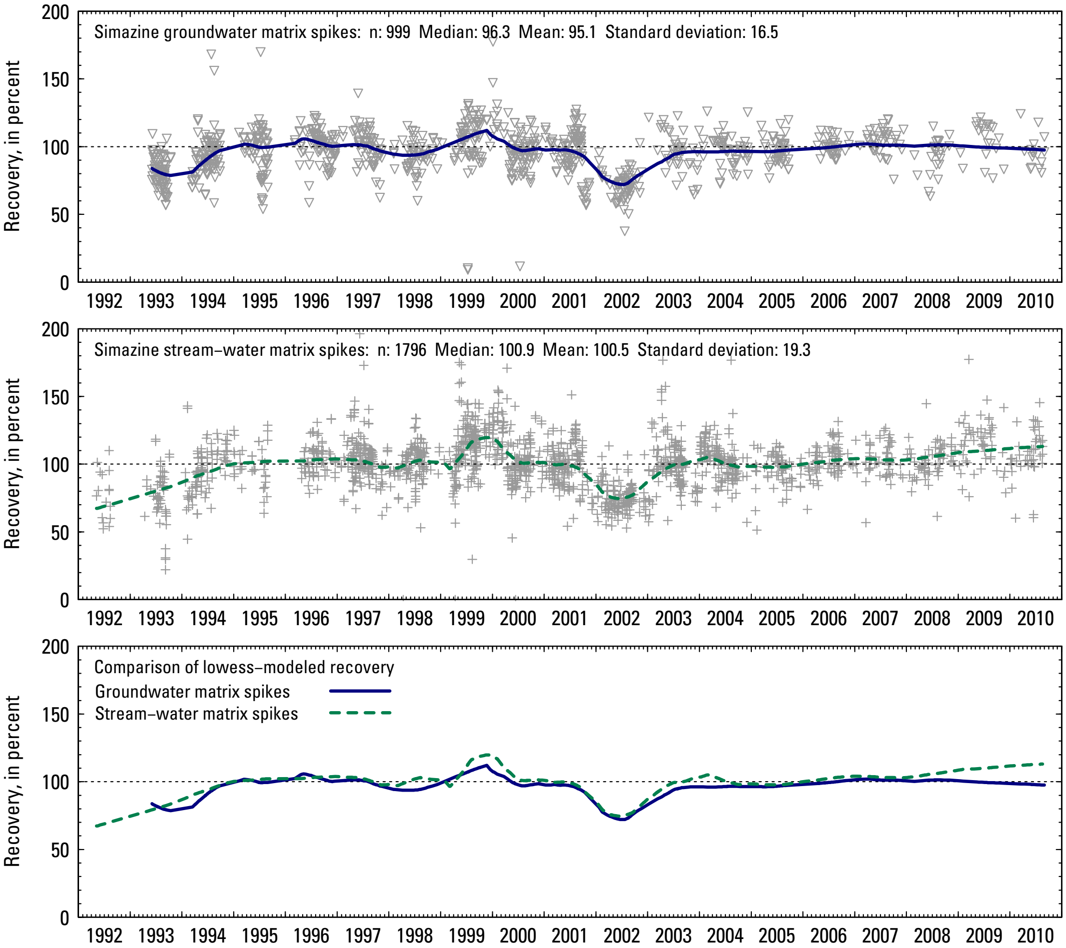
National Water-Quality Assessment Program

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2010



Data Series 630

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

Cover image: Example graphs showing temporal changes in analytical recovery of simazine in groundwater and surface-water matrix spikes from 1992 through 2010. Similar graphs for 43 other pesticides and 8 pesticide degradates are given in appendix 3 of this report.

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2010

By Jeffrey D. Martin and Michael Eberle

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Foreword

The U.S. Geological Survey (USGS) is committed to providing the Nation with reliable 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, 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 quality 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. From 1991 to 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/studies/study_units.html*).

National and regional assessments are ongoing in the second decade (2001–2012) of the NAWQA Program as 42 of the 51 Study Units are selectively reassessed. These assessments extend the findings in the Study Units by determining water-quality 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 studies 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. In addition, national syntheses of information on pesticides, volatile organic compounds (VOCs), nutrients, 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.

William H. Werkheiser

USGS Associate Director for Water

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Conversion Factors and Abbreviations

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.

