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NATIONAL SYNTHESIS ON VOLATILE ORGANIC COMPOUNDS

Volatile Organic Compound Matrix Spike Recoveries for Ground- and Surface-Water Samples, 1997–2001

Scientific Investigations Report 2005–5225

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

Front cover photographs:

Top photo: U.S. Geological Survey hydrologic technician spiking a surface-water sample at Clear Creek, Golden, Colorado. Photograph by Chris Lindley.

Middle photo: U.S. Geological Survey hydrologist spiking a sample within the sample processing chamber. Photograph by Barbara Rowe.

Bottom photo: U.S. Geological Survey chemist loading vials into auto sampler, National Water Quality Laboratory, Denver, Colorado. Photograph by Barbara Rowe.

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By Barbara L. Rowe, Gregory C. Delzer, David A. Bender, and John S. Zogorski

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Foreword

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

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

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

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

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

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

Robert M. Hirsch
Associate Director for Water

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Abbreviations and Acronyms Used in This Report

1994 and 1997 NAWQA Study Units:

ACAD	Acadian-Pontchartrain Drainages
ALMN	Allegheny-Monongahela River
CAZB	Central Arizona Basins
COOK	Cook Inlet Basin
DELR	Delaware River Basin
EIWA	Eastern Iowa Basins
GRSL	Great Salt Lake Basins
HPGW	High Plains Regional Ground Water Study
KANA	Kanawha-New River Basins
LERI	Lake Erie-Lake St. Clair Drainages
LINJ	Long Island-New Jersey Coastal Drainages
LIRB	Lower Illinois River Basin
LTEN	Lower Tennessee River Basin
MIAM	Great and Little Miami River Basins
MISE	Mississippi Embayment
MOBL	Mobile River Basin
NECB	New England Coastal Basins
NROK	Northern Rockies Intermontane Basins
OAHU	Oahu
PUGT	Puget Sound Drainages
SACR	Sacramento River Basin
SANA	Santa Ana Basin
SANT	Santee River Basin and Coastal Drainages
SCTX	South Central Texas
SOFL	Southern Florida Drainages
UCOL	Upper Colorado River Basin
UIRB	Upper Illinois River Basin
UMIS	Upper Mississippi River Basin
UTEN	Upper Tennessee River Basin
YELL	Yellowstone River Basin
CAS	Chemical Abstract Service
FMS	Field matrix spike

FMSR	Field matrix spike replicate
IQR	Interquartile range
IUPAC	International Union of Pure and Applied Chemistry
LMS	Laboratory matrix spike
LRS	Laboratory reagent spike
NAWQA	National Water-Quality Assessment Program
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
P&T GC/MS	Purge and trap gas chromatography/mass spectrometry
QC	Quality control
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	Volatile organic compound
µg/L	Microgram per liter
µL	Microliter
°C	Degrees Celsius
°F	Degrees Fahrenheit

Definitions for This Report

Term	Definition
Accuracy	The degree of agreement of a measured value with the true or expected value of the quality of concern.
Analyte	The substance being qualified and quantified in the analysis.
Bias	A systematic error inherent in a method or caused by some artifact or idiosyncrasy of the measurement system. Bias may be either positive or negative.
Degradation	Decomposition of a compound into defined intermediate or end product(s).
Field matrix effects	The effect of organic matter, organic and inorganic constituents, or other factors in the ground and surface water on purging efficiency during analytical processes.
Percent recovery	The result of a measured concentration in a water sample that, when compared to the theoretical concentration, is expressed as a percentage of its theoretical concentration.
Precision	The degree of mutual agreement of independent measurements as a result of repeated application of the process under specified conditions. Precision is inversely related to variability (the greater the variability, the smaller the precision).

Term	Definition
Reagent water	Deionized water that is continuously purged at the National Water Quality Laboratory with ultrapure nitrogen and assumed to be void of the analytes of interest. Used, in part, for laboratory reagent spikes and laboratory set blanks.
Spike types:	
Field matrix spike (FMS)	A ground- or surface-water sample fortified (spiked) in the field with a known concentration of selected compounds. Used to assess the degradation of compounds in a sample.
Field matrix spike replicate (FMSR)	A duplicate ground- or surface-water sample spiked in the field at virtually the same time and with the same known concentration of selected compounds as the paired field matrix spike. Sample is spiked and processed in the same manner as the field matrix spike such that the samples are expected to be essentially identical in composition. Comparison between recovery of a field matrix spike replicate to the recovery of the paired field matrix spike provides a measure of the variability attributed to the spiking procedure, field handling, transport, and analysis.
Laboratory matrix spike (LMS)	A ground- or surface-water sample that is not spiked until reaching the laboratory. The sample is spiked by laboratory personnel with the same known concentration of selected compounds using the same water as the paired field matrix spike and the field matrix spike replicate (if sampled). The laboratory matrix spike is analyzed at the same time and in the same manner as the field matrix spike samples. When paired with a field matrix spike, can be used to assess compound degradation during transport to the laboratory.
Laboratory reagent spike (LRS)	A sample of reagent water that is spiked with a known concentration of selected compounds in the laboratory and is analyzed with each set of ground-water, surface-water, or quality-control samples. A single laboratory reagent spike (often referred to as a set spike) is intended to measure bias in the analytical method for that specific set of samples. Bias in the analytical method is indicated if the measured concentration does not equal the theoretical concentration. Multiple laboratory reagent spikes can be pooled through time and across multiple instruments and analysts to provide information on bias in the analytical method. Laboratory reagent spikes also measure possible bias from other sources including the spike solution, spiking equipment and technique, and contamination. Comparison of recoveries from laboratory matrix spikes with those from paired laboratory reagent spikes can be used to assess matrix effects.
Theoretical concentration	A calculated concentration based on the known mass of chemical constituents that are added to a known volume of water.
Variability	The degree of variation (random error) in independent measurements as the result of repeated application of the process under specified conditions.

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Abstract

The U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program used field matrix spikes (FMSs), field matrix spike replicates (FMSRs), laboratory matrix spikes (LMSs), and laboratory reagent spikes (LRSs), in part, to assess the quality of volatile organic compound (VOC) data from water samples collected and analyzed in more than 50 of the Nation's largest river basins and aquifers (Study Units). The data-quality objectives of the NAWQA Program include estimating the extent to which variability, degradation, and matrix effects, if any, may affect the interpretation of chemical analyses of ground- and surface-water samples. In order to help meet these objectives, a known mass of VOCs was added (spiked) to water samples collected in 25 Study Units. Data within this report include recoveries from 276 ground- and surface-water samples spiked with a 25-microliter syringe with a spike solution containing 85 VOCs to achieve a concentration of 0.5 microgram per liter. Combined recoveries for 85 VOCs from spiked ground- and surface-water samples and reagent water were used to broadly characterize the overall recovery of VOCs. Median recoveries for 149 FMSs, 107 FMSRs, 20 LMSs, and 152 LRSs were 79.9, 83.3, 113.1, and 103.5 percent, respectively.

Spike recoveries for 85 VOCs also were calculated individually. With the exception of a few VOCs, the median percent recoveries determined from each spike type for individual VOCs followed the same pattern as for all VOC recoveries combined, that is, listed from least to greatest recovery—FMSs, FMSRs, LRSs, and LMSs. The median recoveries for individual VOCs ranged from 63.7 percent to 101.5 percent in FMSs; 63.1 percent to 101.4 percent in FMSRs; 101.7 percent to 135.0 percent in LMSs; and 91.0 percent to 118.7 percent in LRSs.

Additionally, individual VOC recoveries were compared among paired spike types, and these recoveries were used to evaluate potential bias in the method. Variability associated with field spiking, field handling, transport, and analysis was assessed by comparing recoveries between 107 pairs of FMR and FMSR samples. For most VOCs, FMSR recoveries were greater than the paired FMS recoveries. This may result from routinely processing the FMS sample first, allowing a more fluid and efficient technique when processing the FMSR. Degradation was examined by comparing VOC recoveries between 20 pairs of FMS and LMS samples. For all VOCs, the LMS recoveries were greater than FMS recoveries. However, data presented in a previously published VOC stability study were interpreted, and recoveries indicated that VOC degradation should not affect the recovery for most VOCs monitored by the NAWQA Program. Matrix effects were examined by comparing VOC recoveries from 20 pairs of LMS and LRS samples. With the exception of two VOCs, individual recoveries were not significantly different between LMSs and LRSs, indicating that most VOC recoveries are not affected by matrix effects. Additionally, matrix effects should be negligible due to the analytical technique (purge and trap capillary column gas chromatography/mass spectrometry) used for VOC analysis at the U.S. Geological Survey National Water Quality Laboratory (NWQL).

