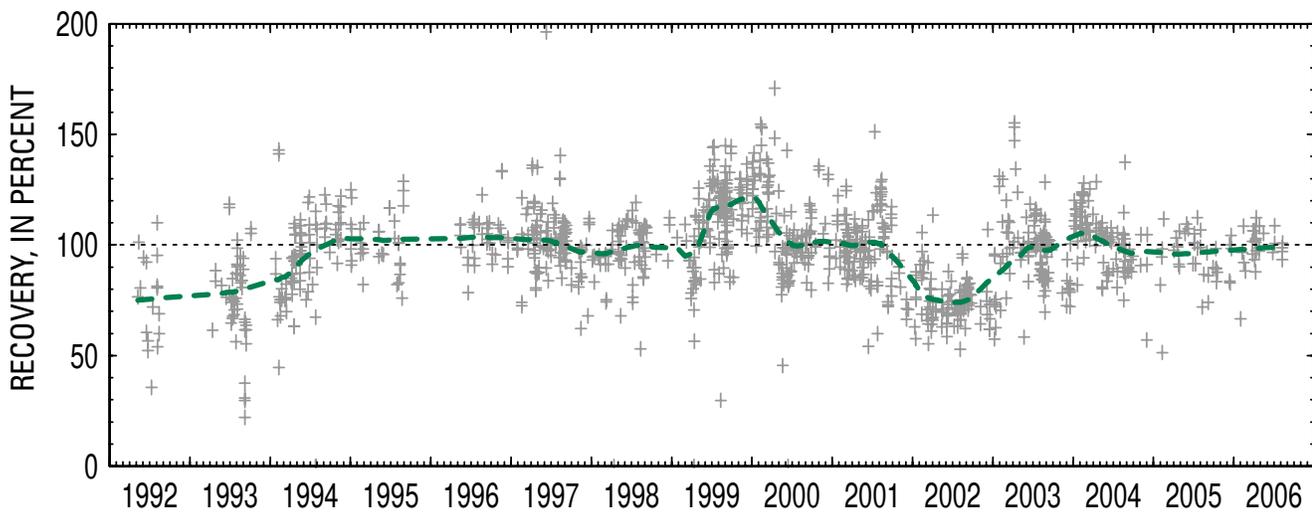


National Water-Quality Assessment Program

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2006



Scientific Investigations Report 2009–5189

Cover image: Example graph showing temporal changes in the recovery of a pesticide in stream–water matrix spikes. Similar graphs for 44 pesticides and 8 pesticide degradates are given in appendix 5 of this report.

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By Jeffrey D. Martin, Wesley W. Stone, Duane S. Wydoski, and
Mark W. Sandstrom

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Scientific Investigations Report 2009–5189

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

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KEN SALAZAR, Secretary

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with credible scientific information that helps to enhance and protect the overall quality of life and that facilitates effective management of water, biological, energy, and mineral resources (<http://www.usgs.gov>). Information on the Nation's water resources is critical to ensuring long-term availability of water that is safe for drinking and recreation and is suitable for industry, irrigation, and fish and wildlife. Population growth and increasing demands for water make the availability of that water, now measured in terms of quantity and quality, even more essential to the long-term sustainability of our communities and ecosystems.

The USGS implemented the National Water-Quality Assessment (NAWQA) Program in 1991 to support national, regional, State, and local information needs and decisions related to water-quality management and policy (<http://water.usgs.gov/nawqa>). The NAWQA Program is designed to answer: What is the condition of our Nation's streams and groundwater? How are conditions changing over time? How do natural features and human activities affect the quality of streams and groundwater, and where are those effects most pronounced? By combining information on water chemistry, physical characteristics, stream habitat, and aquatic life, the NAWQA Program aims to provide science-based insights for current and emerging water issues and priorities. During 1991–2001, the NAWQA Program completed interdisciplinary assessments and established a baseline understanding of water-quality conditions in 51 of the Nation's river basins and aquifers, referred to as Study Units (<http://water.usgs.gov/nawqa/studyu.html>).

Multiple national and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are reassessed. These assessments extend the findings in the Study Units by determining status and trends at sites that have been consistently monitored for more than a decade, and filling critical gaps in characterizing the quality of surface water and groundwater. For example, increased emphasis has been placed on assessing the quality of source water and finished water associated with many of the Nation's largest community water systems. During the second decade, NAWQA is addressing five national priority topics that build an understanding of how natural features and human activities affect water quality, and establish links between sources of contaminants, the transport of those contaminants through the hydrologic system, and the potential effects of contaminants on humans and aquatic ecosystems. Included are topics on the fate of agricultural chemicals, effects of urbanization on stream ecosystems, bioaccumulation of mercury in stream ecosystems, effects of nutrient enrichment on aquatic ecosystems, and transport of contaminants to public-supply wells. These topical studies are conducted in those Study Units most affected by these issues; they comprise a set of multi-Study-Unit designs for systematic national assessment. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, selected trace elements, and aquatic ecology are continuing.

The USGS aims to disseminate credible, timely, and relevant science information to address practical and effective water-resource management and strategies that protect and restore water quality. We hope this NAWQA publication will provide you with insights and information to meet your needs, and will foster increased citizen awareness and involvement in the protection and restoration of our Nation's waters.

The USGS recognizes that a national assessment by a single program cannot address all water-resource issues of interest. External coordination at all levels is critical for cost-effective management, regulation, and conservation of our Nation's water resources. The NAWQA Program, therefore, depends on advice and information from other agencies—Federal, State, regional, interstate, Tribal, and local—as well as nongovernmental organizations, industry, academia, and other stakeholder groups. Your assistance and suggestions are greatly appreciated.

Matthew C. Larsen
Associate Director for Water

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Conversion Factors

Multiply	By	To obtain
	Volume	
liter (L)	0.2642	gallon (gal)
milliliter (mL)	0.03381	fluid ounce (oz)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)

Concentrations of chemical constituents are given in micrograms per liter (µg/L) or micrograms per milliliter (µg/mL). A microgram is one-millionth of a gram, and a milliliter is one-thousandth of a liter.

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2006

By Jeffrey D. Martin, Wesley W. Stone, Duane S. Wydoski, and Mark W. Sandstrom

Abstract

Recovery is the proportion of a target analyte that is quantified by an analytical method and is a primary indicator of the analytical bias of a measurement. Recovery is measured by analysis of quality-control (QC) water samples that have known amounts of target analytes added (“spiked” QC samples). For pesticides, recovery is the measured amount of pesticide in the spiked QC sample expressed as percentage of the amount spiked, ideally 100 percent. Temporal changes in recovery have the potential to adversely affect time-trend analysis of pesticide concentrations by introducing trends in environmental concentrations that are caused by trends in performance of the analytical method rather than by trends in pesticide use or other environmental conditions.

This report examines temporal changes in the recovery of 44 pesticides and 8 pesticide degradates (hereafter referred to as “pesticides”) that were selected for a national analysis of time trends in pesticide concentrations in streams. Water samples were analyzed for these pesticides from 1992 to 2006 by gas chromatography/mass spectrometry. Recovery was measured by analysis of pesticide-spiked QC water samples. Temporal changes in pesticide recovery were investigated by calculating robust, locally weighted scatterplot smooths (lowess smooths) for the time series of pesticide recoveries in 5,132 laboratory reagent spikes; 1,234 stream-water matrix spikes; and 863 groundwater matrix spikes. A 10-percent smoothing window was selected to show broad, 6- to 12-month time scale changes in recovery for most of the 52 pesticides.

Temporal patterns in recovery were similar (in phase) for laboratory reagent spikes and for matrix spikes for most pesticides. In-phase temporal changes among spike types support the hypothesis that temporal change in method performance is the primary cause of temporal change in recovery. Although temporal patterns of recovery were in phase for most pesticides, recovery in matrix spikes was greater than recovery in reagent spikes for nearly every pesticide. Models of recovery based on matrix spikes are deemed more appropriate for adjusting concentrations of pesticides measured in groundwater and stream-water samples than models based on laboratory reagent spikes because (1) matrix spikes are expected to more

closely match the matrix of environmental water samples than are reagent spikes and (2) method performance is often matrix dependent, as was shown by higher recovery in matrix spikes for most of the pesticides.

Models of recovery, based on lowess smooths of matrix spikes, were developed separately for groundwater and stream-water samples. The models of recovery can be used to adjust concentrations of pesticides measured in groundwater or stream-water samples to 100 percent recovery to compensate for temporal changes in the performance (bias) of the analytical method.

Introduction

Analytical recovery is a primary indicator of the analytical bias of a measurement. Analytical recovery (hereafter referred to as “recovery”) is measured by analysis of quality-control (QC) water samples that have known amounts of target analytes added (“spiked” QC samples). For pesticides, recovery is the measured amount of pesticide in the spiked QC sample expressed as a percentage of the amount spiked, ideally 100 percent. Recovery of pesticides in spiked QC water samples is routinely measured by the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL). Pesticide concentrations reported by NWQL are not corrected for recovery. Most environmental laboratories do not correct for recovery (Keith, 1991, p. 116).

Bexfield (2008, p. S228–S230) examined temporal changes in pesticide recovery for water samples analyzed by NWQL during 1993–95 and 2001–3 and found trends in the recovery of pesticides in laboratory reagent spikes. Bexfield noted that temporal changes in recovery had the potential to adversely affect time-trend analysis of pesticide concentrations by introducing trends in environmental concentrations that were caused by trends in performance of the analytical method rather than by trends in pesticide use or other environmental conditions. Temporal changes in recovery in laboratory reagent spikes were modeled (using a smoothing technique similar to that used in this report), and pesticide concentrations in ground-water samples were adjusted to 100-percent recovery prior to time-trend analysis.

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This report presents models of recovery based on recovery in groundwater and stream-water matrix spikes that are intended to be used to adjust pesticide concentrations measured in environmental water samples for temporal changes in recovery for the period 1992–2006. These models are needed for some types of water-quality assessments, such as time-trend analysis. Alternative methods, such as adjusting concentrations on the basis of a single reagent set spike or a single matrix spike for a particular group of environmental samples, are deemed less appropriate because of the considerable variability inherent in the analytical method and, for reagent spikes, a difference in the sample matrix.

Purpose and Scope

This report examines temporal changes in the recovery of 44 pesticides and 8 pesticide degradates (hereafter referred to as “pesticides”) that were selected for a national analysis of time trends in pesticide concentrations in streams (Martin, 2009). Water samples were analyzed for these pesticides from 1992 to 2006 by gas chromatography/mass spectrometry. Recovery of pesticides was measured by analysis of pesticide-spiked QC water samples prepared either by NWQL analysts or by field personnel of the National Water Quality Assessment (NAWQA) Program. Temporal changes in recovery were examined by scatterplot smooths of time series plots of pesticide recovery in 5,132 laboratory reagent spikes; 1,234 stream-water matrix spikes; and 863 groundwater matrix spikes. Models of recovery, based on lowess smooths of matrix spikes, were developed separately for stream-water and groundwater samples. The models of recovery can be used to adjust pesticide concentrations to 100 percent recovery to compensate for temporal changes in the performance of the analytical method. This report describes the procedures used to investigate and model temporal changes in recovery, evaluates the models, identifies regions or sites where recovery is much larger or smaller than “normal,” and provides datasets of measured and modeled recoveries.

Analytical Method for Pesticides

The recovery data discussed in this report are applicable to water-quality samples analyzed during 1992–2006 by NWQL using a gas chromatography/mass spectrometry analytical method (referred to as the “GCMS” method in this report). Pesticides are isolated by C-18 solid-phase extraction (SPE) from filtered water samples and analyzed by capillary-column gas chromatography/mass spectrometry with selected-ion monitoring (Zaugg and others, 1995; Lindley and others, 1996; Madsen and others, 2003). The GCMS method provides low-level analyses for as many as 44 commonly used pesticides and 8 pesticide degradates (table 1). The pesticide ace-tochlor was added to the GCMS method in 1994 (Lindley and others, 1996) and the pesticide fipronil and four degradates of

fipronil were added to the GCMS method in 1999 (Madsen and others, 2003). Analysis of pesticides by GCMS is obtained by requesting a NWQL analytical “schedule” (a suite of pesticides to be measured by one or more analytical methods). The recovery information provided in this report was obtained from samples analyzed by NWQL schedules 2001, 2010, 2003, and 2033.

The GCMS analytical method does not have specified “detection limits” for each pesticide. All detections conclusively identified by retention time and spectral characteristics are quantified (Zaugg and others, 1995, p. 19–21). Nondetections of pesticides (analyses that do not meet identification criteria based on retention time or spectral characteristics) are reported as less than the “reporting level” (for example: < 0.005 µg/L). The types and numerical values of reporting levels used to report nondetections of pesticides analyzed by GCMS have changed through time. Oblinger Childress and others (1999) and Martin (2009) give additional information on reporting procedures for GCMS analytical data.