Abbreviations used in the report

DWH	Data Warehouse
GCMS	gas chromatography/mass spectrometry
lowess	locally weighted scatterplot smooths
NASQAN	National Stream Quality Accounting Network
NAWQA	National Water-Quality Assessment
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
QC	quality control
SPE	solid-phase extraction
USGS	U.S. Geological Survey

Adjustment of Pesticide Concentrations for Temporal Changes in Analytical Recovery, 1992–2010

By Jeffrey D. Martin and Michael Eberle

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 a 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 apparent 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 presents data and models related to 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 through 2010 by gas chromatography/mass spectrometry. Recovery was measured by analysis of pesticide-spiked QC water samples.

Models of recovery, based on robust, locally weighted scatterplot smooths (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 1993–5 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.

Subsequently, Martin and others (2009) did a detailed study of recovery of pesticides in laboratory reagent spikes and in groundwater and stream-water matrix spikes (environmental water samples spiked with known amounts of target analytes) analyzed by NWQL during 1992–2006. As part of that study, Martin and others (2009) developed models of recovery based on recovery in groundwater and stream-water matrix spikes that could be used to adjust pesticide concentrations measured in environmental water samples for temporal changes in recovery for that time period. Such models are needed for certain types of water-quality assessments, including time-trend analysis.

In January 2011, similar procedures were used to obtain, screen, and prepare pesticide data for the period 1992–2010. Models of recovery were developed similar to those reported by Martin and others (2009), and an updated pesticide-dataset trend analysis was developed similar to that reported by Martin (2009).

Purpose and Scope

This report updates and supplements Martin and others (2009) by providing datasets and recomputed models for 1992–2010, an additional 4 years of data. These expanded datasets include analyses resulting from the USGS National Stream Quality Accounting Network (NASQAN), as well as the USGS National Water-Quality Assessment (NAWQA) Program; datasets and models in Martin and others (2009) were based on NAWQA data only.

The 44 pesticides and 8 pesticide degradates (hereafter referred to as "pesticides") were initially selected for a national analysis of time trends in pesticide concentrations in streams (Martin, 2009). Water samples were analyzed for these pesticides from 1992 through 2010 by gas chromatography/mass spectrometry (referred to as the "GCMS" method in this report). Recovery of pesticides was measured by analysis of pesticide-spiked QC water samples prepared by field personnel of either the NAWQA Program or NASQAN. Temporal changes in recovery were examined by scatterplot smooths of time-series plots of pesticide recovery in 1,819 stream-water matrix spikes and 999 groundwater matrix spikes. Models of recovery, based on robust, locally weighted scatterplot smooths (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 provides datasets of measured and modeled recoveries and a brief overview of methods. Additional details about the analytical methods, procedures used to investigate and model temporal changes in recovery, and regional or site-specific variations in recovery can be found in Martin and others (2009).

Analytical Method for Pesticides

The recovery data discussed in this report are applicable to water-quality samples analyzed during 1992–2010 by NWQL using GSMS. Pesticides are isolated from filtered water samples by C-18 solid-phase extraction (SPE) 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 acetochlor 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 the GCMS method 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 the GCMS method 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. Approaches and considerations in the measurement and use of recovery information are presented in Thompson and others (1999), whereas considerations for spiking water samples are given in American Society for Testing and Materials (2000, p. 770–774). Details of recovery procedures germane to the data in this report can be found in Martin and others (2009), but a brief discussion of spike solutions—matrix spikes in particular—is offered here.

Spike solutions of pesticides at known concentrations in solvents are prepared by NWQL personnel or by commercial vendors according to NWQL specifications and 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 provided in appendix 1.

In the original pesticide-recovery study by Martin and others (2009), matrix spikes (as opposed to laboratory-prepared spikes of reagent-grade blank water) were ultimately selected for recovery-model development. Matrix spikes are QC environmental water samples that typically are prepared by scientists responsible for the collection of stream-water and groundwater samples. 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). 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. 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 matrix

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[1] Burns and others (2002) prefer the term "apparent recovery."