The reason for the lower VOC recoveries from FMSs and FMSRs than from LMSs and LRSs may be associated with differences in spiking technique and experience, and to varying environmental conditions at the time of spiking. However, for all spike types, 87 percent of the individual VOC recoveries were within the range of 60 to 140 percent, a range that is considered acceptable by the U.S. Environmental Protection Agency's established analytical method. Additionally, the median recovery for each spike type was within the range of 60 to 140 percent. The excellent VOC recoveries from LMSs and LRSs demonstrate that low VOC concentrations can routinely and accurately be measured by the analytical methods used by the NWQL.

Introduction and Background

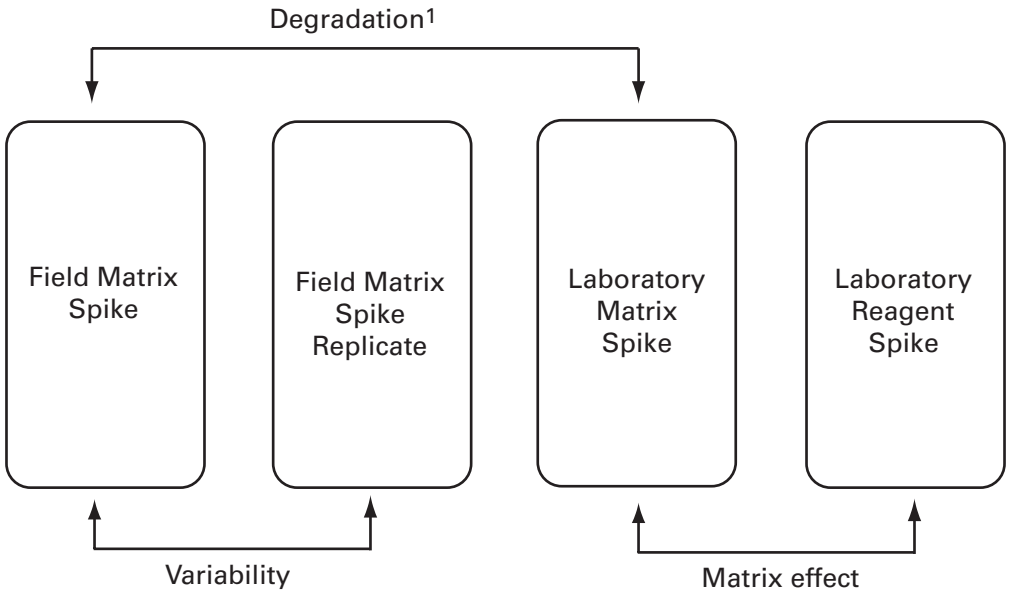
The U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program was designed to assess water-quality status and trends in more than 50 of the Nation's largest river basins and aquifers. For these river basins and aquifers, known as NAWQA Study Units, water-quality information was collected and interpreted, and the data were integrated into a national description of water quality (Gilliom and others, 1995). The data-quality objectives of the NAWQA

Program include estimating the extent to which contamination, measurement variability, degradation, and matrix effects, if any, may affect the interpretation of chemical analyses of ground- and surface-water samples. A known mass of NAWQA analytes (compounds of interest) are added (spiked) to water samples, in part, to document and help ensure the quality of volatile organic compound (VOC) data collected for the NAWQA Program.

A micropipetter was used for VOC field-spiking procedures utilized by the NAWQA Program from 1993 to 1996. In 1996, the National Water Quality Laboratory (NWQL) completed a study assessing VOC recovery from samples spiked with a micropipetter compared to VOC recovery from samples spiked with gas-tight syringes (B.R. Darnel, U.S. Geological Survey, written commun., 1995). Laboratory studies indicated that syringes yielded significantly improved recoveries and precision for spiking water samples. As such, Study Units that began sampling in 1996 were required to utilize a 100-microliter (µL) syringe. Samples were spiked with 13 VOCs to achieve a theoretical concentration of 2.5 micrograms per liter (µg/L). However, some concern was expressed because only 13 of the 85 VOCs analyzed using the NWQL Schedule 2020 (the main VOC analytical schedule used by NAWQA) were being characterized. In addition, the theoretical concentration of 2.5 µg/L was considered very high because most concentrations in ground- and surface-water samples were less than 0.5 µg/L. In response to these concerns, usage of a 25-µL gas-tight syringe with a spike solution containing 85 VOCs designed to achieve a theoretical concentration of 0.5 µg/L in a 40-milliliter water sample was initiated for field-spike sampling in March 1996.

A field matrix spike (FMS) is a water sample that is spiked in the field with a known concentration of VOCs prior to shipment to the laboratory for analysis. Degradation may be indicated if the measured concentration is less than the theoretical concentration. A single FMS, when compared to the theoretical concentration, can be used to estimate VOC degradation. If degradation is suspected, additional FMSs could be collected to confirm the results.

To isolate particular sources of bias, different types of spiked samples are collected, processed, and analyzed, and the recoveries are sequentially compared. For example, a field matrix spike replicate (FMSR) can be prepared in duplicate with a FMS so that both are collected and processed in a manner such that the samples are expected to be essentially identical in composition. A FMSR, when paired to a FMS, is used to estimate the combined variability associated with the field spiking procedure, field handling, transport, and analysis (fig. 1).



[1] Degradation also can be evaluated by comparing field matrix spike recoveries to their own theoretical concentration recovery (100 percent). Also, for this report, additional information on degradation is provided by interpretation of a previously published volatile organic compound stability study (Love and others, 1998).

Figure 1. Schematic showing spike types and how they can be paired to assess variability, degradation, and matrix effects of volatile organic compound recoveries.

Occasionally an additional quality-control sample containing ground or surface water is collected in the field with the FMS and the FMSR, and remains unspiked until reaching the laboratory. The laboratory stores this unspiked sample with the paired FMS and FMSR in the dark at 4°C (39.2°F). This unspiked sample is spiked at the laboratory with the same spike solution that was used for the FMS and the FMSR. This laboratory matrix spike (LMS) is analyzed at the same time and in the same manner as the FMS and the FMSR. The LMS, when paired with a FMS, can be used to assess VOC degradation in samples (fig. 1).

A laboratory reagent spike (LRS) is a sample of reagent water that is spiked with a known concentration of VOCs in the laboratory. LRSs are analyzed with every batch of samples including FMSs, FMSRs, and LMSs. A single LRS (also referred to as a set spike) is intended to measure potential bias in the analytical method for a specific set of samples. Bias in the method is indicated if the recovered concentration does not equal the theoretical concentration. Multiple LRSs can be pooled through time and across multiple instruments and analysts to provide aggregated information on the analytical method. Additionally, LRSs also measure possible bias associated with the spike solution, spiking equipment and technique, degradation, and contamination. Comparison between recoveries of LMSs and the paired LRS can be used to assess matrix effects—the effect of organic matter, organic and inorganic constituents, or other factors in the ground and surface water on analytical purging efficiency (fig. 1).

Volatile Organic Compounds Included in the National Water-Quality Assessment (NAWQA) Program

The analytical schedules used by the NAWQA Program have been periodically updated as knowledge concerning the occurrence and persistence of VOCs in the Nation's ground- and surface-water has increased, and as human-health concerns were considered. VOC analyses were first included in pilot studies of the NAWQA Program (Hirsch and others, 1988) and in the full-scale NAWQA Program (Leahy and Thompson, 1994).

In 1994, members of the VOC National Synthesis Team reviewed VOCs for emphasis in the NAWQA Program in consideration of selected criteria. The selection process for VOC analytes was based on physical properties, human health, aquatic toxicity, concern with depletion of the atmosphere's ozone level, potential bioconcentration in aquatic organisms, and use as oxygenates in gasoline as part of Federally mandated programs (Bender and others, 1999). As a result of this selection procedure, 55 VOCs were identified for emphasis, including 21 halogenated alkanes, 10 halogenated alkenes, 3 aromatic hydrocarbons, 9 alkyl benzenes, 6 halogenated aromatics, 4 ethers, 1 aldehyde, and 1 nitrile. In 1994, the NWQL began development of a new VOC method that included these 55 VOCs emphasized in the NAWQA Program plus an additional 33 analytes (table 1). Initially, 88 analytes were included on the new analytical method, Schedule 2020 (Connor and others, 1998). However, 1,3- and 1,4-dimethylbenzene are listed as one VOC because the compounds co-elute (concentrations are summed) during analysis and consequently are reported as one concentration. Two VOCs were deleted from the schedule due to poor recoveries; ethenyl ethanoate was deleted from the schedule in May 1997, and 2-propenal was deleted from the schedule in April 1998. Consequently, recoveries for 85 VOCs are included in this report. These VOCs are analyzed at the NWQL using purge and trap gas chromatography/mass spectrometry (P&T GC/MS) and offer unequivocal identification of VOCs at sub-microgram per liter detection levels (Connor and others, 1998).