Measurement of Recovery

Recovery, as used in this report, is the ratio of a measured value divided by a reference value.¹ Measurements of recovery provide information on the bias and variability of measurements from the analytical method. Recovery of pesticides analyzed by the GCMS method of NWQL is measured by analysis of spiked QC water samples. Spiked QC samples are prepared by adding small volumes of spike solutions to water samples. Two types of spiked QC samples are routinely analyzed for recovery: (1) laboratory reagent spikes and (2) matrix spikes. Use of the recovery information differs among the type of spikes. Approaches and considerations in the measurement and use of recovery information are presented in Thompson and others (1999). Considerations for spiking water samples are in American Society for Testing and Materials (2000, p. 770–774).

Spike Solutions

Spike solutions of pesticides at known concentrations in solvents are prepared by NWQL personnel or by commercial vendors according to NWQL specifications. Spike solutions are identified by lot number, and pesticide concentrations in spike solutions are certified by NWQL personnel prior to use (U.S. Geological Survey [n.d.]). Pesticide concentrations in most GCMS spike solutions are 1 µg/mL, and 0.1 mL of spike solution typically is added to spiked QC water samples. Pesticide concentrations in most spiked QC water samples are approximately 0.1 µg/L, but some QC samples are spiked at higher concentrations. A dataset of pesticide concentrations in spike solutions is in appendix 1.

¹Burns and others (2002) prefer the term “apparent recovery.”

Table 1. Pesticides analyzed by the GCMS method.

[Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; CAS, Chemical Abstracts Service (table contains CAS Registry Numbers®, a Registered Trademark of the American Chemical Society; CAS recommends the verification of CASRNs through CAS Client ServicesSM); LT-MDL, long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Figure sequence in appendixes 4, 5, 6, and 7	Pesticide	Parameter code	CAS number	Pesticide class	Type of pesticide	Parent pesticide (if degradate)	Maximum LT-MDL (µg/L)
1	Acetochlor	49260	34256-82-1	Acetanilide	Herbicide	NA	0.003
2	Alachlor	46342	15972-60-8	Acetanilide	Herbicide	NA	0.002
3	Atrazine	39632	1912-24-9	Triazine	Herbicide	NA	0.004
4	Azinphos-methyl	82686	86-50-0	Organothiophosphate	Insecticide	NA	0.040
5	Benfluralin	82673	1861-40-1	Dinitroaniline	Herbicide	NA	0.005
6	Butylate	04028	2008-41-5	Thiocarbamate	Herbicide	NA	0.002
7	Carbaryl	82680	63-25-2	Carbamate	Insecticide	NA	0.030
8	Carbofuran	82674	1563-66-2	Carbamate	Insecticide	NA	0.010
9	Chlorpyrifos	38933	2921-88-2	Organothiophosphate	Insecticide	NA	0.003
10	Cyanazine	04041	21725-46-2	Triazine	Herbicide	NA	0.009
11	Dacthal	82682	1861-32-1	Chlorobenzoic acid ester	Herbicide	NA	0.002
12	<i>p,p'</i> -DDE	34653	72-55-9	Organochlorine	Degradate	DDT	0.001
13	Deethylatrazine	04040	6190-65-4	Triazine	Degradate	Atrazine	0.007
14	Desulfinylfipronil	62170	ND	Phenyl pyrazole	Degradate	Fipronil	0.006
15	Desulfinylfipronil amide	62169	ND	Phenyl pyrazole	Degradate	Fipronil	0.015
16	Diazinon	39572	333-41-5	Organothiophosphate	Insecticide	NA	0.003
17	Dieldrin	39381	60-57-1	Organochlorine	Insecticide	NA	0.004
18	2,6-Diethylaniline	82660	579-66-8	Aniline	Degradate	Alachlor	0.003
19	Disulfoton	82677	298-04-4	Organothiophosphate	Insecticide	NA	0.011
20	EPTC	82668	759-94-4	Thiocarbamate	Herbicide	NA	0.002
21	Ethalfuralin	82663	55283-68-6	Dinitroaniline	Herbicide	NA	0.005
22	Ethoprophos	82672	13194-48-4	Organothiophosphate	Insecticide	NA	0.006
23	Fipronil	62166	120068-37-3	Phenyl pyrazole	Insecticide	NA	0.008
24	Fipronil sulfide	62167	120067-83-6	Phenyl pyrazole	Degradate	Fipronil	0.006
25	Fipronil sulfone	62168	120068-36-2	Phenyl pyrazole	Degradate	Fipronil	0.012
26	Fonofos	04095	944-22-9	Organothiophosphate	Insecticide	NA	0.003
27	<i>alpha</i> -HCH	34253	319-84-6	Organochlorine	Degradate	<i>gamma</i> -HCH	0.002
28	<i>gamma</i> -HCH	39341	58-89-9	Organochlorine	Insecticide	NA	0.002
29	Linuron	82666	330-55-2	Urea	Herbicide	NA	0.030
30	Malathion	39532	121-75-5	Organothiophosphate	Insecticide	NA	0.014
31	Metolachlor	39415	51218-45-2	Acetanilide	Herbicide	NA	0.006
32	Metribuzin	82630	21087-64-9	Triazine	Herbicide	NA	0.014
33	Molinate	82671	2212-67-1	Thiocarbamate	Herbicide	NA	0.002
34	Napropamide	82684	15299-99-7	Amide	Herbicide	NA	0.009
35	Parathion	39542	56-38-2	Organothiophosphate	Insecticide	NA	0.005
36	Parathion-methyl	82667	298-00-0	Organothiophosphate	Insecticide	NA	0.008
37	Pebulate	82669	1114-71-2	Ohiocarbamate	Herbicide	NA	0.002
38	Pendimethalin	82683	40487-42-1	Dinitroaniline	Herbicide	NA	0.011
39	<i>cis</i> -Permethrin	82687	54774-45-7	Pyrethroid	Insecticide	NA	0.005
40	Phorate	82664	298-02-2	Prganothiophosphate	Insecticide	NA	0.027

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Table 1. Pesticides analyzed by the GCMS method.—Continued

[Parameter code, the number used to identify a pesticide in the U.S. Geological Survey National Water Information System; CAS, Chemical Abstracts Service (table contains CAS Registry Numbers®, a Registered Trademark of the American Chemical Society; CAS recommends the verification of CASRN's through CAS Client ServicesSM); LT-MDL, long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Figure sequence in appendixes 4, 5, 6, and 7	Pesticide	Parameter code	CAS number	Pesticide class	Type of pesticide	Parent pesticide (if degradable)	Maximum LT-MDL (µg/L)
41	Prometon	04037	1610-18-0	Triazine	Herbicide	NA	0.007
42	Propachlor	04024	1918-16-7	Acetanilide	Herbicide	NA	0.012
43	Propanil	82679	709-98-8	Amide	Herbicide	NA	0.005
44	Propargite	82685	2312-35-8	Sulfite ester	Acaricide	NA	0.011
45	Propyzamide	82676	23950-58-5	Amide	Herbicide	NA	0.002
46	Simazine	04035	122-34-9	Triazine	Herbicide	NA	0.006
47	Tebuthiuron	82670	34014-18-1	Urea	Herbicide	NA	0.008
48	Terbacil	82665	5902-51-2	Uracil	Herbicide	NA	0.020
49	Terbufos	82675	13071-79-9	Organothiophosphate	Insecticide	NA	0.009
50	Thiobencarb	82681	28249-77-6	Thiocarbamate	Herbicide	NA	0.005
51	Triallate	82678	2303-17-5	Thiocarbamate	Herbicide	NA	0.003
52	Trifluralin	82661	1582-09-8	Dinitroaniline	Herbicide	NA	0.005

Laboratory Reagent Spikes

Laboratory reagent spikes are QC water samples prepared at NWQL by chemists. The term “reagent” indicates that the spike solution has been added to sample of “reagent-grade” blank water (as opposed to an environmental water sample). Spiked samples of reagent water are then extracted, eluted, and analyzed for pesticides by use of the same analysis procedures as for environmental samples. One laboratory reagent spike is prepared for each set of 10 environmental samples. “Background” concentrations of pesticides (concentrations in the water sample before the spike solution was added) are known to be less than the reporting level for reagent-grade blank water (blank water is routinely analyzed for pesticides) and were assumed to be zero concentration for the calculation of recovery. Recovery in laboratory reagent spikes is calculated as follows:

$$R = (C_{\text{measured}}/C_{\text{expected}}) \times 100\% \quad (1)$$

where

R is pesticide recovery, in percent,
 C_{measured} is the measured concentration of the pesticide in the spiked sample, in micrograms per liter, and
 C_{expected} is the expected or theoretical concentration of the pesticide in the spiked sample, in micrograms per liter, and is calculated as:

$$C_{\text{expected}} = C_{\text{solution}} \times V_{\text{solution}} / V_{\text{sample}} \quad (2)$$

where

C_{solution} is the concentration of the pesticide in the spike solution, in micrograms per milliliter,
 V_{solution} is the volume of spike solution added to the spiked sample, in milliliters, and
 V_{sample} is the volume of water in the spiked sample, in liters.

Laboratory reagent spikes primarily are used to demonstrate that all sample preparation and analysis processes for the analytical method are in control (Maloney, 2005, p. B.2–B.3).

Matrix Spikes

Matrix spikes are QC water samples prepared by scientists responsible for the collection of stream-water and groundwater samples. The term “matrix” indicates that the spiked solution has been added to an environmental water sample (as opposed to a blank/reagent water sample). Water is collected from the stream or well and processed by use of standard procedures to produce two samples (U.S. Geological Survey, variously dated; Shelton, 1994; Koterba and others, 1995). Spike solution is added to only one of the two water samples, resulting in spiked and unspiked samples (the matrix spike and the “background” sample, respectively). Most matrix spikes were spiked at the field site (field matrix spikes) but about 5.5 percent (114) of the matrix spikes were spiked at the laboratory before analysis (laboratory matrix spikes). Field and laboratory matrix spikes provide similar information on recovery except that field matrix spikes also include the effect of pesticide degradation that might occur during

the time between sample collection and laboratory analysis. Field QC procedures for the NAWQA program are described for groundwater samples in Koterba and others (1995) and for stream-water samples in Mueller and others (1997). In general, approximately 5 percent of the pesticide samples collected for the NAWQA program are field matrix spikes.

Background concentrations of pesticides are measured by pesticide analysis of the unspiked sample. Nondetections of pesticides in the unspiked sample were assumed to be zero concentration for the calculation of recovery. Recovery in field matrix spikes is calculated as follows:

$$R = [(C_{\text{spiked}} - C_{\text{unspiked}}) / C_{\text{expected}}] \times 100\% \quad (3)$$

where

R	is pesticide recovery, in percent,
C_{spiked}	is the measured concentration of the pesticide in the spiked sample, in micrograms per liter,
C_{unspiked}	is the measured concentration of the pesticide in the unspiked sample, in micrograms per liter, and
C_{expected}	is the expected or theoretical concentration of the pesticide in the spiked sample, in micrograms per liter (C_{expected} is defined in eq. 2).

Matrix spikes measure pesticide recovery in environmental water samples and are used to (1) assess performance of the analytical method in environmental waters, (2) identify a stream or aquifer with a problematic water matrix for pesticide analysis (“matrix effects”), and, for field matrix spikes, (3) investigate pesticide degradation during sample shipment to the laboratory. Some water samples have a matrix (the chemical, physical, and biological properties of the water sample) that interferes with pesticide analysis, resulting in pesticide recovery much higher or lower than normal. For example, chlorine in treated water samples degrades some pesticides, resulting in much lower recovery of these pesticides in chlorinated water compared to unchlorinated water (Valder and others, 2008, fig. 7). Comparison of recovery in field matrix spikes among sites can identify sites where the magnitude of matrix effects is more problematic than for other sites.

Sources, Preparation, and Review of Recovery Data

Recovery in laboratory reagent spikes was obtained from NWQL (Stephen R. Glodt, Information Technology Specialist, U.S. Geological Survey, written commun., January 19, 2005; March 7, 2006; and March 14, 2006). Recovery data were reviewed, and questionable values of recovery were referred to NWQL chemists for verification. Questionable recoveries were verified, recalculated, or deleted from the dataset. The

period of laboratory reagent spikes spans September 1993 through September 2005 and contains 5,132 reagent spikes. The date value reported or plotted for laboratory reagent spikes is the date the spiked sample was logged in at NWQL. The sample log-in date was determined from the laboratory ID (a number composed of the calendar year, the numerical day of year (from 1 to 365 or 366), and a sequence number). For laboratory reagent spikes, the sample preparation/extraction date is the same as the sample log-in date. The final reviewed laboratory reagent spike dataset is in appendix 2.