Table 1. Pesticides analyzed by the gas chromatography/mass spectrometry (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 Services^{SM}); LT-MDL, long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Figure number in appendix 3	Pesticide	Parameter code	CAS number	Type of pesticide	Parent pesticide (if degradate)	Maximum LT-MDL (µg/L)
1	Acetochlor	49260	34256-82-1	Herbicide	NA	0.005
2	Alachlor	46342	15972-60-8	Herbicide	NA	0.004
3	Atrazine	39632	1912-24-9	Herbicide	NA	0.004
4	Azinphos-methyl	82686	86-50-0	Insecticide	NA	0.06
5	Benfluralin	82673	1861-40-1	Herbicide	NA	0.007
6	Butylate	04028	2008-41-5	Herbicide	NA	0.002
7	Carbaryl	82680	63-25-2	Insecticide	NA	0.1
8	Carbofuran	82674	1563-66-2	Insecticide	NA	0.03
9	Chlorpyrifos	38933	2921-88-2	Insecticide	NA	0.005
10	Cyanazine	04041	21725-46-2	Herbicide	NA	0.02
11	Dacthal	82682	1861-32-1	Herbicide	NA	0.0038
12	*p,p'*-DDE	34653	72-55-9	Degradate	DDT	0.0013
13	Deethylatrazine	04040	6190-65-4	Degradate	Atrazine	0.007
14	Desulfinylfipronil	62170	ND	Degradate	Fipronil	0.006
15	Desulfinylfipronil amide	62169	ND	Degradate	Fipronil	0.015
16	Diazinon	39572	333-41-5	Insecticide	NA	0.003
17	Dieldrin	39381	60-57-1	Insecticide	NA	0.004
18	2,6-Diethylaniline	82660	579-66-8	Degradate	Alachlor	0.003
19	Disulfoton	82677	298-04-4	Insecticide	NA	0.02
20	EPTC	82668	759-94-4	Herbicide	NA	0.0028
21	Ethalfluralin	82663	55283-68-6	Herbicide	NA	0.005
22	Ethoprophos	82672	13194-48-4	Insecticide	NA	0.008
23	Fipronil	62166	120068-37-3	Insecticide	NA	0.02
24	Fipronil sulfide	62167	120067-83-6	Degradate	Fipronil	0.006
25	Fipronil sulfone	62168	120068-36-2	Degradate	Fipronil	0.012
26	Fonofos	04095	944-22-9	Insecticide	NA	0.005
27	*alpha*-HCH	34253	319-84-6	Degradate	*gamma*-HCH	0.004
28	*gamma*-HCH	39341	58-89-9	Insecticide	NA	0.007
29	Linuron	82666	330-55-2	Herbicide	NA	0.03
30	Malathion	39532	121-75-5	Insecticide	NA	0.014
31	Metolachlor	39415	51218-45-2	Herbicide	NA	0.01
32	Metribuzin	82630	21087-64-9	Herbicide	NA	0.014
33	Molinate	82671	2212-67-1	Herbicide	NA	0.002
34	Napropamide	82684	15299-99-7	Herbicide	NA	0.009
35	Parathion	39542	56-38-2	Insecticide	NA	0.01
36	Parathion-methyl	82667	298-00-0	Insecticide	NA	0.008
37	Pebulate	82669	1114-71-2	Herbicide	NA	0.008
38	Pendimethalin	82683	40487-42-1	Herbicide	NA	0.011
39	*cis*-Permethrin	82687	54774-45-7	Insecticide	NA	0.007
40	Phorate	82664	298-02-2	Insecticide	NA	0.027
41	Prometon	04037	1610-18-0	Herbicide	NA	0.007
42	Propachlor	04024	1918-16-7	Herbicide	NA	0.012
43	Propanil	82679	709-98-8	Herbicide	NA	0.007

Table 1. Pesticides analyzed by the gas chromatography/mass spectrometry (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 CASRNs through CAS Client Services^{SM}); LT-MDL, long-term method detection level; µg/L, microgram per liter; NA, not applicable; ND, not determined]

Figure number in appendix 3	Pesticide	Parameter code	CAS number	Type of pesticide	Parent pesticide (if degradate)	Maximum LT-MDL (µg/L)
44	Propargite	82685	2312-35-8	Acaricide	NA	0.02
45	Propyzamide	82676	23950-58-5	Herbicide	NA	0.0021
46	Simazine	04035	122-34-9	Herbicide	NA	0.006
47	Tebuthiuron	82670	34014-18-1	Herbicide	NA	0.014
48	Terbacil	82665	5902-51-2	Herbicide	NA	0.02
49	Terbufos	82675	13071-79-9	Insecticide	NA	0.009
50	Thiobencarb	82681	28249-77-6	Herbicide	NA	0.008
51	Triallate	82678	2303-17-5	Herbicide	NA	0.003
52	Trifluralin	82661	1582-09-8	Herbicide	NA	0.009

spikes are expected to more closely match the matrix of environmental water samples than are reagent spikes, and method performance is often matrix dependent, as has been shown by higher recovery in matrix spikes for most of the pesticides (Martin and others, 2009).