Purpose and Scope

The purpose of this report is to summarize VOC matrix spike recoveries for ground- and surface-water samples collected from 25 Study Units for the NAWQA Program during 1997–2001. Recoveries from FMSs, FMSRs, LMSs, and LRSs are evaluated to broadly characterize the overall performance of the VOC spiking procedure used for ground- and surface-water samples. This is accomplished by evaluating recoveries from 85 VOCs combined to assess major patterns and central tendencies of spike recoveries from ground- and surface-water samples. A total of 428 spiked samples are evaluated including recoveries from 149 FMSs, 107 FMSRs, 20 LMSs, and 152 LRSs. Of these spiked samples, 209 were from ground water and include 115 FMSs, 83 FMSRs, and 11 LMSs. Sixty-seven were from surface water and include 34 FMSs, 24 FMSRs, and 9 LMSs. The 152 LRSs were spiked at the NWQL and accompanied each FMS, FMSR, and/or LMS. The recovery of these LRSs also are examined.

After careful evaluation, data from ground-water and surface-water spike samples were combined, and recoveries of these spiked samples also are evaluated and compared for 85 individual VOCs to assess: (1) variability, (2) degradation, and (3) matrix effects. Variability is characterized by examining recoveries from 107 FMS and FMSR pairs. Degradation is characterized through general evaluation of FMSs and by comparing recoveries from 20 FMSs to LMSs. In addition, degradation is further evaluated using data from a previously published VOC stability study and calculating the recoveries. Matrix effects are characterized by comparing recoveries from 20 LMSs to LRSs.

Acknowledgments

The authors acknowledge and thank the many people who assisted in preparing this report. This study and assessment would not have been possible without the project personnel from Study Units who conscientiously and routinely collect ground- and surface-water samples and prepare field-spike samples. The authors also thank the persons at the NWQL, who not only developed the method of analyses for VOCs, but also performed the many laboratory analyses of VOC samples. These persons include Sonja Abney, Brooke Connor, Debbie Hobbs, Lucinda Murtagh, Mary Noriega, and Donna Rose.

Table 1. Volatile organic compounds analyzed by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program.

[PCODE, U.S. Geological Survey parameter code; CAS no., Chemical Abstract Services number; IUPAC, International Union of Pure and Applied Chemistry; NWQL, National Water Quality Laboratory]

PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))	PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))
55 analytes included in NAWQA's National VOC Assessment					
34030	71-43-2	Benzene (C_6H_6)	34501	75-35-4	1,1-Dichloroethene ($C_2H_2Cl_2$) (vinylidene chloride)
32101	75-27-4	Bromodichloromethane ($CHBrCl_2$) (dichlorobromomethane)	77093	156-59-2	*cis*-1,2-Dichloroethene ($C_2H_2Cl_2$) ((Z)-1,2-dichloroethene)
50002	593--2	Bromoethene (C_2H_3Br) (vinyl bromide)	34546	156-60-5	*trans*-1,2-Dichloroethene ($C_2H_2Cl_2$) ((E)-1,2-dichloroethene)
34413	74-83-9	Bromomethane[1] (CH_3Br) (methyl bromide)	34423	75-09-2	Dichloromethane (CH_2Cl_2) (methylene chloride)
77342	104-51-8	*n*-Butylbenzene ($C_{10}H_{14}$) (1-phenylbutane)	34541	78-87-5	1,2-Dichloropropane ($C_3H_6Cl_2$) (propylene dichloride)
34301	108-90-7	Chlorobenzene (C_6H_5Cl) (monochlorobenzene)	34704	10061-01-5	*cis*-1,3-Dichloropropene ($C_3H_4Cl_2$) ((Z)-1,3-dichloropropene)
34311	75-00-3	Chloroethane (C_2H_5Cl) (ethyl chloride)	34699	10061-02-6	*trans*-1,3-Dichloropropene ($C_3H_4Cl_2$) ((E)-1,3-dichloropropene)
39175	75-01-4	Chloroethene (C_2H_3Cl) (vinyl chloride)	77135	95-47-6	1,2-Dimethylbenzene (C_8H_{10}) (*o*-xylene)
34418	74-87-3	Chloromethane[1] (CH_3Cl) (methyl chloride)	85795	108-38-3 106-42-3	1,3-Dimethylbenzene[2] (C_8H_{10}) (*m*-xylene) and 1,4-Dimethylbenzene[2] (C_8H_{10}) (*p*-xylene)
82625	96-12-8	1,2-Dibromo-3-chloropropane ($C_3H_5Br_2Cl$) (dibromochloropropane, DBCP)	77128	100-42-5	Ethenylbenzene (C_8H_8) (styrene)
32105	4-48-1	Dibromochloromethane ($CHBr_2Cl$) (chlorodibromomethane)	50004	637-92-3	2-Ethoxy-2-methylpropane ($C_6H_{14}O$) (ethyl *tert*-butyl ether, ETBE)
77651	106-93-4	1,2-Dibromoethane ($C_2H_4Br_2$) (ethylene dibromide, EDB)	34371	100-41-4	Ethylbenzene (C_8H_{10}) (phenylethane)
34536	95-50-1	1,2-Dichlorobenzene ($C_6H_4Cl_2$) (*o*-dichlorobenzene)	39702	87-68-3	1,1,2,3,4,4-Hexachloro-1,3-butadiene (C_4Cl_6) (hexachlorobutadiene)
34566	541-73-1	1,3-Dichlorobenzene ($C_6H_4Cl_2$) (*m*-dichlorobenzene)	34396	67-72-1	1,1,1,2,2,2-Hexachloroethane (C_2Cl_6) (carbon hexachloride)
34571	106-46-7	1,4-Dichlorobenzene ($C_6H_4Cl_2$) (*p*-dichlorobenzene)	50005	994-05-8	2-Methoxy-2-methylbutane ($C_6H_{14}O$) (*tert*-amyl methyl ether, TAME)
34668	75-71-8	Dichlorodifluoromethane[1] (CCl_2F_2) (CFC-12)	78032	1634-04-4	2-Methoxy-2-methylpropane (C_5HO) (methyl *tert*-butyl ether, MTBE)
34496	75-34-3	1,1-Dichloroethane ($C_2H_4Cl_2$) (ethylidene chloride)	34010	108-88-3	Methylbenzene (C_7H_8) (toluene)
32103	107-06-2	1,2-Dichloroethane ($C_2H_4Cl_2$) (ethylene dichloride)	77223	98-82-8	(1-Methylethyl)benzene (C_9H) (isopropylbenzene)

Table 1. Volatile organic compounds analyzed by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program.—Continued

[PCODE, U.S. Geological Survey parameter code; CAS no., Chemical Abstract Services number; IUPAC, International Union of Pure and Applied Chemistry; NWQL, National Water Quality Laboratory]

PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))	PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))
55 analytes included in NAWQA's National VOC Assessment—Continued					
34696	91-20-3	Naphthalene ($C_{10}H_8$)	77613	87-61-6	1,2,3-Trichlorobenzene ($C_6H_3Cl_3$)
81577	108-20-3	2,2′-oxybis[propane] ($C_6H_{14}O$) (diisopropyl ether, DIPE)	34551	0-82-1	1,2,4-Trichlorobenzene ($C_6H_3Cl_3$)
34210	107-02-8	2-Propenal[3] (C_3H_4O) (acrolein)	34506	71-55-6	1,1,1-Trichloroethane ($C_2H_3Cl_3$) (methylchloroform)
34215	107-13-1	2-Propenenitrile (C_3H_3N) (acrylonitrile)	34511	79-00-5	1,1,2-Trichlorethane ($C_2H_3Cl_3$) (vinyl trichloride)
77224	103-65-1	*n*-Propylbenzene (C_9H) (1-phenylpropane)	39180	79-01-6	Trichloroethene (C_2HCl_3) (trichloroethylene, TCE)
34475	7-18-4	Tetrachloroethene (C_2Cl_4) (perchloroethene, PCE)	34488	75-69-4	Trichlorofluoromethane (CCl_3F) (CFC-11)
32102	56-23-5	Tetrachloromethane (CCl_4) (carbon tetrachloride)	32106	67-66-3	Trichloromethane ($CHCl_3$) (chloroform)
32104	75-25-2	Tribromomethane ($CHBr_3$) (bromoform)	77443	96-18-4	1,2,3-Trichloropropane ($C_3H_5Cl_3$) (allyl trichloride)
77652	76-13-1	1,1,2-Trichloro-1,2,2-trifluoroethane ($C_2Cl_3F_3$) (CFC-113)	77222	95-63-6	1,2,4-Trimethylbenzene (C_9H) (pseudocumene)
Other NWQL analytes					
81555	108-86-1	Bromobenzene (C_6H_5Br) (phenyl bromide)	77057	108-05-4	Ethenyl ethenoate[4] (vinyl acetate)
77297	74-97-5	Bromochloromethane (CH_2BrCl) (methylene chlorobromide)	77220	611-14-3	1-Ethyl-2-methylbenzene (C_9H) (2-ethyltoluene)
81595	78-93-3	2-Butanone (C_4H_8O) (methyl ethyl ketone, MEK)	73570	97-63-2	Ethyl 2-methyl-2-propenoate ($C_6H_{10}O_2$) (ethyl methacrylate)
77041	75-15-0	Carbon disulfide (CS_2)	77103	591-78-6	2-Hexanone (C_6HO) (butyl methyl ketone, MBK)
77275	95-49-8	1-Chloro-2-methylbenzene (C_7H_7Cl) (*o*-chlorotoluene)	77424	74-88-4	Iodomethane[1] (CH_3I) (methyl iodide)
77277	106-43-4	1-Chloro-4-methylbenzene (C_7H_7Cl) (*p*-chlorotoluene)	77356	99-87-6	1-Isopropyl-4-methylbenzene ($C_{10}H_{14}$) (*p*-isopropyltoluene)
78109	107-05-1	3-Chloro-1-propene (C_3H_5Cl) (allyl chloride)	81597	80-62-6	Methyl 2-methyl-2-propenoate ($C_5H_8O_2$) (methyl methacrylate)
30217	74-95-3	Dibromomethane ($CH_2Br_{2)}$ (methylene bromide)	78133	108-10-1	4-Methyl-2-pentanone (C_6HO) (isobutyl methyl ketone, MIK)
73547	110-57-6	*trans*-1,4-Dichloro-2-butene ($C_4H_6Cl_2$) ((E)-1,4-dichloro-2-butene)	81593	6-98-7	2-Methyl-2-propenenitrile (C_4H_5N) (methyl acrylonitrile)

Table 1. Volatile organic compounds analyzed by the U.S. Geological Survey's National Water-Quality Assessment (NAWQA) Program.—Continued

[PCODE, U.S. Geological Survey parameter code; CAS no., Chemical Abstract Services number; IUPAC, International Union of Pure and Applied Chemistry; NWQL, National Water Quality Laboratory]

PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))	PCODE	CAS no.	IUPAC compound name (chemical formula) (common name(s))
		Other NWQL analytes—Continued			
77173	142-28-9	1,3-Dichloropropane ($C_3H_6Cl_2$) (trimethylene dichloride)	49991	96-33-3	Methyl-2-propenoate ($C_4H_6O_2$) (methyl acrylate)
77170	594-20-7	2,2-Dichloropropane ($C_3H_6Cl_2$)	77350	135-98-8	(1-Methylpropyl)benzene ($C_{10}H_{14}$) (*sec*-butylbenzene)
77168	563-58-6	1,1-Dichloropropene ($C_3H_4Cl_2$)	81576	60-29-7	1,1′-Oxybisethane ($C_4H_{10}O$) (diethyl ether)
77353	98-06-6	(1,1-Dimethylethyl)benzene (*tert*-butylbenzene)	81552	67-64-1	2-Propanone (C_3H_6O) (acetone)
81607	109-99-9	1,4-Epoxybutane (C_4H_8O) (tetrahydrofuran)	77562	630-20-6	1,1,1,2-Tetrachloroethane ($C_2H_2Cl_4$)
34516	79-34-5	1,1,2,2-Tetrachloroethane ($C_2H_2Cl_4$)	77221	526-73-8	1,2,3-Trimethylbenzene (C_9H) (hemimellitene)
49999	488-23-3	1,2,3,4-Tetramethylbenzene ($C_{10}H_{14}$) (prehitene)	77226	108-67-8	1,3,5-Trimethylbenzene (C_9H) (mesitylene)
50000	527-53-7	1,2,3,5-Tetramethylbenzene ($C_{10}H_{14}$) (isodurene)			

[1]Detections of these compounds are reported by the U.S. Geological Survey National Water-Quality Laboratory as estimated concentrations (E-coded).

[2]Analytical results are reported by the U.S. Geological Survey National Water-Quality Laboratory as the sum of concentrations for these two compounds.

[3]Deleted from list of volatile organic compounds analyzed by the U.S. Geological Survey National Water-Quality Laboratory in April 1998 because of poor performance after installation of new equipment.

[4] Deleted from list of volatile organic compounds analyzed by the U.S. Geological Survey National Water-Quality Laboratory in May 1997 due to erratic analytical results.

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Methodology

This section provides information on methods used to evaluate variability, degradation, and matrix effects of VOCs in spike samples. The collection guidelines for FMS, FMSR, and LMS samples and procedures for LRSs are summarized. The data set is described. Methods used to calculate percent recoveries for FMSs, FMSRs, LMSs, and LRSs are presented along with a description of the basic statistical approach used to evaluate variability, degradation, and matrix effects. Finally, methods used to determine recoveries from data previously published in a VOC stability study in consideration of analytical variability (instrument drift) are presented.

Collection Guidelines for Field and Laboratory Quality-Control Samples

The protocol and recommended quality-control (QC) procedures for the NAWQA Program were designed to reduce inconsistencies and to enhance the quality of data used in various assessments. Koterba and others (1995) described NAWQA protocols and recommended procedures for collection of ground-water samples and quality-control samples. FMSs and FMSRs were to be collected at a minimum of 2 well sites in a 30-well network. Mueller and others (1997) described

quality-control design for surface-water sampling. Spiking was to be scheduled to cover a broad range of hydrologic conditions. Recommended frequencies for routine QC sampling for all surface-water sites each year included: (1) one FMS per site prepared when environmental concentrations of the spiked analytes were expected to be low, that is, no more than 10 percent of the expected concentration in the spiked sample; (2) one FMSR per site when VOC concentrations were expected to be high; and (3) at a minimum, three spiked samples per year.

All of the field-spike samples were collected in accordance with the procedures outlined in the National Field Manual for the Collection of Water Quality (U.S. Geological Survey, 1997–2004). For preparation of matrix spikes, a ground- or surface-water sample was collected for spiking. From this sample, one FMS and one FMSR were each spiked in the field with 85 VOCs. A portion of the sample remained unspiked and was submitted to the NWQL to prepare the LMS. All samples collected for spiking were preserved with a 1:1 solution of $HCl:H_2O$ to a pH of 2.0 to inhibit microbiological activity and were chilled with ice during shipment to the laboratory. Upon receipt at the laboratory, samples were stored in a refrigerator until analysis. The LMS was spiked at the laboratory just prior to analysis, within a timeframe of 2 to 40 hours. All QC samples were analyzed within 14 days of field collection. Collection guidelines are provided in Shelton (1997), Mueller and others (1997), and Connor and others (1998).

For preparation of LRSs, deionized water was boiled for 1 hour, cooled, and purged with ultrapure grade nitrogen continuously for a minimum of 1 hour. A sample of this water was spiked in the laboratory with a known concentration of selected compounds. LRSs were analyzed with each set of ground- or surface-water samples. A thorough discussion of the NWQL's analytical methods is provided by Connor and others (1998).

Description of Data Set

Samples from 25 Study Units were collected and spiked (fig. 2). Overall, 23,394 individual VOC analytical determinations for the VOCs listed in table 1 were used to analyze, evaluate, and interpret spike recoveries. Field-spike data and other QC samples were reviewed by the NAWQA Study Units, stored in the local USGS National Water Information System (NWIS) database, and aggregated nationally in the NAWQA Data Warehouse.