Recovery in matrix spikes was calculated from spiked environmental water samples and the associated unspiked water samples collected for the NAWQA program and stored in the NAWQA Data Warehouse (DWH). NAWQA water-quality data were obtained from DWH data managers (Nathaniel L. Booth, Information Technology Specialist, U.S. Geological Survey, written commun., September 22, 2006). Any water-quality sample in the DWH with analyses of one or more pesticides of interest was retrieved along with selected supporting sample information.

Matrix spikes were identified on the basis of sample codes stored with the data. The associated unspiked environmental sample for each matrix spike was identified by locating the environmental sample collected at the same station number and date as the matrix spike. Twenty-six field matrix spikes had more than one possible associated unspiked environmental sample. Analytical results and sample comments stored with the data were reviewed, and the associated unspiked sample was identified (usually the environmental sample closest in time to the spiked sample).

The volume of the spiked sample, the volume of spike solution added to the spiked sample, and the concentration of the pesticide in the spike solution are critical values for calculation of recovery. The concentration of the pesticide in the spike solution must be determined from the lot number of the spike solution (U.S. Geological Survey [n.d.]). The volume of the spiked sample is measured by NWQL and stored with the data. The volume of spike solution added and the lot number of the spike solution are entered into the database by field or laboratory personnel (depending on who does the spiking). Data for spike volume and lot number for many matrix spikes were missing or incorrect and were inferred from sample date, from other matrix spikes collected by field personnel, and by review of initial recovery calculations.

A total of 2,168 matrix spike samples were identified in the dataset. Of these, 30 were removed from the dataset because no matching unspiked environmental sample was identified, 4 were removed because sample volume was missing, 24 were removed because the spike solution apparently was not added to the matrix spike, 7 were removed because the spiked sample volume was less than 400 mL, and 6 were removed because recoveries of pesticides were 3 to 7 times greater than the expected recovery—most likely because more spike solution was added than indicated in the data. These sample deletions resulted in a dataset of 2,097 matrix spikes.

High background concentrations of pesticides resulted in invalid estimates of recovery for some matrix spikes. In the presence of high background concentrations, the additional concentration from spiking may be indistinguishable from the normal analytical variability of measurements at high concentrations. Recoveries calculated from matrix spikes under these conditions may be much higher or lower (even negative) than is typical for the method. Review of plots of recovery versus background concentrations showed that occurrences of very high (greater than 200 percent) or low (less than 50 percent) recoveries were more frequent at background concentrations of 0.5 µg/L or higher than at concentrations less than 0.5 µg/L. Recoveries were deleted from the dataset if background concentrations were greater than or equal to 0.5 µg/L and recovery was less than 50 percent or greater than 200 percent². This criterion removed 76 recoveries from the dataset.

Recoveries for several pesticides were 3 or more times greater than expected. Recoveries in excess of 300 percent were assumed to be unrepresentative of method performance and were removed from the dataset (table 2)³. Recoveries less than 0 percent were set to 0 percent. Finally, the spike volume for eight matrix spike samples was increased from 0.1 mL to 0.2 mL because these matrix spikes likely were spiked twice. The final reviewed matrix spike dataset comprises 2,097 samples and 49,749 estimates of pesticide recovery and spans the period May 1992 through August 2006. The date value reported or plotted for matrix spikes is the sample-collection date. For matrix spikes, the sample preparation/extraction date typically is 2 to 6 days after the sample-collection date. Pesticide recovery in matrix spikes is summarized in table 3. The final reviewed matrix spike dataset is in appendix 3.

Temporal Changes in Recovery

Temporal changes in pesticide recovery were investigated by calculating robust, locally weighted scatterplot smooths (termed “lowess” or “lowess smooths”) for the time series of pesticide recoveries. Lowess smooths were used to model changes in recovery as a function of time and to compare the timing and magnitude of temporal changes in recovery among the different types of spiked quality-control samples. This section of the report (1) describes the lowess procedure, (2) compares temporal changes in recovery between reagent and matrix spikes, (3) states the justification for selecting matrix spikes for models of recovery, (4) describes the magnitude of temporal changes in recovery of pesticides in matrix spikes, (5) compares temporal changes in recovery between groundwater and stream-water matrix spikes, (6) states the justification for modeling temporal changes in recovery separately for

² The 50- and 200-percent recovery thresholds were subjectively selected to retain typical values of recovery (those apparently not adversely affected by high background concentrations).

³ Removal of recoveries in excess of 300 percent had negligible effects on models of recovery.

Table 2. Pesticide recoveries in excess of 300 percent that were deleted from the matrix spike dataset.

Pesticide	Number of recoveries deleted	Median recovery deleted (percent)	Maximum recovery deleted (percent)
Carbaryl	102	361	1853
Carbofuran	49	396	1373
Azinphos-methyl	37	352	570
Terbacil	19	336	462
<i>cis</i> -Permethrin	18	320	351
Propargite	11	325	654
Tebuthiuron	9	430	5342
Linuron	8	345	1198
Propachlor	8	535	4465
Molinate	3	990	1697
Pebulate	2	631	795
2,6-Diethylaniline	1	368	368
Atrazine	1	412	412
Dieldrin	1	786	786
Parathion-methyl	1	330	330

groundwater and stream-water sample matrices, (7) assesses model performance, and (8) discusses limitations of recovery models.

Robust, Locally Weighted Scatterplot Smooths (lowess smooths)

The lowess procedure (Cleveland, 1979; Cleveland and McGill, 1985, p. 833) is particularly useful in showing the shape of the relationship between two variables in a scatterplot of large sample size (Helsel and Hirsch, 2002, p. 289). Lowess iteratively fits at least 2^n weighted least-squares regressions (Helsel and Hirsch, 2002, p. 287) to the n number of recoveries in the time series to estimate the center of the recoveries as a function of time. The shape of the smooth is not determined by assuming a particular model of the relation between recovery and time; rather, the shape is completely determined by the pattern of the data and the length of the smoothing window (Helsel and Hirsch, 2002, p. 45–47, 289). The length of the smoothing window controls the amount of curvature in the smooth—longer windows have less curvature than shorter windows. Weights in the regression equations are a function of (1) the distance (time, in this application) between a point and the center of the smoothing window (the point to be fit) and (2) the magnitude of the residual error from the previous regression (Helsel and Hirsch, 2002, p. 287–288). Locally weighted regression ensures that recoveries closer in time to the date to be fit have more weight than those more distant in time. The robustness feature of lowess ensures that little weight is assigned to outliers (recoveries much greater or smaller than the center of the recoveries).

Table 3. Pesticide recovery in matrix spikes, 1992–2006.

[GW, Groundwater; SW, Stream water]

Pesticide	Medium	Number of matrix spikes	Date of first spike	Date of last spike	Statistics of recovery (percent)			
					Mean	Standard deviation	Median	Interquartile range
Acetochlor	GW	651	6/20/1995	8/9/2006	103.1	14.1	102.7	15.3
Acetochlor	SW	1040	8/8/1995	8/10/2006	112.0	13.4	111.3	16.5
Alachlor	GW	861	6/3/1993	8/9/2006	101.6	14.7	102.4	15.7
Alachlor	SW	1232	5/8/1992	8/10/2006	110.7	14.6	110.0	16.8
Atrazine	GW	840	6/3/1993	8/9/2006	99.6	16.3	100.0	17.4
Atrazine	SW	1210	5/8/1992	8/10/2006	103.1	18.8	102.4	18.4
Azinphos-methyl	GW	857	6/3/1993	8/9/2006	102.9	51.6	98.2	64.1
Azinphos-methyl	SW	1158	5/8/1992	8/10/2006	144.7	53.1	141.0	69.2
Benfluralin	GW	863	6/3/1993	8/9/2006	77.7	18.8	77.3	21.9
Benfluralin	SW	1195	5/8/1992	8/10/2006	86.0	16.1	85.4	18.2
Butylate	GW	786	6/3/1993	11/4/2004	95.9	14.9	95.3	13.1
Butylate	SW	1125	5/8/1992	4/20/2005	102.2	15.1	100.8	14.7
Carbaryl	GW	825	6/3/1993	8/9/2006	130.7	59.3	123.4	74.1
Carbaryl	SW	1166	5/8/1992	8/10/2006	141.9	57.1	137.1	71.4
Carbofuran	GW	798	6/3/1993	8/9/2006	127.5	46.8	120.1	53.3
Carbofuran	SW	1140	5/8/1992	8/10/2006	137.6	45.3	129.2	48.9
Chlorpyrifos	GW	862	6/3/1993	8/9/2006	90.7	17.4	91.6	16.7
Chlorpyrifos	SW	1192	5/8/1992	8/10/2006	97.0	15.0	97.6	15.8
Cyanazine	GW	816	6/3/1993	8/9/2006	102.9	24.5	103.6	27.0
Cyanazine	SW	1179	5/8/1992	8/10/2006	110.3	25.7	111.5	29.7
Dacthal	GW	863	6/3/1993	8/9/2006	103.4	17.6	102.7	16.8
Dacthal	SW	1213	4/14/1993	8/10/2006	105.3	14.9	104.7	16.0
<i>p,p'</i> -DDE	GW	786	6/3/1993	11/4/2004	69.3	13.4	68.6	16.6
<i>p,p'</i> -DDE	SW	1084	5/8/1992	4/20/2005	61.1	12.4	61.0	14.4
Deethylatrazine	GW	839	6/3/1993	8/9/2006	47.2	20.8	45.6	29.5
Deethylatrazine	SW	1230	5/8/1992	8/10/2006	48.6	21.5	46.6	28.4
Desulfnylfipronil	GW	101	1/8/2003	8/9/2006	106.5	27.4	102.4	22.7
Desulfnylfipronil	SW	204	12/9/2002	8/10/2006	115.4	23.7	111.5	29.4
Desulfnylfipronil amide	GW	101	1/8/2003	8/9/2006	97.6	43.1	93.6	45.6
Desulfnylfipronil amide	SW	204	12/9/2002	8/10/2006	120.5	48.2	108.2	73.3
Diazinon	GW	862	6/3/1993	8/9/2006	94.0	16.5	95.0	16.1
Diazinon	SW	1228	5/8/1992	8/10/2006	99.2	14.9	99.7	14.1
Dieldrin	GW	860	6/3/1993	8/9/2006	94.0	16.7	92.6	18.5
Dieldrin	SW	1194	5/8/1992	8/10/2006	99.0	15.2	98.1	18.2
2,6-Diethylaniline	GW	862	6/3/1993	8/9/2006	91.1	16.2	91.4	15.0
2,6-Diethylaniline	SW	1195	5/8/1992	8/10/2006	89.0	16.3	89.5	16.5
Disulfoton	GW	816	6/3/1993	8/9/2006	72.6	34.3	71.4	29.1
Disulfoton	SW	1136	5/8/1992	8/10/2006	67.1	30.5	67.1	35.1
EPTC	GW	816	6/3/1993	8/9/2006	92.8	13.6	93.4	12.4
EPTC	SW	1138	5/8/1992	8/10/2006	94.3	13.3	94.2	12.8
Ethalfuralin	GW	786	6/3/1993	11/4/2004	88.7	23.5	87.2	22.7
Ethalfuralin	SW	1086	5/8/1992	4/20/2005	100.1	19.9	98.3	24.8
Ethoprophos	GW	816	6/3/1993	8/9/2006	93.6	17.7	93.2	20.1
Ethoprophos	SW	1137	5/8/1992	8/10/2006	103.3	17.5	101.8	21.8
Fipronil	GW	101	1/8/2003	8/9/2006	107.3	36.0	103.4	38.5
Fipronil	SW	204	12/9/2002	8/10/2006	147.9	45.7	134.7	70.8

8 Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2006

Table 3. Pesticide recovery in matrix spikes, 1992–2006.—Continued

[GW, Groundwater; SW, Stream water]