Most matrix spikes analyzed by the NWQL were spiked at the field site (field matrix spikes). In general, approximately 5 percent of the pesticide samples collected for the NAWQA and NASQAN Programs 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:

$$R = [(C_{spiked} - C_{unspiked}) / C_{expected}] \times 100\ \% \qquad (1)$$

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, and is calculated as

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

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.

Sources, Preparation, and Review of Recovery Data

Recovery in matrix spikes was calculated from concentration data for spiked environmental water samples and the associated unspiked water samples that are stored in the NAWQA Data Warehouse (DWH). Water-quality data were obtained from DWH data managers (Jessica L. Thompson, Information Technology Specialist, U.S. Geological Survey, written commun., January 19, 2011). Any water-quality sample in the DWH with analyses of one or more pesticides of interest was retrieved along with selected supporting sample information. Procedures for identification of the matrix spikes and associated ancillary information are described in Martin and others (2009).

A total of 2,902 matrix spike samples were identified in the 1992–2010 dataset. Of these, 42 were removed from the dataset because no matching unspiked environmental sample was identified, 7 were removed because the spiked-sample volume was less than 400 mL, 5 were removed because of the use of an unidentified high-concentration spike solution, 2 were removed because too few pesticides were detected in the sample, 15 were removed because recoveries of pesticides were 2 to 20 times less than the expected recovery, and 13 were removed because recoveries of pesticides were 3 to 7 times greater than the expected recovery. Recoveries of pesticides much greater than or less than expected were assumed to be caused by improper spiking techniques. These sample deletions resulted in a dataset of 2,818 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 0.3 µg/L or higher than at concentrations lower than 0.3 µg/L. Recoveries were deleted from the dataset if background concentrations were greater than or equal to 0.3 µg/L and recovery was less than 50 percent or greater than 200 percent.[2] This criterion resulted in removal of 164 recoveries from the dataset (22 for groundwater and 142 for surface water).

Recoveries for several pesticides were 5 or more times greater than expected. Fifty-three recoveries in excess of 500 percent were assumed to be unrepresentative of method performance and were removed from the dataset.[3] Forty recoveries less than 0 percent were set to 0 percent. The final reviewed matrix spike dataset comprises 2,818 samples and 125,374 estimates of pesticide recovery and spans the period May 1992 through August 2010. 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. The final reviewed matrix spike dataset is provided in appendix 2.

Temporal Changes in Recovery

Temporal changes in pesticide recovery were investigated by calculating 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 groundwater and stream-water matrix spikes. Details about the lowess procedure and its application to the previous 1992–2006 dataset are given in Martin and others (2009). The remainder of this section focuses on pesticide recovery for the expanded 1992–2010 dataset.

Recovery was modeled by using PROC LOESS of SAS/STAT version 8, typically 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). The 10-percent window was used to model broad changes in recovery over a 6- to 12-month time scale for 48 of the 52 pesticides. A 25-percent window was used to model similar changes for fipronil and the four fipronil degradates because of a much reduced period of data. 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.

Boxplots (Helsel and Hirsch, 2002, p. 25) are used to show the distributions of measured recovery in figure 2 and appendix 3. 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 (commonly termed “outliers”) are *omitted* in order to emphasize statistics of central tendency in these figures.

Magnitude of Temporal Changes in Recovery in Matrix Spikes

The magnitude of temporal change in recovery during 1992–2010 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 modeled recovery in groundwater matrix spikes ranged from 14.6 percent for fipronil sulfone to 159.0 percent for *cis*-permethrin (table 2). The median amount of temporal change was 30.0 percent. The magnitude of temporal change in modeled recovery in stream-water matrix spikes ranged from 10.6 percent for *p,p'*-DDE to 126.3 percent for carbaryl (table 2). The median amount of temporal change was 37.2 percent.

Results of the temporal-change analysis are depicted for each pesticide in appendix 3; figure 2 is a sample illustration (for simazine) from that appendix.

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[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). Recovery thresholds of 25 and 100 percent were used for deethylatrazine because deethylatrazine typically has about 50 percent recovery.

[3] Removal of recoveries in excess of 500 percent had negligible effects on models of recovery.