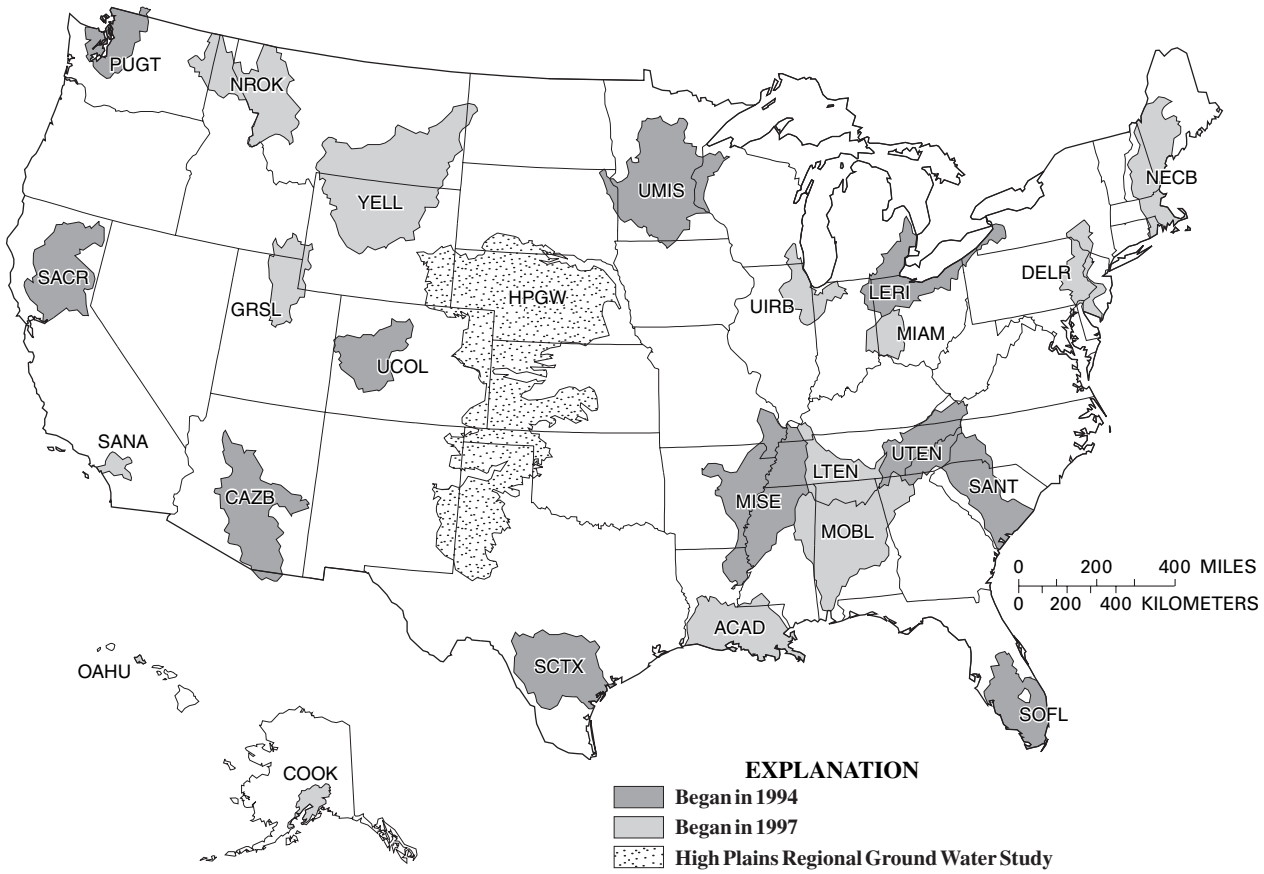


Figure 2. Location and implementation dates of National Water-Quality Assessment (NAWQA) Program Study Units that collected field quality-control samples used in this report to assess the recoveries of volatile organic compounds.

Data included are those spiked samples analyzed from July 14, 1997, through December 3, 2001 (table 2). Five additional 1994 NAWQA Study Units participated in the field-spiking program during this timeframe. However, data indicated that field spiking by these Study Units was not completed with the 25-µL syringe. Consequently the field-spiking data collected by the Allegheny-Monongahela River (ALMN), Eastern Iowa Basins (EIWA), Kanawha-New River Basins (KANA), Lower Illinois River Basin (LIRB), and Long Island-New Jersey Coastal Drainages (LINJ) were not included in this report.

Data for this report include VOC recoveries from 276 spiked ground-water and surface-water samples including 149 FMSs, 107 FMSRs, and 20 LMSs (table 2). In addition, recoveries from 152 LRSs that were analyzed at the same time as each FMS, FMSR, and LMS are included herein. The data are inclusive of all samples that were spiked and analyzed with the exception of four concentrations. These extreme outliers were deleted from the data set because recoveries for 2-butanone were 1,520.3 percent for one FMS and 1,511.9 percent for one FMSR; and recoveries for trichloroethene were 0.6 percent for one FMS and for one FMSR. Also, samples generally were spiked with 85 compounds; however, the number of VOCs within a spiked sample occasionally was only 84 compounds. This occurred because some vendor-prepared lots did not include 1,2,3,4-tetramethylbenzene in the spike solution.

More ground-water samples (209) were spiked than surface-water samples (67) (table 2). The number of spikes, type of spikes, and distribution of collection varied among the 25 Study Units. Some variation can be attributed to the starting date of water-sample collection, the receipt date of analytical data from the NWQL, and/or the submission date of data to the NAWQA QC database.

Calculations for Percent Recoveries From Spiked Samples

Spiked samples typically are evaluated as a percentage of the theoretical concentration. That is, a known mass of select chemical constituents are added to a known volume of water, which may or may not already contain the same constituent(s). The amount of the added mass recovered through sample analyses is characterized as a percentage. As such, the percent recovery of VOC concentrations for FMSs, FMSRs, LMSs, and LRSs were calculated as follows:

$$\text{Percent recovery} = \frac{100(C_{Spiked} - C_{Sample})}{C_{theoretical}}$$

where

C_{Spiked} = the measured concentration in the spiked sample, in micrograms per liter;

C_{Sample} = the measured concentration that is present in the unspiked water sample, in micrograms per liter; and

$C_{theoretical}$ = the theoretical concentration of the sample, in micrograms per liter.

Statistical Approach to Data Set

A preliminary statistical and visual examination of data was completed to determine the central tendency of recoveries from spike samples. Recoveries were examined to determine if data are normally distributed and to determine if data should be analyzed by parametric statistical methods or by nonparametric statistical methods. To determine if the data from spike samples had a normal distribution, quantile plots were developed for FMS, FMSR, and LMS recoveries (fig. 3). With the exception of some extreme outliers, distribution of VOC recoveries for all spike types generally follow a normal distribution. Additionally, the chi-square goodness-of-fit test (Ott and Longnecker, 2001) indicates that FMS, FMSR, and LMS recoveries had normal distributions; however, because some extreme outliers are apparent in the data (fig. 3), nonparametric analyses, such as median values, are predominantly used for statistical analyses of spike recoveries in this report.

To determine if ground- and surface-water samples could be combined to report VOC recoveries from FMSs, FMSRs, and LMSs, statistical and visual examinations of data were completed. For statistical examination of data between ground- and surface-water samples and among spike types, the mean and median recoveries were computed for FMSs, FMSRs, and LMSs (table 3). To ensure that the central tendency for ground- and surface-water recoveries represents a true median of the population, a 95-percent confidence interval for medians was calculated using the method described by Ott and Longnecker (2001). With the exception of FMS recoveries from surface-water samples, the range of the confidence interval for the median of spiked samples is narrow (1.2 to 3.6 percent), indicating that the stated value generally reflects the true median of the data. The mean and median values for ground-water samples compared to surface-water samples are very similar for recoveries from FMSs, FMSRs, and LMSs (table 3).

Additionally, boxplots as described by Helsel and Hirsch (1992) were prepared to visually examine the similarities between ground- and surface-water recoveries. The boxplots provide summaries of (1) the median or the center line of data depicted in the box; (2) variation or spread indicated by the interquartile range (IQR) shown by the box height; (3) the skewness as shown in the relative size of box halves; and (4) presence or absence of unusual values such as outliers extending beyond the box.