Pesticide	Medium	Number of matrix spikes	Date of first spike	Date of last spike	Statistics of recovery (percent)			
					Mean	Standard deviation	Median	Interquartile range
Fipronil sulfide	GW	101	1/8/2003	8/9/2006	104.2	27.7	102.0	20.5
Fipronil sulfide	SW	204	12/9/2002	8/10/2006	116.6	21.7	113.9	23.1
Fipronil sulfone	GW	101	1/8/2003	8/9/2006	93.7	28.3	89.7	29.6
Fipronil sulfone	SW	204	12/9/2002	8/10/2006	108.7	25.2	103.0	37.3
Fonofos	GW	861	6/3/1993	8/9/2006	89.9	18.2	90.3	15.9
Fonofos	SW	1193	5/8/1992	8/10/2006	94.8	16.8	96.2	17.3
<i>alpha</i> -HCH	GW	786	6/3/1993	11/4/2004	93.5	14.6	93.8	16.9
<i>alpha</i> -HCH	SW	1085	5/8/1992	4/20/2005	96.6	13.4	95.7	15.1
<i>gamma</i> -HCH	GW	783	6/3/1993	11/4/2004	95.9	16.0	96.2	17.0
<i>gamma</i> -HCH	SW	1084	5/8/1992	4/20/2005	99.8	15.6	99.1	17.7
Linuron	GW	781	6/3/1993	11/4/2004	110.4	41.3	105.6	44.5
Linuron	SW	1080	5/8/1992	4/20/2005	113.2	39.4	109.8	45.4
Malathion	GW	863	6/3/1993	8/9/2006	93.0	23.1	94.5	26.4
Malathion	SW	1231	5/8/1992	8/10/2006	103.8	24.6	103.6	29.6
Metolachlor	GW	856	6/3/1993	8/9/2006	105.3	15.4	104.9	16.3
Metolachlor	SW	1218	5/8/1992	8/10/2006	110.5	16.6	110.1	18.3
Metribuzin	GW	863	6/3/1993	8/9/2006	83.4	20.7	85.5	24.8
Metribuzin	SW	1233	5/8/1992	8/10/2006	91.4	19.5	92.7	23.8
Molinate	GW	814	6/3/1993	8/9/2006	96.3	13.7	96.2	11.9
Molinate	SW	1138	5/8/1992	8/10/2006	100.3	12.7	99.9	12.5
Napropamide	GW	786	6/3/1993	11/4/2004	98.1	16.2	97.2	16.7
Napropamide	SW	1086	5/8/1992	4/20/2005	108.1	16.5	107.0	20.5
Parathion	GW	786	6/3/1993	11/4/2004	96.9	24.3	96.2	26.0
Parathion	SW	1084	5/8/1992	4/20/2005	115.3	26.0	112.8	30.6
Parathion-methyl	GW	863	6/3/1993	8/9/2006	93.3	27.6	90.8	28.5
Parathion-methyl	SW	1190	5/8/1992	8/10/2006	111.5	27.0	108.4	31.7
Pebulate	GW	784	6/3/1993	11/4/2004	94.4	13.5	95.2	11.2
Pebulate	SW	1086	5/8/1992	4/20/2005	98.7	13.2	98.0	12.3
Pendimethalin	GW	863	6/3/1993	8/9/2006	83.2	24.5	81.8	27.9
Pendimethalin	SW	1195	5/8/1992	8/10/2006	103.6	24.4	103.0	30.6
<i>cis</i> -Permethrin	GW	847	6/3/1993	8/9/2006	72.7	41.0	62.5	24.3
<i>cis</i> -Permethrin	SW	1192	5/8/1992	8/10/2006	56.0	29.7	52.4	19.7
Phorate	GW	862	6/3/1993	8/9/2006	72.9	21.7	75.0	22.7
Phorate	SW	1192	5/8/1992	8/10/2006	72.6	22.8	75.3	25.6
Prometon	GW	861	6/3/1993	8/9/2006	93.6	20.5	95.4	19.5
Prometon	SW	1229	5/8/1992	8/10/2006	102.9	19.5	103.5	19.8
Propachlor	GW	781	6/3/1993	11/4/2004	104.4	17.3	104.6	19.6
Propachlor	SW	1083	5/8/1992	4/20/2005	116.3	17.8	115.6	20.2
Propanil	GW	812	6/3/1993	8/9/2006	103.5	18.1	104.4	21.2
Propanil	SW	1140	5/8/1992	8/10/2006	114.0	18.0	114.6	24.0
Propargite	GW	802	6/3/1993	8/9/2006	96.4	34.2	90.8	34.0
Propargite	SW	1147	5/8/1992	8/10/2006	109.9	33.5	107.3	36.2
Propyzamide	GW	861	6/3/1993	8/9/2006	92.2	16.1	93.1	18.9
Propyzamide	SW	1193	5/8/1992	8/10/2006	102.4	15.0	102.6	17.0
Simazine	GW	863	6/3/1993	8/9/2006	93.9	17.7	95.4	21.4
Simazine	SW	1220	5/8/1992	8/10/2006	98.1	20.2	99.1	23.0

Table 3. Pesticide recovery in matrix spikes, 1992–2006.—Continued

[GW, Groundwater; SW, Stream water]

Pesticide	Medium	Number of matrix spikes	Date of first spike	Date of last spike	Statistics of recovery (percent)			
					Mean	Standard deviation	Median	Interquartile range
Tebuthiuron	GW	838	6/3/1993	8/9/2006	110.4	29.9	110.6	40.2
Tebuthiuron	SW	1181	5/8/1992	8/10/2006	119.5	33.9	119.0	38.2
Terbacil	GW	778	6/3/1993	11/4/2004	96.0	42.8	91.0	41.4
Terbacil	SW	1072	5/8/1992	4/20/2005	112.6	42.4	109.1	50.1
Terbufos	GW	863	6/3/1993	8/9/2006	78.4	19.9	79.1	21.2
Terbufos	SW	1190	5/8/1992	8/10/2006	83.3	18.4	83.8	16.7
Thiobencarb	GW	812	6/3/1993	8/9/2006	101.5	15.7	102.6	17.3
Thiobencarb	SW	1140	5/8/1992	8/10/2006	104.8	13.4	104.5	15.0
Triallate	GW	786	6/3/1993	11/4/2004	93.2	14.7	93.7	14.9
Triallate	SW	1086	5/8/1992	4/20/2005	98.2	13.4	98.1	14.5
Trifluralin	GW	863	6/3/1993	8/9/2006	80.4	20.1	78.8	21.6
Trifluralin	SW	1195	5/8/1992	8/10/2006	90.5	17.6	90.0	21.0

Recovery was modeled using PROC LOESS of SAS/STAT version 8 with a 10-percent smoothing window (SAS Institute Inc. [n.d.]). A smoothing window of 10 percent means that 10 percent of the data points in the time series of recoveries were used for the locally weighted regression. The length of the smoothing window is subjectively chosen depending on the use of the smooth (Helsel and Hirsch, 2002, p. 288). During initial investigations, smoothing windows of 1, 2, 5, 10, and 20 percent were compared. The 10-percent window was selected to model broad changes in recovery over a 6- to 12-month time scale for most of the 52 pesticides. Shorter smoothing windows showed sudden, abrupt changes in recovery that were considered less appropriate for correcting concentrations for trend analysis because of (1) the relatively large variability of recovery inherent in the analytical method, (2) the increased influence of an irregular/uneven time series of spikes for short smoothing windows, and (3) the increased probability that matrix effects associated with particular water matrices would influence models of temporal changes in recovery. The 10-percent smoothing window is appropriate for modeling changes in recovery over a 6- to 12-month time scale but has no implications for the frequency of environmental samples that can be analyzed for time trends. Trend analysis of weekly, monthly, or annual time series of recovery-adjusted concentrations all are appropriate—depending on the trend-analysis technique and the characteristics of the time series. The time period associated with the smoothing window varies with data density—the window is narrower when data are dense and is wider when data are sparse. Based on the median number of spikes per year, the typical time period associated with the 10-percent smoothing window was 16.0 months for reagent spikes, 16.8 months for matrix spikes, 15.6 months for groundwater matrix spikes, and 16.5 months for stream-water matrix spikes.

Boxplots (Helsel and Hirsch, 2002, p. 25) are used to show the distributions of measured recovery, modeled recovery, or differences in modeled recovery in some of the figures and appendixes that follow. Boxplots are explained in figure 1. Whiskers for boxplots shown in this report are drawn from the quartiles (the 25th and 75th percentiles) to the most distant value that does not exceed 1.5 times the interquartile range from the quartile. Values that exceed 1.5 times the interquartile range from the quartile are termed “outliers” and are shown as a short, horizontal line segment. Outliers are *not* shown in the boxplots in appendixes 4 and 5 in order to emphasize statistics of central tendency in these figures.

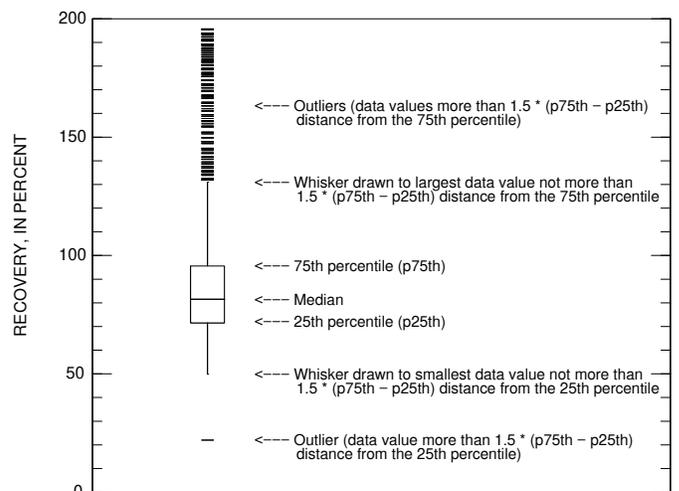


Figure 1. Explanation of boxplots used to depict distributions of recovery. Outliers are not shown in appendix 4 and appendix 5. In some figures, the number of measurements is shown at the top or bottom of the boxplot.

Comparison of Reagent Spikes and Matrix Spikes

Temporal patterns in recovery were similar for laboratory reagent spikes and for matrix spikes for most individual pesticides and are shown in 52 figures in appendix 4. In general, the pattern of increases and decreases in modeled recovery for both types of spikes was temporally in phase. (See, for example, figs. A4–7 (carbaryl), A4–13 (deethylatrazine), and A4–46 (simazine).) In-phase temporal changes among spike types supports the hypothesis that temporal changes in method performance (which would affect both types of spikes) is the primary cause of temporal changes in recovery rather than temporal changes in the matrix of water samples spiked or other causes.

Some of the differences in the timing of temporal changes in recovery between reagent and matrix spikes were most apparent at the beginning or end of the modeled period and were attributed to differences in the starting or ending dates of the reagent and matrix spikes. (See, for example, figs. A4–11 (dacthal), A4–29 (linuron), and A4–38 (pendimethalin).) Temporal patterns for fipronil (fig. A4–23) and its associated degradates (figs. A4–14, A4–15, A4–24, and A4–25,) were less in phase than most pesticides, most likely because the 10-percent smoothing window was too narrow and allowed too much curvature in the smooth for the limited number of spikes for these compounds. Recovery of several pesticides in the early to mid-1990s was much lower than recovery in subsequent years, reflecting early improvements to the analytical method for these pesticides. (See, for example, figs. A4–13 (deethylatrazine), A4–29 (linuron), and A4–32 (metribuzin).)

Other temporal patterns of recovery were evident and most likely were associated with changes in instrumentation, equipment, reagents, procedures, or personnel. Prometon, for example, exhibited a period of low recoveries in reagent spikes prior to 1998 (fig. 4A–41). After 1997, recoveries in reagent spikes increased as a result of the addition of salt to the blank water used to make reagent spikes (salt increased the ionic strength of the blank water). Simazine exhibited a sharp increase in recovery in reagent spikes during 2003 (fig. A4–46) that resulted from a change in the solvent in the vendor-supplied spike solutions used to prepare reagent spikes. In March 1995, the elution solvent (the solvent used to remove pesticides from solid-phase extraction cartridges) was changed from hexane:isopropanol to ethyl acetate, and small increases in recovery were observed for diazinon (fig. A4–16), linuron (fig. A4–29), *cis*-permethrin (fig. A4–39), propachlor (fig. A4–42), and propanil (fig. A4–43). Recovery of deethylatrazine (fig. A4–13) is generally low because it is not completely retained on the C-18 SPE column using the 1-L sample volume (Zaugg and others, 1995), and the temporal changes in recovery are most likely related to use of different lots of the SPE columns that have small differences in retention efficiency.

Although temporal patterns of recovery were in phase for most pesticides, recovery in matrix spikes was greater than

recovery in reagent spikes for nearly every pesticide (fig. 2; appendix 4). The difference in recovery between the types of spikes was quantified by subtracting the modeled recovery in reagent spikes from the modeled recovery in matrix spikes for each day with modeled recovery for both types of spikes. The medians of the differences in modeled recovery were more than 5 percent larger in matrix spikes for 35 of the 52 pesticides and more than 10 percent larger for 14 of the 52 pesticides (fig. 2). The largest median difference in recovery (48 percent) was for azinphos-methyl.