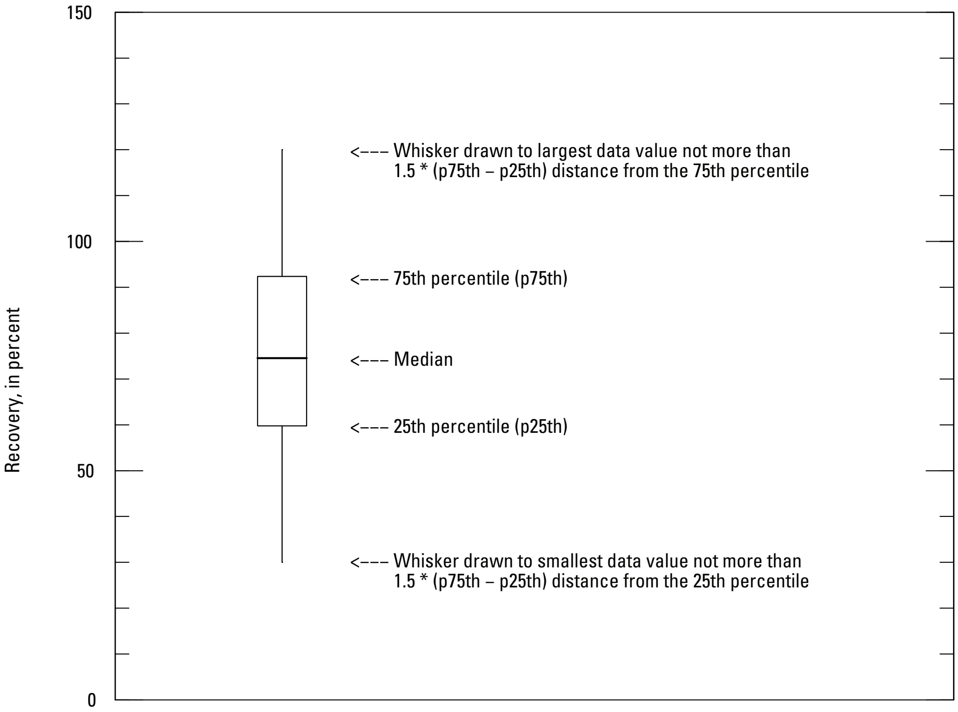

Figure 1. Explanation of boxplots used to depict distributions of recovery. The number of measurements is shown at the top or bottom of the boxplot. Values more extreme than the whiskers are not shown.

Table 2. Summary statistics of temporal change in modeled recovery from the 1992–2010 pesticide dataset.

[SW, surface water; GW, groundwater]

Figure number in appendix 3	Parameter code	Pesticide	Temporal change in modeled recovery (percent)								Median difference in modeled recovery (SW–GW, in percent)
			Groundwater				Surface water				
			Median	Range	Minimum	Maximum	Median	Range	Minimum	Maximum	
1	49260	Acetochlor	102.8	19.0	93.2	112.2	113.0	31.0	102.1	133.1	9.8
2	46342	Alachlor	103.0	15.8	95.9	111.7	111.3	30.4	99.4	129.8	8.0
3	39632	Atrazine	100.6	24.1	87.4	111.6	102.4	26.9	85.9	112.8	2.2
4	82686	Azinphos-methyl	102.5	95.5	49.3	144.8	139.9	92.8	78.5	171.4	38.8
5	82673	Benfluralin	77.0	31.8	57.9	89.7	84.6	37.7	59.8	97.5	8.7
6	04028	Butylate	96.5	19.5	84.0	103.5	101.1	24.7	82.6	107.3	4.0
7	82680	Carbaryl	116.5	126.1	63.3	189.5	125.7	126.3	74.5	200.9	10.0
8	82674	Carbofuran	116.9	79.1	76.3	155.5	126.2	56.1	101.4	157.4	10.6
9	38933	Chlorpyrifos	92.5	15.6	86.0	101.6	99.1	23.3	80.9	104.2	5.6
10	04041	Cyanazine	103.8	32.9	83.2	116.2	108.2	56.2	86.2	142.4	7.7
11	82682	Dacthal	103.7	41.6	96.5	138.0	105.6	15.8	99.2	115.0	2.3
12	34653	*p,p'*-DDE	68.7	29.7	59.8	89.5	61.7	10.6	56.9	67.6	−7.3

Table 2. Summary statistics of temporal change in modeled recovery from the 1992–2010 pesticide dataset.—Continued