Table 2. Number of ground- and surface-water field matrix spikes, field matrix spike replicates, and laboratory matrix spikes for each of the 25 Study Units.

[FMS, field matrix spike; FMSR, field matrix spike replicate; LMS, laboratory matrix spike; NS, not sampled]

Study Unit abbreviation	Study Unit	Number of spiked samples						Total
		Ground water			Surface water			
		FMS	FMSR	LMS	FMS	FMSR	LMS	
ACAD	Acadian-Pontchartrain Drainages	3	3	3	1	1	NS	11
CAZB	Central Arizona Basins	2	2	NS	NS	NS	NS	4
COOK	Cook Inlet Basin	2	2	2	1	1	1	9
DELR	Delaware River Basin	5	2	NS	9	NS	NS	16
GRSL	Great Salt Lake Basins	10	10	NS	1	1	NS	22
HPGW	High Plains Regional Ground Water Study	19	9	NS	NS	NS	NS	28
LERI	Lake Erie-Lake St. Clair Drainages	NS	NS	NS	1	1	NS	2
LTEN	Lower Tennessee River Basin	1	1	1	NS	NS	NS	3
MIAM	Great and Little Miami River Basins	3	3	2	NS	NS	2	10
MISE	Mississippi Embayment	7	5	NS	NS	NS	NS	12
MOBL	Mobile River Basin	1	1	NS	4	4	1	11
NECB	New England Coastal Basins	8	3	NS	NS	NS	NS	11
NROK	Northern Rockies Intermontane Basins	2	2	1	NS	NS	NS	5
OAHU	Oahu	4	4	NS	1	1	1	11
PUGT	Puget Sound Drainages	6	6	NS	2	1	NS	15
SACR	Sacramento River Basin	NS	NS	NS	1	1	NS	2
SANA	Santa Ana Basin	11	7	NS	7	7	NS	32
SANT	Santee River Basin and Coastal Drainages	1	NS	1	1	1	1	5
SCTX	South Central Texas	3	2	NS	1	1	1	8
SOFL	Southern Florida Drainages	4	4	NS	1	1	NS	10
UCOL	Upper Colorado River Basin	3	3	NS	NS	NS	NS	6
UIRB	Upper Illinois River Basin	2	2	NS	NS	NS	NS	4
UMIS	Upper Mississippi River Basin	5	3	1	2	2	2	15
UTEN	Upper Tennessee River Basin	3	NS	NS	NS	NS	NS	3
YELL	Yellowstone River Basin	10	9	NS	1	1	NS	21
	Totals	115	83	11	34	24	9	276

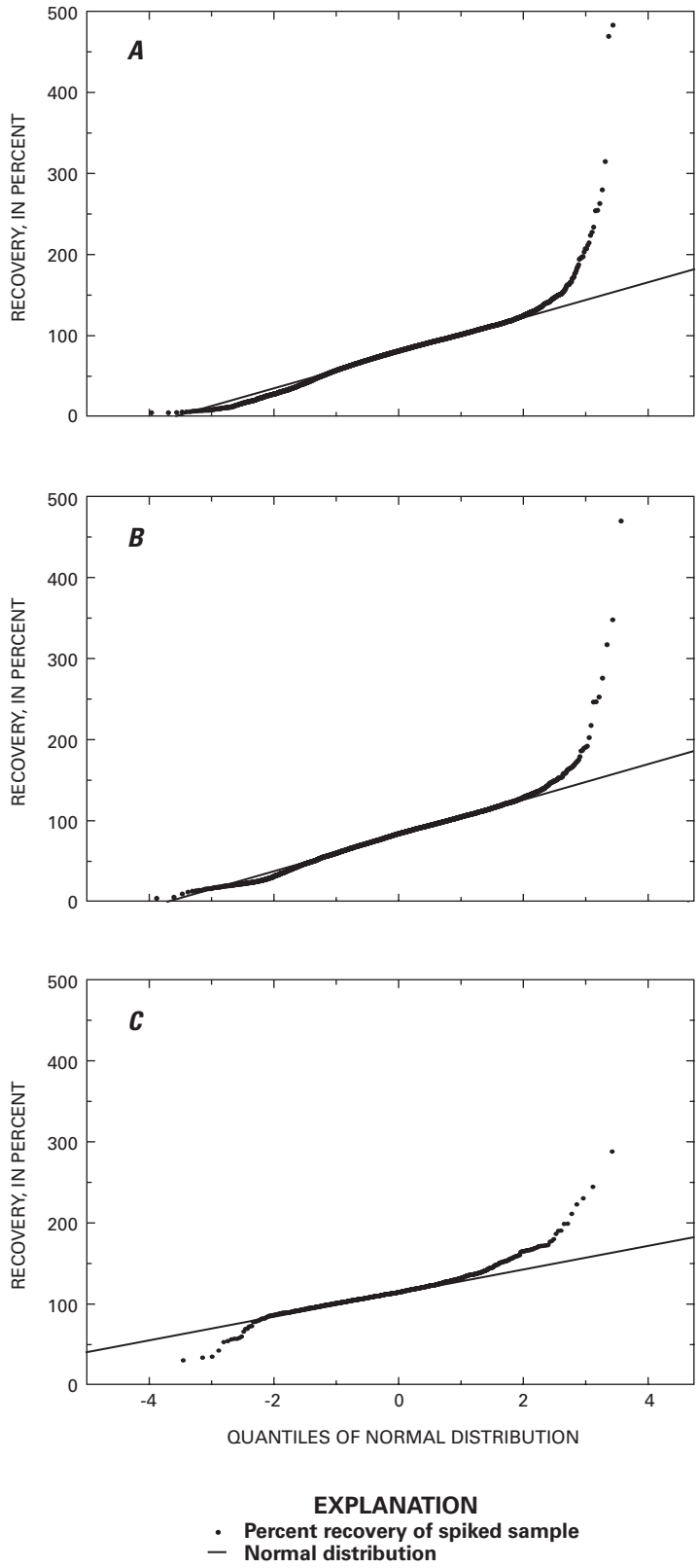


Figure 3. Plots comparing percentiles of volatile organic compound recoveries to quantiles of normal distribution for (*A*) field matrix spikes; (*B*) field matrix spike replicates; and (*C*) laboratory matrix spikes.

Table 3. Mean and median recoveries and confidence intervals for median recoveries for field matrix spikes, field matrix spike replicates, and laboratory matrix spikes from ground- and surface-water samples.

[n, number of individual VOC recoveries by sample]

Ground water n = 17,720			Surface water n = 5,674		
Mean	Median	Confidence interval for median	Mean	Median	Confidence interval for median
Field matrix spike					
79.9	81.0	80.4 to 81.6	77.1	76.5	72.8 to 88.2
Field matrix spike replicate					
83.0	83.1	82.4 to 83.8	77.1	83.9	82.6 to 85.0
Laboratory matrix spike					
115.2	113.6	112.6 to 114.9	116.1	112.1	108.5 to 112.1

As discussed by Helsel and Hirsch (1992), the 75th, 50th (median), and 25th percentiles split the data into four equal-sized quarters. The 75th percentile, also called the upper quartile (the top of the "box" in a boxplot) is a value that exceeds no more than 75 percent of the data and is exceeded by no more than 25 percent of the data. The 25th percentile (the bottom of the "box" in a boxplot), or lower quartile, is a value that exceeds no more than 25 percent of the data and is exceeded by no more than 75 percent of the data. The median, or 50th percentile, is the central value of the distribution when the data are ranked in order of the magnitude (the line between the top and the bottom of the box). The range between the 25th and 75th percentiles is considered the IQR.

As shown in figure 4, and previously demonstrated (table 3), the medians for ground-water and surface-water samples between spike types are similar. As shown in the boxplots in figure 4, the variability of ground-water FMS recoveries and surface-water FMS recoveries is similar as indicated by the IQR spread, and the medians are centered in the boxes indicating a symmetric distribution of recoveries. Comparison of mild and extreme outliers is visually difficult because the number of recoveries from ground-water samples is greater than the number of recoveries from surface-water samples. Consequently, outliers, in general, may appear to be more prevalent for ground-water spikes than for surface-water spikes. Comparison between ground- and surface-water FMSR recoveries (fig. 4) indicates that the variability of recovery is similar. Data for ground-water FMSR recoveries are symmetrically distributed about the median. However, the median for surface-water FMSR recoveries is located in the upper portion of the IQR indicating a greater number of recoveries exist on the lower side of the median within the box than on the upper side. Although the medians of LMS recoveries for ground- and surface-water samples are similar (fig. 4), the variability of recovery is greater for surface water than for ground water.