Greater recovery in matrix spikes compared to reagent spikes reflects known analytical problems for some pesticides in the analytical method. Azinphos-methyl (fig. A4–4), carbofuran (fig. A4–8), and carbaryl (fig. A4–7) have some of the largest median differences in recovery between laboratory reagent spikes and matrix spikes (fig. 2) and are prone to degradation in the injection port of the gas chromatograph (Zaugg and others, 1995). Significant enhancement in chromatographic response can occur for some analytes when matrix components fill active sites in the injection port, thus reducing analyte degradation/sorption in matrix spikes compared to reagent spikes that do not have matrix components. Reduced degradation/sorption results in higher recovery in matrix samples (Anastassiades and others, 2003; Poole, 2007). The pesticide *cis*-permethrin (fig. A4–39) is relatively hydrophobic, and the sample matrix likely increases recovery either by decreasing its solubility (“salting-out effect”) or by preventing it from sorbing to the walls of the glass sample bottle.

Degradation of pesticides in water samples during shipment to the laboratory has the potential to produce a negative bias in the measured concentration of pesticides in water samples. Given that pesticide recovery in matrix spikes is greater than in reagent spikes and that most matrix spikes were spiked in the field prior to shipment to the laboratory, degradation of pesticides does not appear to be a significant loss process affecting most water samples. Nonetheless, degradation might be a significant loss process in some matrices. In view of the variability of recovery inherent in the analytical method, a series of paired laboratory-spiked and field-spiked water samples would be needed to estimate degradation in a particular matrix.

Models of recovery based on matrix spikes are deemed more appropriate for adjusting concentrations of pesticide measured in groundwater and stream-water samples than models based on laboratory reagent spikes. Although there are many more laboratory reagent spikes than matrix spikes, the number and temporal distribution of matrix spikes is sufficient to model changes in recovery over a 6- to 12-month time scale. Models of recovery based on matrix spikes were selected because (1) matrix spikes are expected to more closely match the matrix of environmental water samples than are reagent spikes and (2) method performance is often matrix dependent, as was shown by higher recovery in matrix spikes for most of the pesticides (fig. 2).

Given that temporal patterns of recovery were in phase for most pesticides, models of recovery based on either type of spike could be used to adjust measured concentrations in water samples for the purposes of time-trend analysis of concentrations (where relative change in concentrations through time is the issue). For other purposes, such as estimates of mass flux in rivers or comparisons of concentrations to regulatory standards (where the true concentration in the environmental water sample is the issue), adjusted concentrations based on models of recovery in matrix spikes are expected to yield a better estimate of the true concentration in environmental water samples than those based on models of reagent spikes.

Magnitude of Temporal Changes in Recovery in Matrix Spikes

The magnitude of temporal change in recovery during 1992–2006 was quantified for each pesticide by calculating the range of lowess-modeled recovery for all days within the time period of the first matrix spike to the last matrix spike, inclusive. The magnitude of temporal change in recovery ranged from 17 percent (*p,p'*-DDE) to 138 percent (desulfinylfipronil amide) (fig. 3). The median amount of temporal change was 36 percent.

Comparison of Groundwater and Stream-Water Matrix Spikes

In consideration of the systematic difference in recovery between reagent spikes and matrix spikes for most pesticides, recovery was modeled separately for groundwater and stream-water matrix spikes. As was seen in the comparison of reagent and matrix spikes, the pattern of increases and decreases in modeled recovery for groundwater and stream-water matrix spikes was temporally in phase for most pesticides. (See, for example, figs. A5–13 (deethylatrazine), A5–19 (disulfoton), and A5–47 (tebuthiuron).) Temporal changes in recovery were less in phase for some pesticides—especially for pesticides with highly variable recovery—most likely because of differences in data density (the number of spikes) between groundwater and stream-water matrix spikes for some periods of time. (See, for example, figs. A5–4 (azinphos-methyl), A5–7 (carbaryl), and A5–8 (carbofuran).) In general, relatively more groundwater spikes than stream-water spikes were collected during June through October, whereas relatively more stream-water than groundwater spikes were collected during December through April.

Recovery in stream-water matrix spikes was greater than recovery in groundwater spikes for nearly every pesticide (fig. 4; appendix 5). The medians of the differences in modeled recovery were more than 5 percent larger in stream-water spikes for 31 of the 52 pesticides and more than 10 percent larger for 14 of the 52 pesticides (fig. 4). The smallest median difference in recovery (-11 percent) was for *cis*-permethrin, and the largest median difference in recovery (41 percent) was for azinphos-methyl. Given the systematic differences in recovery between groundwater and stream-water matrix spikes for most pesticides, models of recovery used to adjust pesticide concentrations in environmental water samples should be matrix specific.

The median differences in recovery of the 52 pesticides between reagent spikes and matrix spikes (fig. 2.) and between groundwater and stream-water matrix spikes (fig. 4) were highly correlated (fig. 5). Pesticides with higher recovery in matrix spikes than in reagent spikes generally had higher recovery in stream-water matrix spikes than in groundwater matrix spikes. The reason for the correlation might be that the matrix of reagent water is more similar to groundwater than to stream water. Potentially important matrix characteristics might be ionic strength, dissolved organic carbon, or pH. Three pesticides were notable outliers in the correlation: desulfinylfipronil and desulfinylfipronil amide had higher recoveries in stream water than in groundwater but had similar recoveries in reagent water and matrix water, whereas *cis*-permethrin had higher recoveries in groundwater than in stream water but had higher recoveries in matrix water than in reagent water (figs. 2, 4, and 5). The lower recovery of *cis*-permethrin in stream samples might be related to dissolved organic carbon, which can affect retention of hydrophobic compounds during extraction. The hydrophobic pesticides are hypothesized to bind to dissolved organic carbon in the stream samples and thus be less available for interaction with the C-18 phase of the SPE column (Wijayaratne and Means, 1984). Streams typically have higher concentrations of dissolved organic carbon than groundwater does, so the effect on recovery would be greater for stream water.

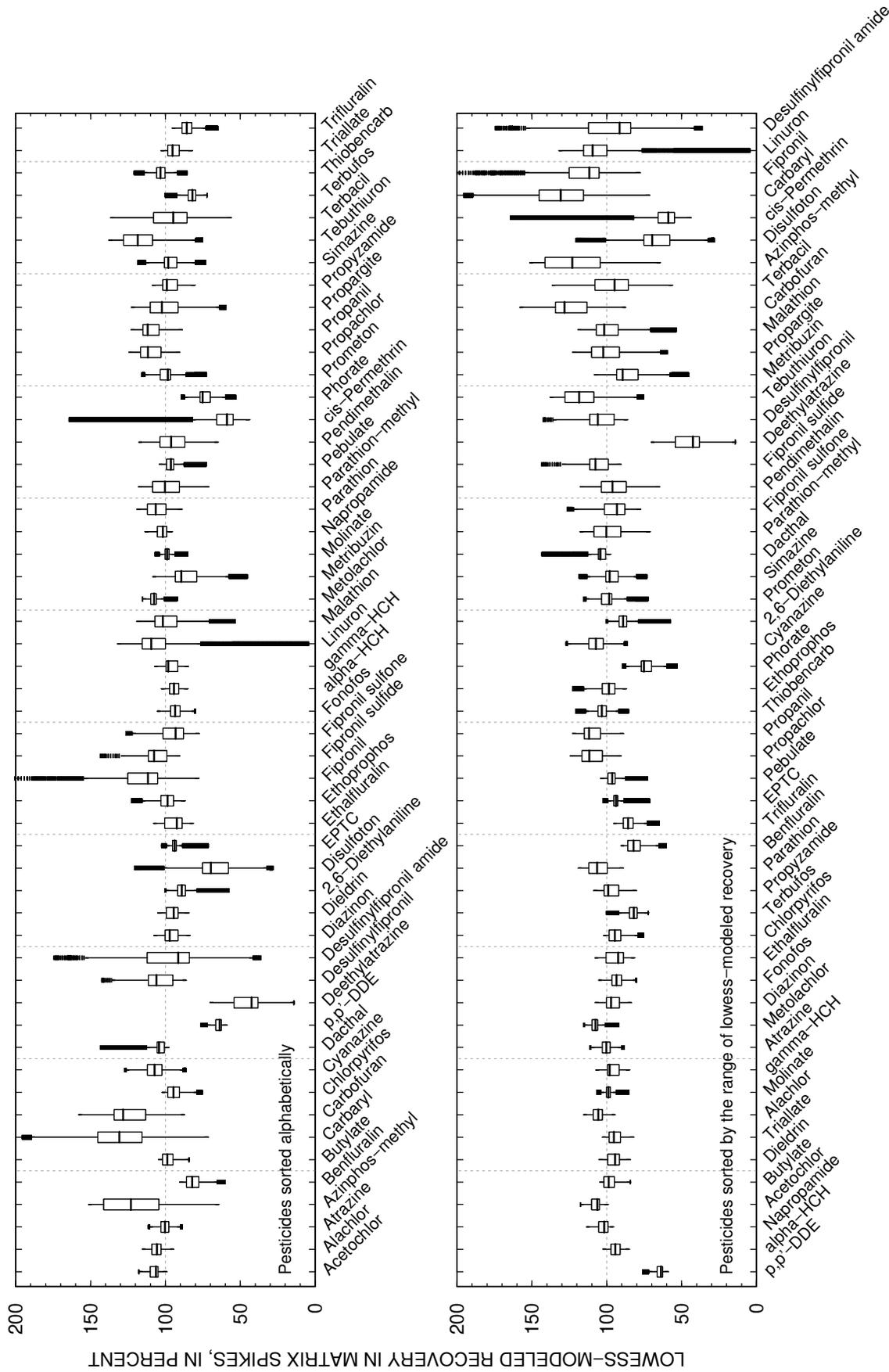


Figure 3. Range of modeled temporal changes in recovery in matrix spikes. Boxplots show the range of lowess-modeled recovery, by pesticide, for each day in the time period from the first matrix spike to the last matrix spike, inclusive. Boxplots are explained in figure 1. (The maximum modeled recovery for fipronil, 205.4 percent, is not shown in the figure.)

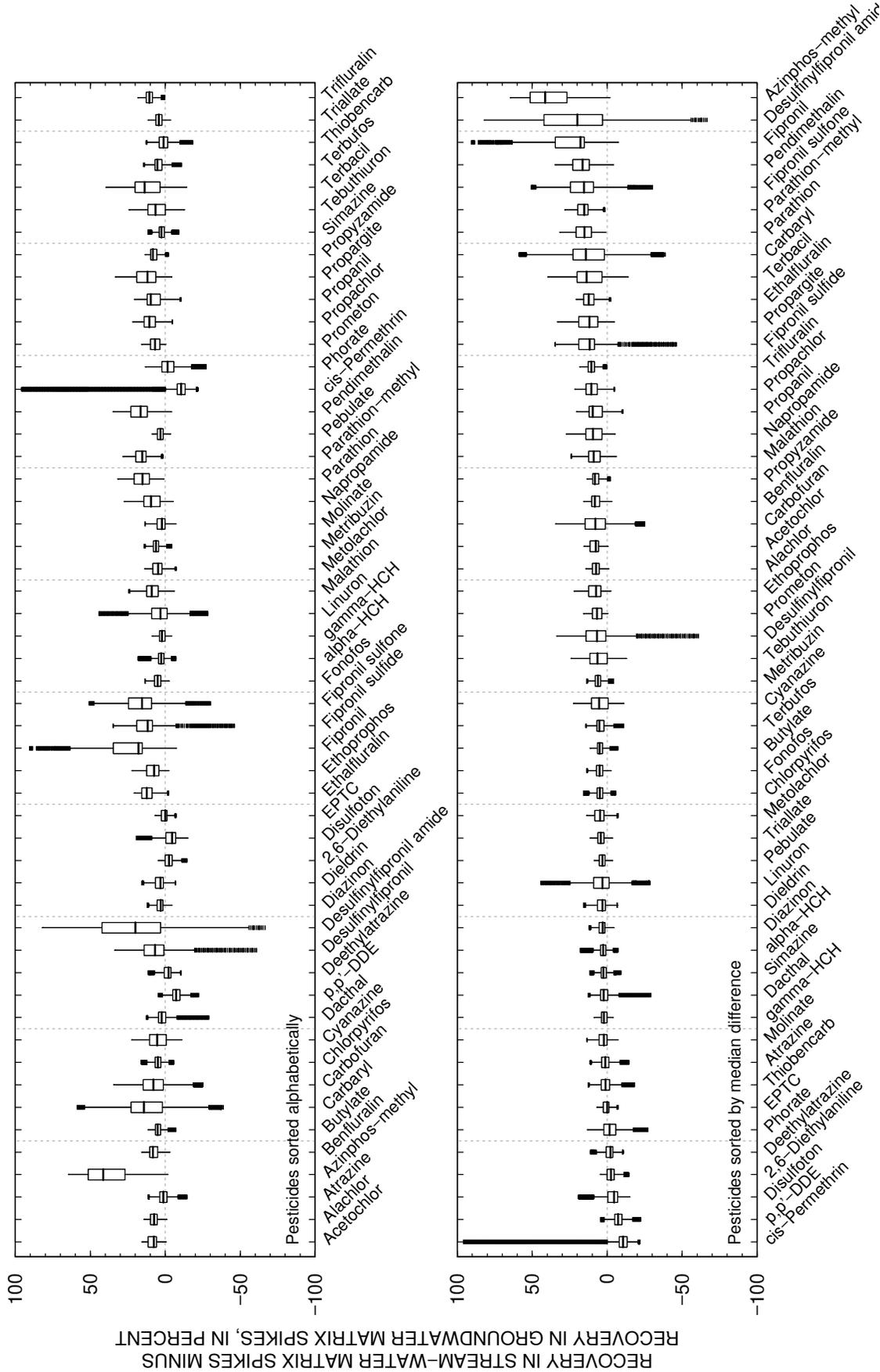


Figure 4. Differences in modeled recovery between groundwater and stream-water matrix spikes. Difference in recovery was calculated as recovery in stream-water matrix spikes minus recovery in groundwater matrix spikes for each date with modeled recovery for both types of spikes. Boxplots are explained in figure 1. (Differences greater than 100 percent recovery or less than -100 percent recovery are not shown).