Figure number in appendix 3	Parameter code	Pesticide	Temporal change in modeled recovery (percent)								Median difference in modeled recovery (SW–GW, in percent)
			Groundwater				Surface water				
			Median	Range	Minimum	Maximum	Median	Range	Minimum	Maximum	
13	04040	Deethylatrazine	46.7	62.4	24.0	86.4	41.2	84.2	11.3	95.5	−1.9
14	62170	Desulfinylfipronil	99.7	23.5	90.4	114.0	107.8	31.4	97.0	128.4	9.2
15	62169	Desulfinylfipronil amide	94.1	25.0	78.1	103.1	116.8	81.1	80.5	161.6	24.8
16	39572	Diazinon	95.3	25.3	81.0	106.4	99.8	26.7	86.9	113.6	5.1
17	39381	Dieldrin	94.2	18.1	82.2	100.3	95.9	20.9	86.5	107.4	2.5
18	82660	2,6-Diethylaniline	91.8	17.2	85.3	102.5	88.9	36.2	62.7	98.9	−2.2
19	82677	Disulfoton	72.7	88.7	37.0	125.7	68.3	72.7	31.2	103.9	−4.9
20	82668	EPTC	94.2	18.7	84.3	103.0	94.9	33.1	69.3	102.4	0.7
21	82663	Ethalfluralin	85.8	30.9	68.7	99.6	94.7	29.4	82.0	111.4	10.5
22	82672	Ethoprophos	97.1	31.0	82.1	113.1	103.7	54.4	85.9	140.3	9.4
23	62166	Fipronil	101.5	23.9	89.3	113.2	130.6	116.0	67.3	183.4	30.1
24	62167	Fipronil sulfide	98.6	17.0	91.4	108.4	114.5	39.1	103.6	142.7	18.6
25	62168	Fipronil sulfone	84.3	14.6	79.5	94.1	97.9	39.9	87.9	127.8	14.8
26	04095	Fonofos	91.4	20.0	78.3	98.2	96.4	28.9	79.6	108.5	5.1
27	34253	*alpha*-HCH	93.7	23.5	79.1	102.6	95.7	17.0	86.9	103.9	2.2
28	39341	*gamma*-HCH	97.0	23.3	84.2	107.4	99.3	21.7	85.8	107.5	1.6
29	82666	Linuron	108.6	119.4	28.6	148.0	114.9	123.0	13.4	136.4	4.4
30	39532	Malathion	98.1	37.9	72.2	110.1	106.3	63.6	60.7	124.4	8.6
31	39415	Metolachlor	104.5	14.7	100.7	115.4	110.5	23.6	97.7	121.2	5.3
32	82630	Metribuzin	88.1	44.5	54.6	99.2	91.2	76.0	45.5	121.5	6.4
33	82671	Molinate	98.4	20.3	83.9	104.2	100.5	29.5	80.0	109.5	3.0
34	82684	Napropamide	96.7	15.5	90.3	105.8	106.6	36.5	94.7	131.2	9.0
35	39542	Parathion	96.3	31.8	78.8	110.6	112.5	31.0	93.5	124.5	14.6
36	82667	Parathion-methyl	90.7	27.3	75.4	102.6	104.2	53.9	70.7	124.7	16.5
37	82669	Pebulate	95.0	15.2	85.7	100.9	97.9	35.3	73.4	108.7	2.8
38	82683	Pendimethalin	87.5	41.1	62.8	104.0	104.5	48.9	76.8	125.7	15.7
39	82687	*cis*-Permethrin	67.5	159.0	50.0	209.1	54.1	46.6	41.0	87.6	−10.3
40	82664	Phorate	74.3	31.8	57.2	89.0	73.6	27.9	54.0	82.0	−2.6
41	04037	Prometon	95.5	30.9	80.6	111.5	102.0	48.4	70.8	119.2	6.7
42	04024	Propachlor	106.0	36.5	81.1	117.6	116.8	35.3	93.7	129.0	10.6
43	82679	Propanil	108.1	32.5	84.4	116.9	116.9	62.7	86.5	149.2	10.4
44	82685	Propargite	93.2	36.7	69.3	106.1	109.4	56.1	84.2	140.4	17.3
45	82676	Propyzamide	96.2	26.8	76.9	103.8	103.6	38.7	80.2	119.0	7.8
46	04035	Simazine	98.2	37.9	72.1	110.0	101.0	51.2	67.5	118.7	2.7
47	82670	Tebuthiuron	115.3	72.0	74.4	146.4	123.3	98.5	78.5	177.0	9.6
48	82665	Terbacil	93.3	111.6	47.9	159.6	97.7	84.5	56.7	141.2	13.7
49	82675	Terbufos	78.7	32.3	65.7	97.9	84.2	27.7	71.1	98.8	4.8
50	82681	Thiobencarb	105.8	23.8	94.1	117.8	105.4	36.7	87.5	124.2	2.9
51	82678	Triallate	94.3	18.9	81.6	100.5	98.3	32.9	83.8	116.7	3.9
52	82661	Trifluralin	80.7	30.2	63.3	93.5	90.4	39.1	66.4	105.4	9.8