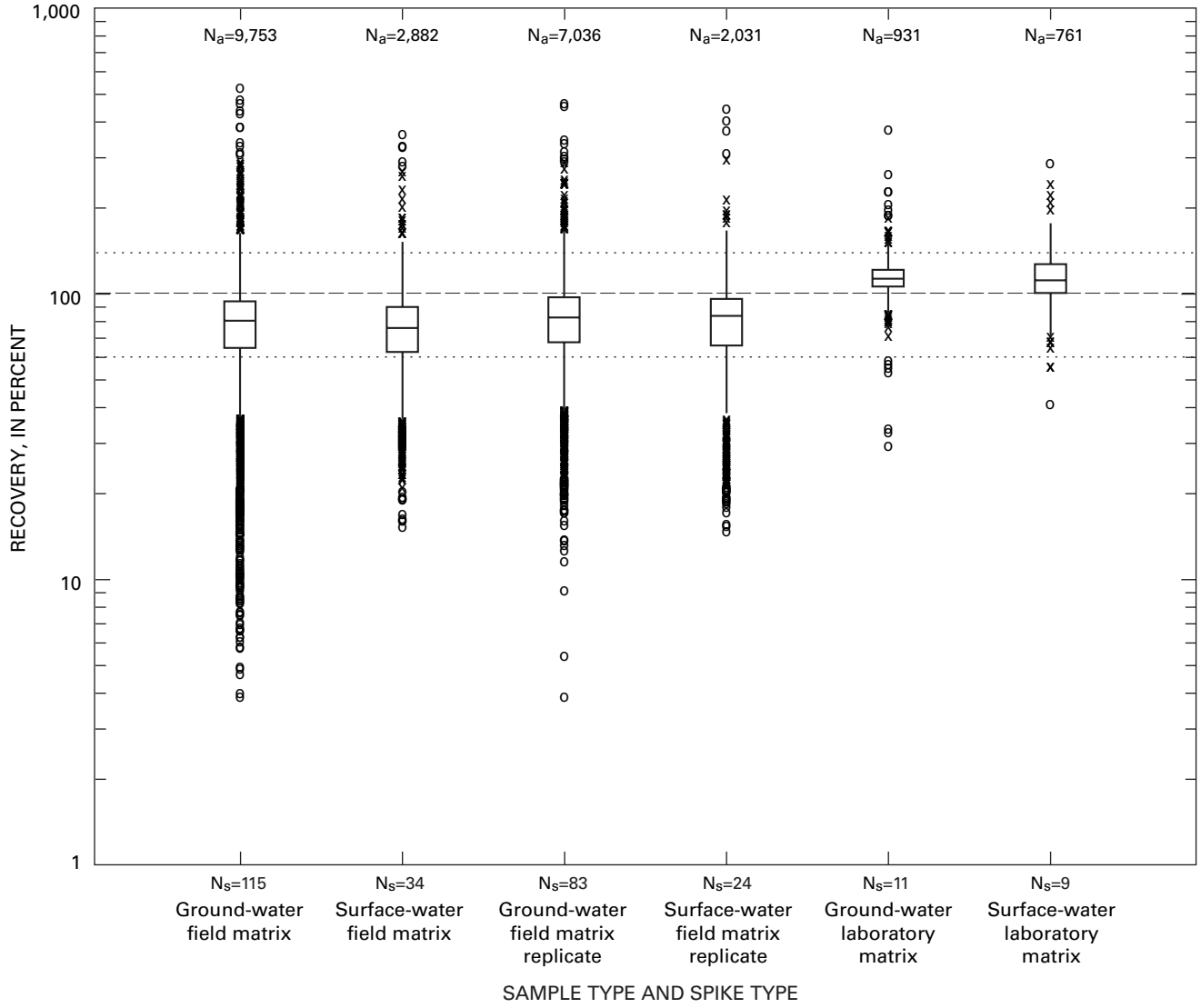
Although minor differences may exist in recoveries between ground- and surface-water spike samples, statistical and visual examinations indicate that recoveries between spike types for ground- and surface-water samples are similar. For this report, ground- and surface-water samples are combined for FMS, FMSR, and LMS recoveries.

Methods Used for Interpretation of a Stability Study of Volatile Organic Compounds in Preserved Samples

The long-term stability of low VOC concentrations in samples was addressed in a study conducted at the NWQL, and analytical results (no interpretation) were presented by Love and others (1998). Interpretation of the data presented by Love and others (1998) is contained herein to better characterize VOC degradation and stability.

To assess stability of VOCs at low concentrations, surface-water and ground-water samples were spiked in the laboratory with 85 VOCs (table 1) to achieve a theoretical concentration of 0.5 µg/L. To assess degradation of VOCs over a period of time, about 45 replicate spike ground-water samples and 45 replicate spike surface-water samples were processed and stored, 5 of which were analyzed at selected time intervals including days 0, 14, 28, 37, 47, 56, 112, 156, and 216. On day 0, an unspiked ground-water sample and an unspiked surface-water sample were analyzed to measure VOC concentrations in the original samples (C_{Sample}). The five replicate spiked ground- and surface-water samples were selected randomly and analyzed at each time interval. Three replicate LRSs also were analyzed at the same times as the spiked-water samples to assess daily analytical variability.

Love and others (1998) did not calculate percent recoveries for data collected for the VOC stability study. As such, surface- and ground-water spike recoveries (hereafter referred to as LMS_{adj}) were calculated and compared to LRS recoveries. For this study, the intent of LRS recoveries was to measure instrument drift on the days in which LMS_{adj} samples were analyzed. Thus, LMS_{adj} recoveries were calculated in consideration of LRS concentrations to take into account daily analytical variability due to laboratory equipment that could potentially affect VOC recovery. For example, if LRSs had high recoveries, the LMS_{adj} concentrations also would have been artificially high without accounting for the LRSs. To account for this, the LMS_{adj} recoveries were decreased proportionately to account for inflated LRS recoveries. Similarly, if LRSs had low recoveries, the LMS_{adj} concentrations were increased proportionately. Adjustment of the LMS_{adj} recoveries relative to the LRSs was completed to ensure that any apparent increase or decrease in recoveries was due to actual changes in VOC concentrations and not due to normal instrument drift.



EXPLANATION

- N_a Number of analytical determinations
- N_s Number of samples
- o Outlier data value greater than 3 times the interquartile range outside the quartile
- × Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile
- Data value less than or equal to 1.5 times the interquartile range outside the quartile
- 75th percentile
- Median
- 25th percentile
- Interquartile range
- ——— One-hundred percent recovery
- ····· Boundaries of plus or minus 40 percent of complete recovery

Figure 4. Volatile organic compound percent recoveries for ground- and surface-water field matrix spikes, field matrix spike replicates, and laboratory matrix spikes. Samples were spiked using a 25-microliter syringe with a spike solution of 85 VOCs designed to achieve a concentration of 0.5 microgram per liter.

The percent recovery for individual VOCs from the data reported by Love and others (1998) was calculated by the steps shown in table 4. Although the example shown is for adjusted recoveries for an individual VOC on day 14, these steps for calculation of LMS_{adj} recoveries were completed for individual VOCs at all specified time intervals, including days 0, 14, 28, 37, 47, 56, 112, 156, and 216. For the stability study, the mean was used to report the central tendency of the values because only three replicate LRSs were used. The results of the study provided information about the stability of low concentrations of VOCs in samples preserved with hydrochloric acid, chilled at 4°C (39.2°F), and kept in the dark prior to analysis.

Table 4. Calculations for adjusted percent recovery for volatile organic compounds (VOCs) from laboratory matrix spikes (LMSs).

Step 1: Calculation of mean VOC concentration of five replicate samples:

$$C_{mean\ rep14,\ 1\text{-}5} = \frac{\sum C_{rep14,\ 1\text{-}5}}{n} - C_{sample}$$

where

$C_{mean\ rep14,\ 1\text{-}5}$ = mean concentration of replicate spikes 1, 2, 3, 4, and 5 on day 14;

$\sum$ = summation;

$C_{rep14,\ 1\text{-}5}$ = concentration of replicate spikes 1, 2, 3, 4, and 5 on day 14;

$n = 5$ = number of spiked replicates; and

C_{sample} = concentration that is present in the unspiked water sample.