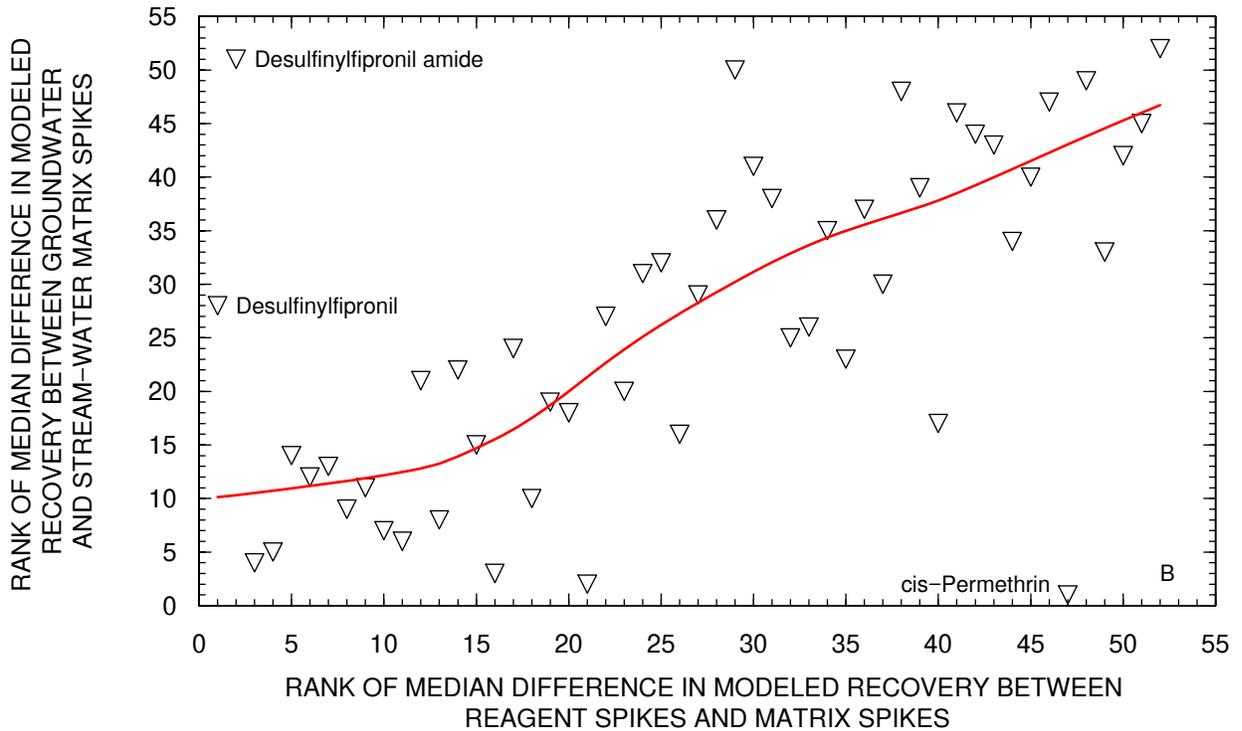
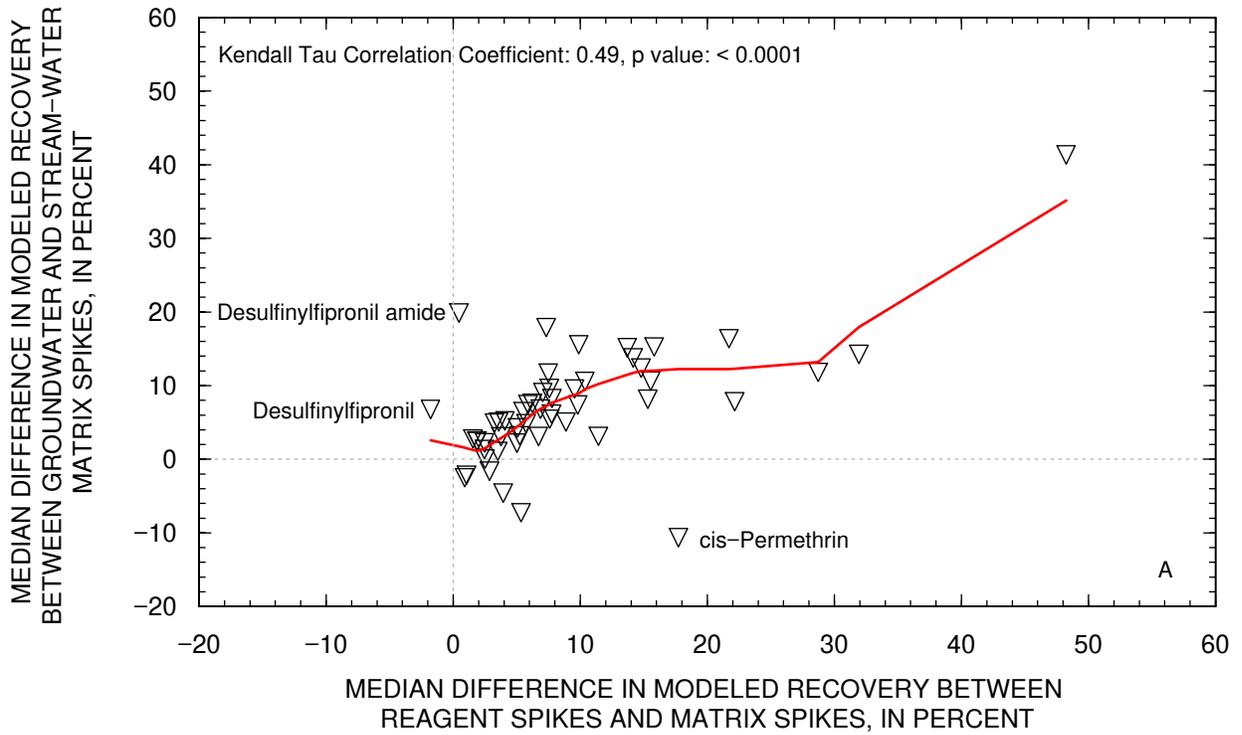


Figure 5. Relation of differences in recovery between groundwater and stream-water matrix spikes to differences in recovery between reagent spikes and matrix spikes for 52 pesticides. Positive differences (panel A) indicate greater recovery in stream-water matrix spikes than in groundwater matrix spikes or indicate greater recovery in matrix spikes than in reagent spikes.

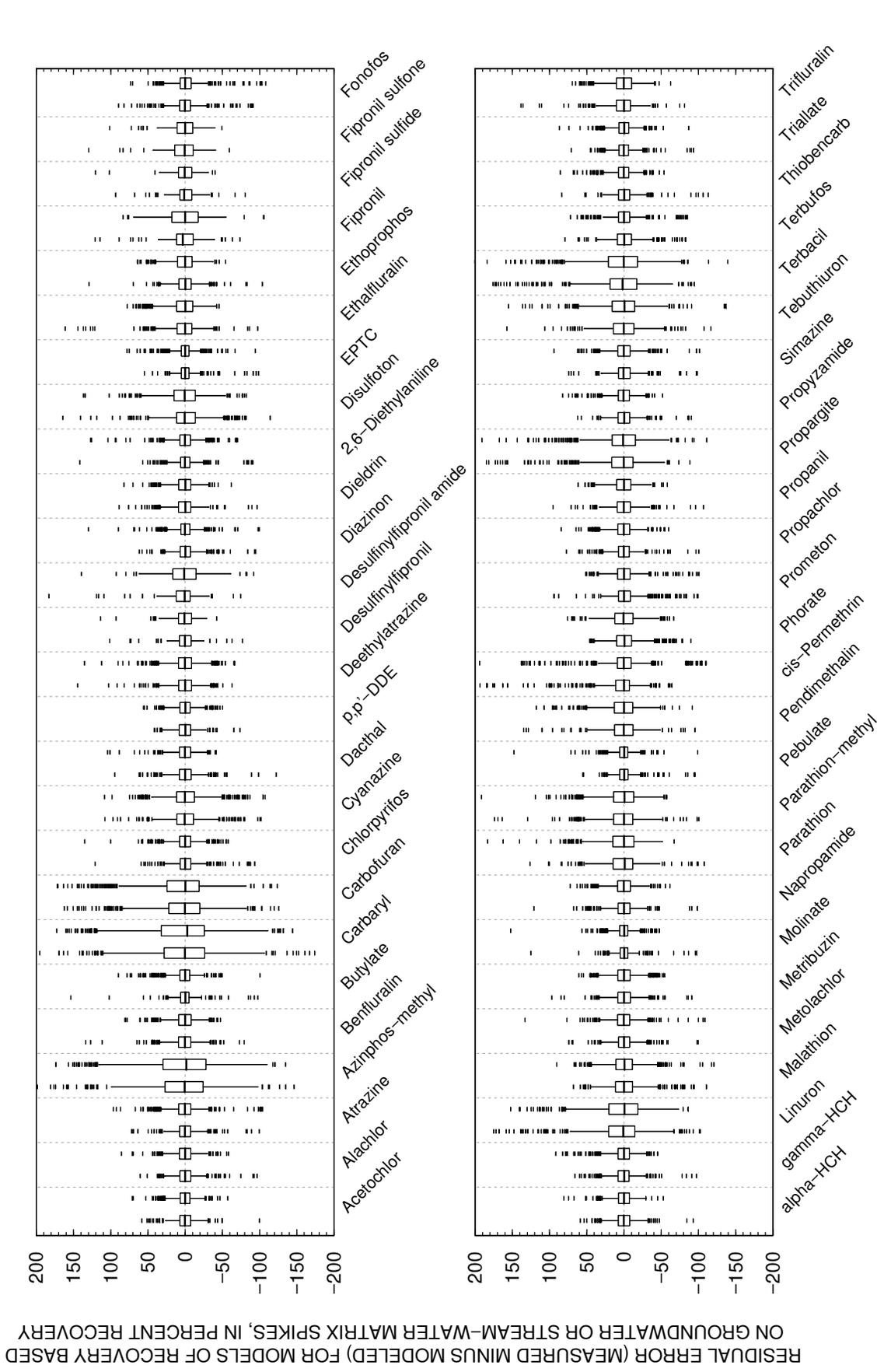


Figure 6. Distribution of residual errors in models of recovery based on groundwater or stream-water matrix spikes. Errors for groundwater are plotted on the left side of the panel and errors for stream water are plotted on the right side. Lowess models of recovery are shown in appendix 5. Boxplots are explained in figure 1. (Residual errors greater than 200 percent or less than -200 percent are not shown).

Model Performance

Model performance was evaluated by examining the distribution of residual errors (measured recovery minus modeled recovery) in recovery modeled from groundwater and stream-water matrix spikes (fig. 6). In general, residual errors were symmetric about zero and were similarly distributed for groundwater and stream-water models. This is expected because lowess models the center of the data, and the robustness feature of lowess ensures that little weight is assigned to outliers. Pesticides with the smallest residual errors included butylate, diazinon, EPTC, molinate, and pebulate, whereas those with the largest residual errors included azinphos-methyl, carbaryl, carbofuran, linuron, and terbacil. Pesticides with the largest residual errors are those that exhibit the most variability in recovery in the analytical method.