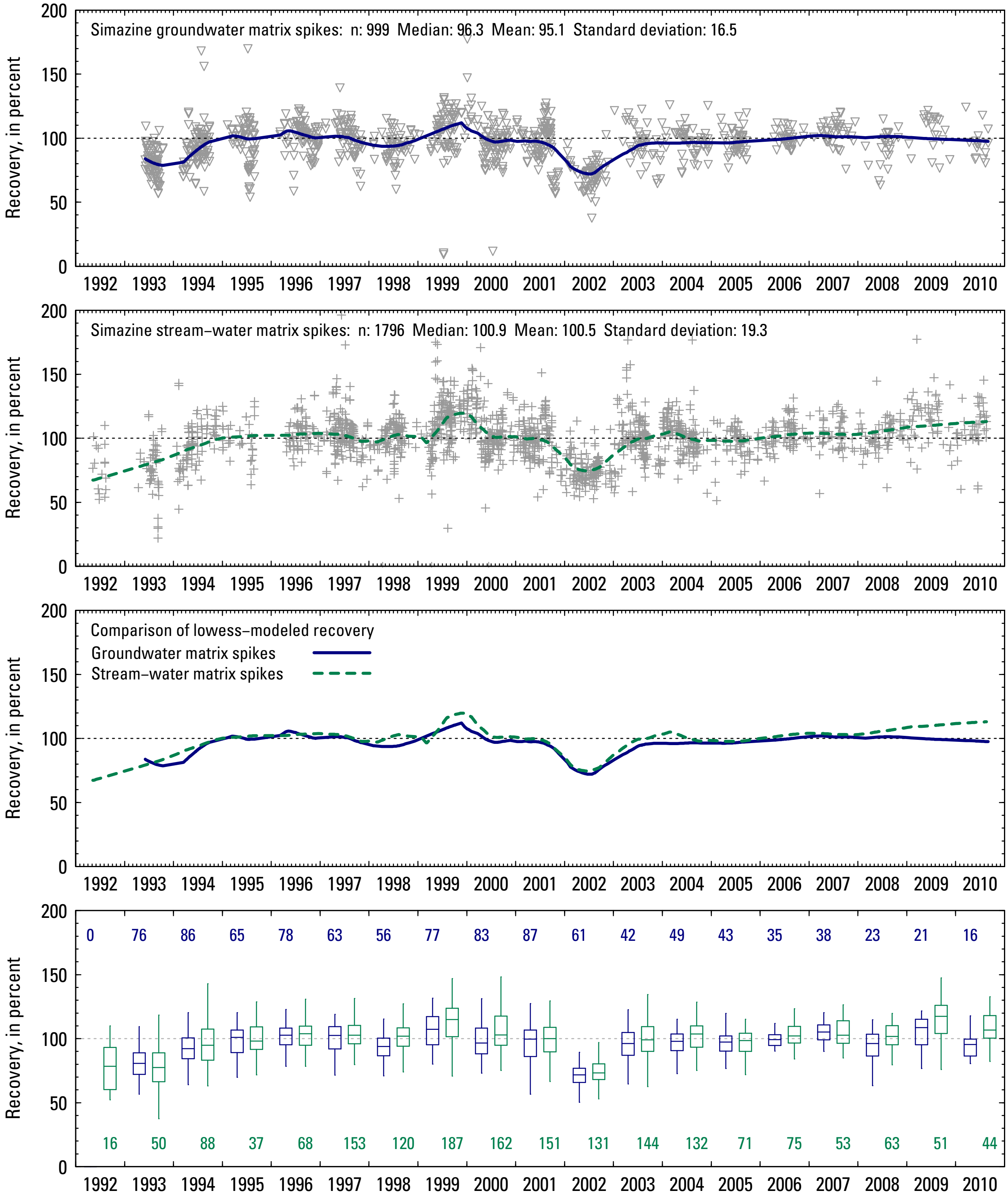

Figure 2. Example comparison of temporal changes (in the recovery of simazine) in groundwater matrix spikes and in stream-water matrix spikes. In the bottom graph, boxplots for groundwater matrix spikes are plotted in the first half of the year and boxplots for stream-water matrix spikes are plotted in the second half of the year. The number of groundwater spikes is shown at the top of the plot and the number of stream-water spikes is shown at the bottom of the plot. Boxplots are explained in figure 1. (Recoveries greater than 200 percent are not shown.)

Comparison of Groundwater and Stream-Water Matrix Spikes

Recovery was modeled separately for groundwater and stream-water matrix spikes. As was seen in the modeling of the 1992–2006 dataset (Martin and others, 2009), 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, appendix figs. 3–13 (deethylatrazine), 3–19 (disulfoton), and 3–47 (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, appendix figs. 3–4 (azinphos-methyl), 3–7 (carbaryl), and 3–8 (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.

As noted in the results from the original analysis 1992–2006 data (Martin and others, 2009) recovery in stream-water matrix spikes was greater than recovery in groundwater spikes for nearly every pesticide (appendix 3). The medians of the differences in modeled recovery in stream-water spikes were more than 5 percent larger for 32 of the 52 pesticides and more than 10 percent larger for 14 of the 52 pesticides (table 2). The smallest median difference in recovery (−10.3 percent) was for *cis*-permethrin, and largest median difference in recovery (38.8 percent) was for azinphos-methyl (table 2). 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.

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 1992–2010 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 and stream-water matrix spikes are provided in appendixes 4 and 5, 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 4 and 5.

Martin (2009, p. 15–17) presents an example application of recovery adjustment for trend analysis. All detected concentrations were adjusted for recovery. Recovery adjustment for nondetected concentrations was dependent on the class of nondetection. Two classes of nondetections were identified: “routine” and “raised.” The large majority of nondetections in the data set were routine nondetections that result when pesticide identification criteria based on retention time and spectral characteristics were not met. These nondetections were reported as censored concentrations at the “routine” reporting level (for example, <0.005 µg/L). A small number of samples, however, had matrix effects or other analytical difficulties that interfered with pesticide identification. These nondetections were reported as censored concentrations at a “raised” reporting level (for example, <0.03 µg/L, six times greater than the routine reporting level). None of the nondetections at “routine” reporting levels were adjusted for recovery. Nondetections at “raised” reporting levels were adjusted for recovery. Detected concentrations that were downward adjusted to concentrations less than the routine reporting level were not censored at the concentration of the routine reporting level.

Concentrations should be adjusted as follows:

$$C_{adjusted} = [C_{measured} / (R_{predicted} / 100)] \qquad (3)$$

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

$R_{predicted}$ is the lowess-modeled recovery, in percent (the “predict” variable in the data files in appendixes 4 and 5).

Users of the recovery-adjustment models should review the “Model Performance” and “Limitations of Modeled Recovery” sections of Martin and others (2009). 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). Recovery-adjusted concentrations should ***not*** be stored in USGS National Water Information System (NWIS) databases.

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 a 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 apparent 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 (1) examines temporal changes in the recovery of 44 pesticides and 8 pesticide degradates (“pesticides”) that were selected for a national analysis of time trends in pesticide concentrations in streams (Martin, 2009) and (2) provides updates for datasets previously compiled for 1992–2006 by Martin and others (2009). The data source for the current compilation is water samples analyzed for these pesticides from 1992 through 2010 by gas chromatography/mass spectrometry. Recovery of pesticides was measured by analysis of pesticide-spiked QC water samples (“matrix spikes”) prepared by field personnel of the U.S. Geological Survey’s National Water Quality Assessment Program and National Stream Quality Accounting Network. Temporal changes in pesticide recovery were investigated by calculating robust, locally weighted scatterplot smooths (lowess smooths) for the time series of pesticide recoveries in 1,819 stream-water matrix spikes and 999 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.

Models of recovery, based on lowess smooths of matrix spikes, were developed separately for groundwater and stream-water samples. Temporal changes in recovery were similarly distributed in groundwater and surface water for most pesticides but 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.

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/ds/630/*.

Appendix 1. Data File of Pesticide Concentrations in Spike Solutions

Appendix 2. Data File of Recovery of Pesticides in Matrix Spikes

Appendix 3. Comparison of Temporal Changes in Recovery of Pesticides in Groundwater Matrix Spikes and in Stream-Water Matrix Spikes

Appendix 4. Data File of Modeled Recovery of Pesticides in Groundwater, 1992–2010

Appendix 5. Data File of Modeled Recovery of Pesticides in Stream Water, 1992–2010

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