Model performance also was evaluated for groundwater matrix spikes and for stream-water matrix spikes by NAWQA Study Unit (appendix 6, fig. 7) and for stream-water matrix spikes by stream-water site for the 67 sites with 7 or more matrix spikes (appendix 7). The distributions of residual errors for each group (Study Unit or stream-water site) were plotted as side-by-side boxplots and PROC TTEST of SAS/STAT version 8 (SAS Institute Inc. [n.d.]) was used to determine whether the mean of the residuals for each group was significantly different from zero ($p < 0.01$). T-tests were done for groups with two or more residuals. A mean residual error significantly different from zero ($p < 0.01$) by more the 10 percent was selected as a threshold to identify “potentially important” recovery model bias for a Study Unit or stream-water site. The 10-percent threshold ensures that groups are not identified as having recovery model bias simply because of a large sample size.

Application of the 10-percent threshold to the 4,686 t-tests done by media and Study Unit (appendix 6) identified 231 combinations of Study Unit and pesticide with potentially important recovery model bias (92 for groundwater and 139 for stream water). Pesticides that exhibited frequent model bias for Study Units include *cis*-permethrin (fig. A6–39) and carbaryl (fig. A6–7) for groundwater and malathion (fig. A6–30), propargite (fig. A6–44), and terbacil (fig. A6–48) for stream water.

Some Study Units had a large number of pesticides with potentially important recovery model bias (number of pesticides in parenthesis): PODL (9), ALBE (8), ALMN (7), and COOK (7) for groundwater and OAHU (21), OZRK (19), LINJ (13), and LERI (11) for stream water (appendix 6; fig. 7). Within a Study Unit and media, the direction of potentially important model bias typically was consistent across pesticides. For example, all 21 of the OAHU and all 19 of the OZRK pesticides in stream-water matrix spikes were biased low, whereas all 13 of the LINJ and all 11 of the LERI pesticides in stream-water matrix spikes were biased high. For groundwater, 21 Study Units had two or more pesticides with model bias; and in 16 of the Study Units, the direction of bias was consistent across pesticides. For stream water, 21 Study Units had two or more pesticides with model bias; and

in 17 of the Study Units, the direction of bias was consistent across pesticides. The reasons why (1) some Study Units have many pesticides with potentially important recovery model bias and (2) the direction of bias typically is consistent across pesticides within a Study Unit and media is not known but might be associated with the chemical, physical, or biological properties of water common in the Study Unit (matrix effects) or, for some Study Units such as OAHU, a small number of matrix spikes.

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery

Pesticide recovery in groundwater and stream water was modeled by lowess for each day in the 1992–2006 period. Recovery for dates prior to the first matrix spike was modeled by assigning the lowess-modeled recovery for the date of the first spike to all previous dates. Recovery for dates after the last matrix spike was modeled by assigning the lowess-modeled recovery for the date of the last spike to all subsequent dates. Modeled recovery was extrapolated beyond the period of record for spikes in order to provide an estimate of the recovery for environmental samples collected beyond the period of record for matrix spikes.

Data files of modeled recovery in groundwater matrix spikes and in stream-water matrix spikes are in appendix 8 and appendix 9, respectively. Data files of modeled recovery may be used to adjust concentrations of pesticides measured in groundwater or stream-water samples to 100 percent recovery. The sample-collection date of the water sample should be matched with the “dates” variable in the data files in appendixes 8 and 9. In general, nondetections of pesticides should not be adjusted for recovery. See Martin, 2009, p. 15–17, for an example application of recovery adjustment for trend analysis.

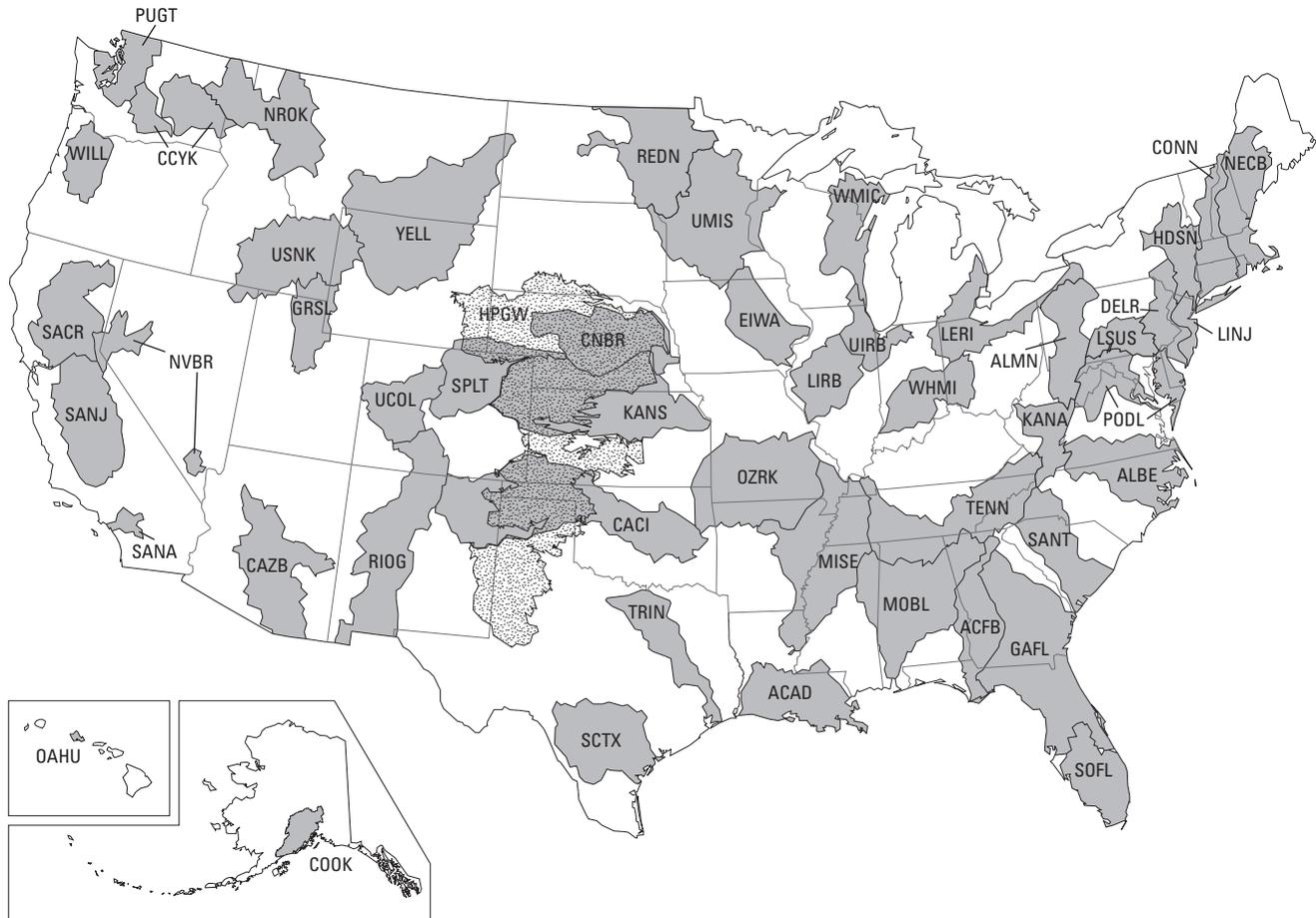
Concentrations should be adjusted as follows:

$$C_{\text{adjusted}} = (C_{\text{measured}} / [R_{\text{predicted}} / 100]) \quad (4)$$

where

C_{adjusted}	is the recovery-adjusted concentration of the pesticide in the water sample, in micrograms per liter,
C_{measured}	is the measured concentration of the pesticide in the water sample, in micrograms per liter, and
$R_{\text{predicted}}$	is the lowess-modeled recovery, in percent (the “predict” variable in the data files in appendixes 8 and 9).

Model users should clearly state in their reports that concentration data have been adjusted for modeled recovery in matrix spikes and should consider publishing both unadjusted and recovery-adjusted data, as was done in Martin (2009, appendix 5a).



Study Units

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

Figure 7. Study Units of the National Water-Quality Assessment (NAWQA) Program, 2009.

Limitations of Modeled Recovery

The models of recovery presented in this report are useful for adjusting pesticide concentrations to 100 percent recovery, but model users should be cognizant of some of the limitations of the models. This section of the report discusses (1) model limitations related to potentially important model bias for selected regions or sites and (2) potential bias for pesticide concentrations substantially different from those that were typically spiked.

The Study Unit and stream-water site residual-error analysis identified potentially important recovery model bias on a regional or site scale (see section “Model Performance”). Study Units and stream-water sites with a recovery model bias, as identified in appendixes 6 and 7, also can be considered regions or sites where recovery in matrix spikes is much larger or smaller than in the majority of matrix spikes (perhaps because of matrix effects). Application of the recovery models to regions or sites with potentially important recovery model bias is not expected to adversely affect time-trend analysis for these regions or sites because, even though the recovery-adjustment factor may be biased, time-trend analysis primarily assesses relative changes in concentrations through time and a uniform bias would not affect trend analysis. More caution should be used in the application of the recovery models to regions or sites with potentially important recovery model bias for other analysis objectives, such as mass-balance studies or comparisons of concentrations to water-quality benchmarks. Options include (1) development of alternative models, (2) application of the existing, biased model if the recovery-adjustment factor from the model is much greater than the recovery model bias, or (3) application of the existing, biased model with a supplementary correction for model bias.

The vast majority of matrix spikes used to develop models of recovery were spiked at concentrations that increased background pesticide concentrations (if any) by approximately 0.1 µg/L. Recoveries at concentrations much higher or lower than 0.1 µg/L are not well documented by matrix spikes. An experiment was done in 1997 and 1998 to investigate recovery of 16 selected pesticides at spiked concentrations of 2 to 20 µg/L. All stream-water matrix spikes collected from March through December 1997 and from June through October 1998 were classified as “high” or “normal” concentration spikes, and recoveries were plotted as side-by-side boxplots (fig. 8) to investigate the influence of concentration on recovery. “High” spiked concentrations were 2 to 6 µg/L for all pesticides except alachlor, cyanazine, dacthal, deethylatrazine, and metolachlor which were spiked at 3 to 10 µg/L; and atrazine, which was spiked at 3 to 20 µg/L. (Lot numbers for high-concentration spike solutions are 65605 and 75100 (appendix 1), and concentrations spiked can be determined from information in appendix 3.)

T-tests of the effect of spiked concentration on recovery showed no significant difference in recovery ($p < 0.01$) for butylate, carbaryl, dacthal, deethylatrazine, malathion, prometon, propargite, or simazine (table 4). Recovery was significantly larger in high concentration than normal concentration spikes for acetochlor, alachlor, atrazine, diazinon, and metolachlor and was significantly smaller for carbofuran, cyanazine, and metribuzin. For pesticides with significant differences in recovery, the difference in mean recovery between the concentration classes ranged from 10 percent for diazinon and metolachlor to 54 percent for carbofuran (table 4).

For most of the pesticides with significant differences in recovery between concentration classes, recovery bias was in the same direction for both normal-concentration and high-concentration spikes, but recovery in normal-concentration spikes was closer to 100 percent recovery than recovery in high-concentration spikes (fig. 8). For these pesticides, application of the recovery models will adjust high concentrations in the correct direction, but the modeled adjustment factors are insufficient (too small) to fully adjust high concentrations to 100 percent recovery; that is, application of the recovery models to high concentrations will produce adjusted concentrations that are closer to the expected “true” environmental concentration than the unadjusted data. For carbofuran and cyanazine, however, recovery in high-concentration spikes is biased low (cyanazine) or not biased (carbofuran), whereas recovery in normal-concentration spikes is biased high (fig. 8). Application of the recovery models (a generally downward adjustment in concentration) to high concentrations of carbofuran and cyanazine is expected to produce adjusted concentrations that are more biased than the unadjusted high concentrations.

Users of the recovery models should understand the distribution of high pesticide concentrations in their datasets prior to application of the models, particularly for time-trend analysis. For example, given a time series where cyanazine concentrations start high and end low (a downward trend), application of the cyanazine recovery model is expected to produce a time series of adjusted concentrations where the initial high concentrations are biased low but the later low concentrations are not biased. Trend tests on the adjusted time series will result in trend slopes that are biased low. Options for addressing situations where recovery at high concentration is not biased or where recovery bias between normal and high concentrations is in opposite directions include (1) application of the recovery model only to low concentrations and (2) application of the recovery model to all concentrations, with a supplementary correction for model bias at high concentrations.

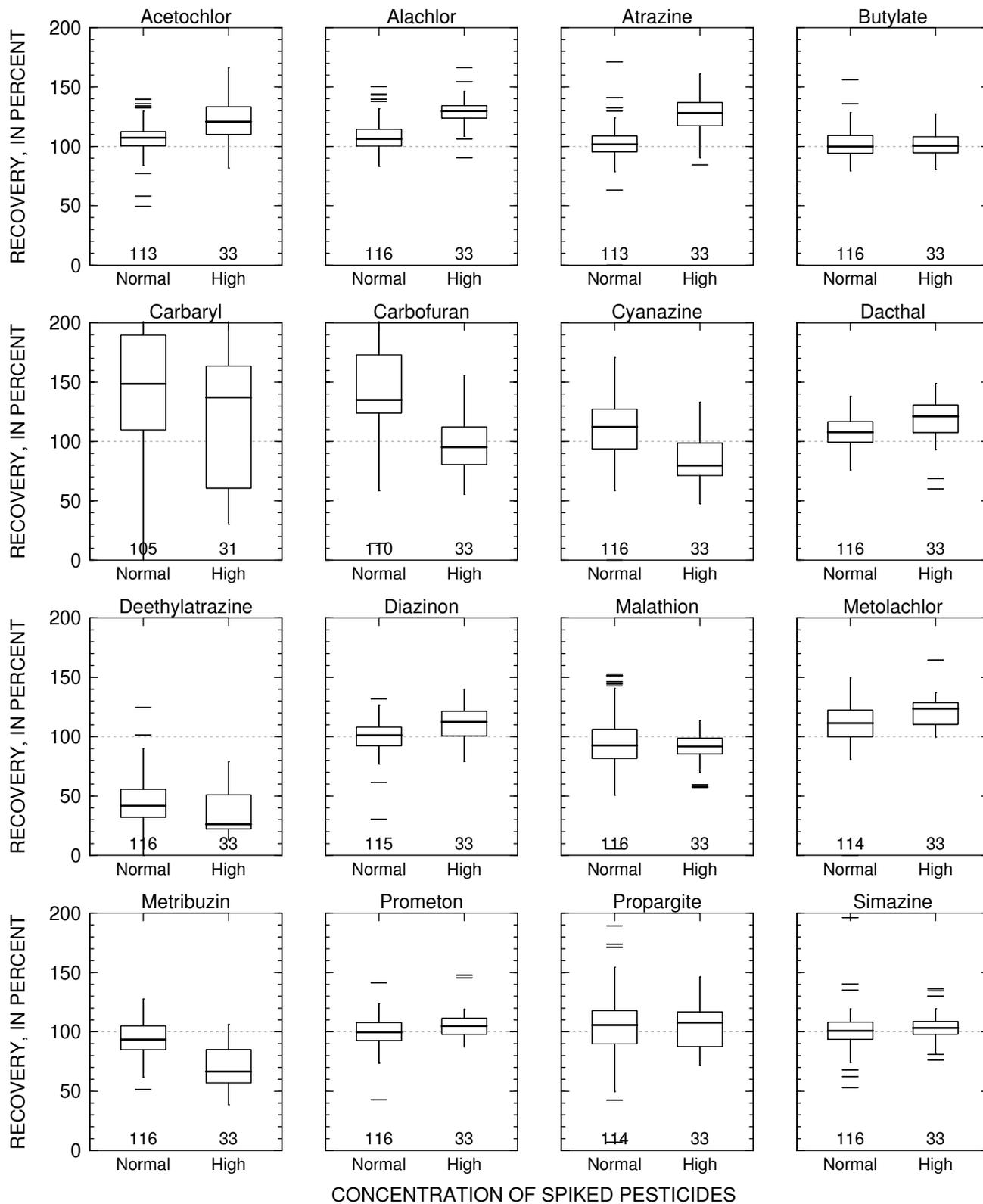


Figure 8. Comparison of recovery of 16 pesticides spiked at normal concentrations (0.09 to 0.5 µg/L) to recovery at high concentrations (2 to 20 µg/L). The number of matrix spikes is shown at the bottom of the boxplot. Boxplots are explained in figure 1. (Recoveries greater than 200 percent are not shown).

Table 4. Results of t-tests for differences in recovery of 16 pesticides spiked at normal concentrations (0.09 to 0.5 µg/L) and at high concentrations (2 to 20 µg/L).

[p, the probability of obtaining a t-test result as extreme as that obtained solely by chance]

Pesticide	"Normal" concentration stream-water matrix spikes			"High" concentration stream-water matrix spikes			Results of t-tests	
	Number	Mean recovery (percent)	Concentration spiked (µg/L)	Number	Mean recovery (percent)	Concentration spiked (µg/L)	p	Difference in mean recovery, high minus normal (percent)
Acetochlor	113	106.5	0.1–0.3	33	121.0	2–6	0.0002	14.5
Alachlor	116	108.1	0.1–0.5	33	128.0	3–10	0.0001	19.9
Atrazine	113	102.0	0.1–0.5	33	124.9	3–20	0.0001	22.9
Butylate	116	102.2	0.09–0.5	33	101.8	2–6	0.87	-0.4
Carbaryl	105	147.2	0.1–0.5	31	121.5	2–6	0.051	-25.7
Carbofuran	110	149.7	0.09–0.5	33	96.0	2–6	0.0001	-53.7
Cyanazine	116	112.2	0.09–0.5	33	84.9	3–10	0.0001	-27.3
Dacthal	116	107.4	0.09–0.5	33	118.6	3–10	0.019	11.2
Deethylatrazine	116	44.8	0.1–0.5	33	35.9	3–10	0.026	-8.9
Diazinon	115	100.1	0.09–0.5	33	110.5	2–6	0.0013	10.4
Malathion	116	94.0	0.1–0.5	33	89.7	2–6	0.19	-4.3
Metolachlor	114	110.2	0.09–0.5	33	120.5	3–10	0.0008	10.3
Metribuzin	116	94.1	0.09–0.5	33	70.2	2–6	0.0001	-23.9
Prometon	116	100.0	0.1–0.5	33	106.5	2–6	0.017	6.5
Propargite	114	106.0	0.09–0.5	33	104.7	2–6	0.76	-1.3
Simazine	116	100.9	0.1–0.5	33	104.2	2–6	0.29	3.3

Future Investigations

This study examined temporal changes in pesticide recovery in laboratory reagent spikes and in groundwater and stream-water matrix spikes and concluded that similar patterns of change in these types of spikes were consistent with temporal changes in the performance (bias) of the GCMS analytical method. Matrix effects also were identified as important factors influencing recovery, and models of temporal changes in recovery were developed separately for groundwater and surface-water samples. Potentially important model bias was evaluated by NAWQA Study Unit and, for sites with sufficient data, by stream-water site. Although matrix effects were addressed by separating groundwater and stream-water spikes and assessing model bias by groups of sites, it is highly unlikely that all of the sites in a group or all of the samples at a site have the same matrix. The chemical, physical, and biological properties of the individual water sample undoubtedly influence pesticide recovery in that sample. Future investigations of recovery should attempt to determine the specific matrix factors that most influence pesticide recovery. It is beyond the scope of this section to suggest the specific analytical approach to develop an understanding of important matrix factors, but a multivariate approach that examines the influence of the water-quality constituents and properties that are routinely measured when pesticides are measured is a logical starting point.

Summary

Recovery is a primary indicator of the analytical bias of a measurement. For pesticides, recovery is measured by analysis of quality-control (QC) water samples that have known amounts of pesticides added ("spiked" QC samples). Recovery is the measured amount of pesticide in the spiked QC sample expressed as percentage of the amount spiked, ideally 100 percent. Temporal changes in recovery have the potential to adversely affect time-trend analysis of pesticide concentrations by introducing trends in environmental concentrations that are caused by trends in performance of the analytical method rather than by trends in pesticide use or other environmental conditions.

This report examines temporal changes in the recovery of 44 pesticides and 8 pesticide degradates (hereafter referred to as "pesticides") that were selected for a national analysis of time trends in pesticide concentrations in streams (Martin, 2009). Water samples were analyzed for these pesticides from 1992 to 2006 by gas chromatography/mass spectrometry. Recovery of pesticides was measured by analysis of pesticide-spiked QC water samples prepared either by analysts of the National Water Quality Laboratory or by field personnel of the National Water Quality Assessment Program. Temporal changes in pesticide recovery were investigated by calculating robust, locally weighted scatterplot smooths (lowess smooths)

for the time series of pesticide recoveries in 5,132 laboratory reagent spikes; 1,234 stream-water matrix spikes; and 863 groundwater matrix spikes. A 10-percent smoothing window was selected to show broad changes in recovery over a 6- to 12-month time scale for most of the 52 pesticides. The time period associated with the smoothing window varies with data density—but was typically about 15 to 17 months for most pesticides.

Temporal patterns in recovery were similar (in phase) for laboratory reagent spikes and for matrix spikes for most pesticides. In-phase temporal changes among spike types supports the hypothesis that temporal changes in method performance (which would affect both types of spikes) is the primary cause of temporal changes in recovery rather than temporal changes in the matrix of water samples spiked or other causes. Although temporal patterns of recovery were in phase for most pesticides, recovery in matrix spikes was greater than recovery in reagent spikes for nearly every pesticide. Recovery was more than 5 percent larger in matrix spikes for 35 of the 52 pesticides and more than 10 percent larger for 14 of the 52. Models of recovery based on matrix spikes are deemed more appropriate for adjusting concentrations of pesticides measured in groundwater and stream-water samples than models based on laboratory reagent spikes. Models of recovery based on matrix spikes were selected because (1) matrix spikes are expected to more closely match the matrix of environmental water samples than are reagent spikes and (2) method performance is often matrix dependent, as was shown by higher recovery in matrix spikes for many of the pesticides.

Models of recovery, based on lowess smooths of matrix spikes, were developed separately for groundwater and stream-water samples. The distribution of residual errors in recovery modeled from matrix spikes were, in general, symmetric about zero and similarly distributed for groundwater and stream-water models. This is expected because lowess models the center of the data, and the robustness feature of lowess ensures that little weight is assigned to outliers.

Model performance was evaluated for groundwater matrix spikes and for stream-water matrix spikes by NAWQA Study Unit and for stream-water matrix spikes by stream-water site for the 67 sites with 7 or more matrix spikes. The distributions of residual errors for each group were plotted as side-by-side boxplots, and t-tests were used to determine whether the mean of the residuals for each group was significantly different from zero ($p < 0.01$). Potentially important recovery model bias for a Study Unit or stream-water site is indicated where mean residual error is significantly different from zero ($p < 0.01$) and differs from zero by more the 10 percent for a Study Unit or a stream-water site.

Some Study Units had a large number of pesticides with potentially important recovery model bias. Within a Study Unit, the direction of potentially important model bias typically was consistent across pesticides. The reasons why (1) some Study Units have many pesticides with potentially important recovery model bias and (2) the direction of bias typically is consistent across pesticides within a Study Unit is

not known but might be associated with the chemical, physical, or biological properties of water common in the Study Unit (matrix effects) or, for some Study Units, a small number of matrix spikes.

Pesticide recovery in groundwater and stream water was modeled by lowess for each day in the 1992–2006 period. Recovery for dates prior to the first spike was modeled by assigning the lowess-modeled recovery for the date of the first spike to all previous dates. Recovery for dates after the last spike was modeled by assigning the lowess-modeled recovery for the date of the last spike to all subsequent dates. Modeled recovery was extrapolated beyond the period of record for spikes in order to provide an estimate of the recovery for environmental samples collected beyond the period of record for spikes. The models of recovery can be used to adjust concentrations of pesticides measured in groundwater or stream-water samples to 100 percent recovery to compensate for temporal changes in the performance (bias) of the analytical method. Model users should clearly state in their reports that concentration data have been adjusted for modeled recovery and should consider publishing both unadjusted and recovery-adjusted data.

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Appendixes

Appendixes are separate online documents, accessible at <http://pubs.usgs.gov/sir/2009/5189/>.

1. Data file of pesticide concentrations in spike solutions
2. Data file of recovery of pesticides in laboratory reagent spikes
3. Data file of recovery of pesticides in matrix spikes
4. Comparison of temporal changes in recovery of pesticides in laboratory reagent spikes and in matrix spikes
5. Comparison of temporal changes in recovery of pesticides in groundwater matrix spikes and in stream-water matrix spikes
6. Distribution of residual errors in models of recovery by NAWQA Study Unit
7. Distribution of residual errors in modeled recovery for selected stream-water sites
8. Data file of modeled recovery of pesticides in groundwater, 1992–2006
9. Data file of modeled recovery of pesticides in stream water, 1992–2006