Step 2: Calculation of the mean VOC recovery of three LRSs:

$$R_{mean\ reag14,\ 1\text{-}3} = \frac{\sum R_{reag14,\ 1\text{-}3}}{n}$$

where

$R_{mean\ reag14,\ 1\text{-}3}$ = mean recovery, in percent, of reagent spikes 1, 2, and 3 on day 14;

$R_{reag14,\ 1\text{-}3}$ = recovery, in percent, of reagent spikes 1, 2, and 3 on day 14; and

$n = 3$ = number of reagent spike recoveries.

Step 3: Calculation of the LMS_{adj14}:

$$LMS_{adj14} = \left(\frac{C_{mean\ rep14,\ 1\text{-}5}}{\frac{\left(\frac{R_{mean\ reag14,\ 1\text{-}3}}{100}\right)}{\text{theoretical concentration}}} \right)$$

where

LMS_{adj14} = adjusted VOC recovery of LMS, in percent, on day 14.

Major Patterns and Central Tendencies of Matrix Spike Recoveries for All Volatile Organic Compounds Combined

One main purpose of this report is to summarize VOC spike recoveries for ground- and surface-water samples collected for the NAWQA Program during 1997–2001. As described in the Methodology section, ground- and surface-water data are combined to characterize VOC recoveries from FMSs, FMSRs, LMSs, and LRSs. Comparison of these spike recoveries are intended to describe major patterns and central tendencies of spike recoveries from ground- and surface-water samples. For these purposes, recoveries from all 85 VOCs are combined for each spike type, and general comparisons are made between the spike types. More detailed discussion of variability, degradation, and matrix effects is described on an individual VOC basis and is presented in the following section.

FMSs, FMSRs, and LMSs were processed by 25 Study Units (fig. 2). Recoveries for each of these spike types by Study Unit are presented in Appendix 1. A total of 12,635 VOC analytical results were available from 149 FMSs collected by 25 Study Units. Of all spike types included herein, FMSs were sampled most frequently (table 2) and had the lowest median recovery of 79.9 percent (fig. 5). The IQR of the recoveries is symmetrical about the median and has minimal variability of recoveries. However, extreme outliers exist, and high values may indicate inflated recoveries for some data. Extreme outliers, as shown in figure 5, could represent recoveries for VOCs that are identified as problem compounds by the NWQL. These compounds do not perform as well as other VOCs in the P&T GC/MS methodology used by the NWQL, and as such, the variability of percent recovery is estimated. These compounds are referred to as permanently "E-coded" and include bromomethane, chloromethane, dichlorodifluoromethane, and iodomethane (Connor and others, 1998).

A total of 9,067 VOC concentrations were measured from 107 FMSRs collected by 24 Study Units (table 2). FMSRs had an overall median recovery of 83.3 percent (fig. 5). Data are centered symmetrically about the median, indicating minimal skewness. Fewer extreme outliers exist for FMSRs than for FMSs. Greater recovery of VOCs from FMSRs than from FMSs could be associated with spiking procedures. When spiking in the field, a routine is established with the FMS sample, resulting in equipment that is in place and a technique that was practiced prior to spiking the replicate.

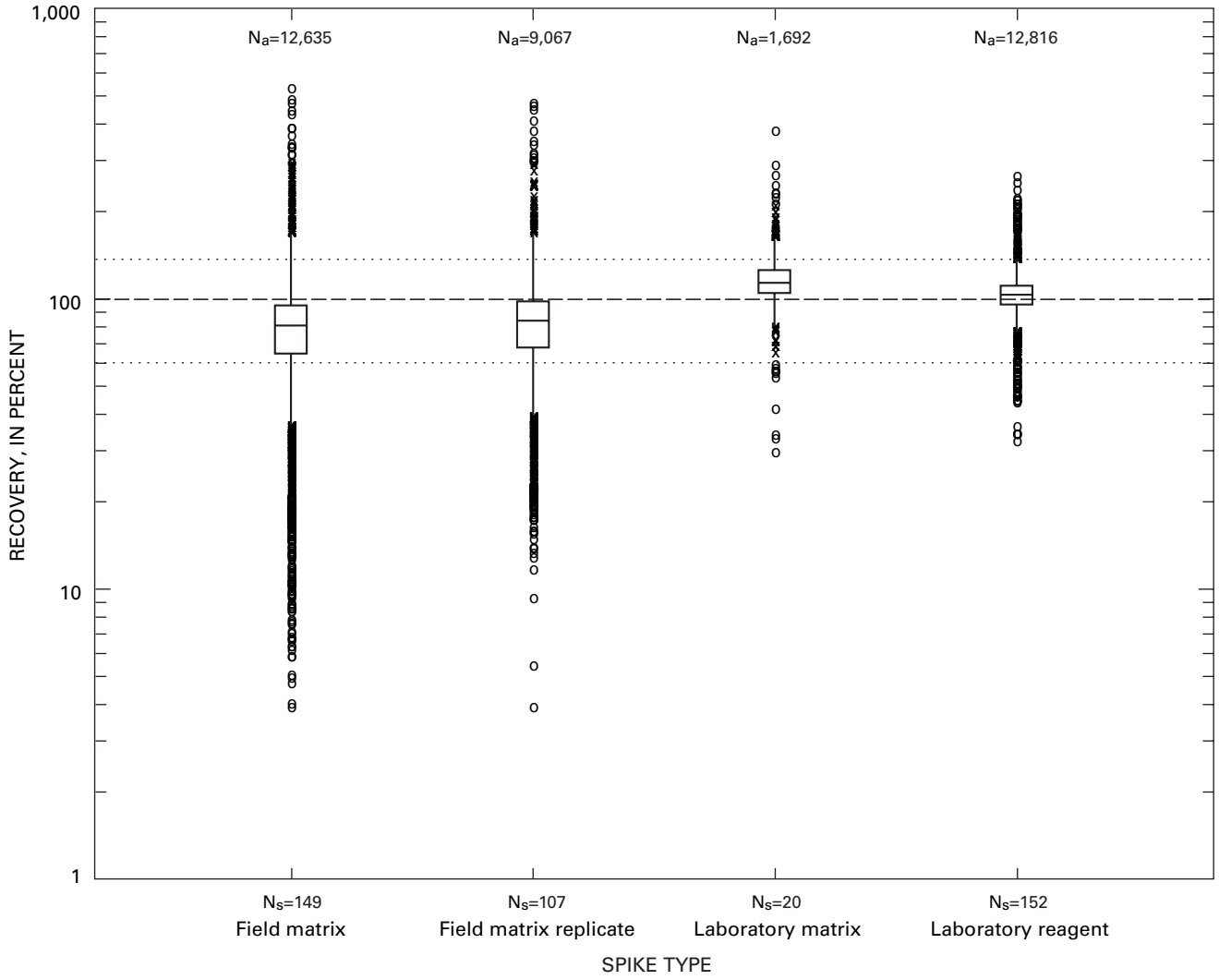
A total of 1,692 analytical results were available for 20 LMSs collected by 10 Study Units (table 2). LMSs had the greatest percent recovery among all spike types with a median recovery of 113.1 percent (fig. 5). The small IQR (difference between the 25th and 75th percentile) and the symmetry and tightness about the median indicate that LMS recoveries had less variability than FMS and FMSR recoveries. The greater precision and recovery of VOCs from LMSs than from FMSs and FMSRs could be credited to several factors. The precision associated with spike recoveries may vary with the technique and the experience of the technician performing the spiking procedure. Most USGS field staff spike markedly fewer samples in a particular year than NWQL personnel who routinely perform the spiking procedure. In addition, environmental conditions, especially temperature and wind, could account for greater variability of VOC recoveries from samples that are spiked in the field than from samples that are spiked in a controlled environment, such as the laboratory. Finally, differences in percent recovery among spike types could have resulted from (1) inadequate hydrochloric acid preservation that fails to eliminate microbial activity; (2) instrument variation; (3) chemical instability; and (4) short-term environmental fluctuations (Connor and others, 1998).

A total of 12,816 analytical results were available for 152 LRSs spiked at the NWQL. The small IQR and the sparse outliers indicate minimal variability in LRS recoveries. The overall median recovery was 103.5 for LRSs indicating that, overall, the analytical method performance by the NWQL is quite accurate.

Variability, Degradation, and Matrix Effects for Individual Volatile Organic Compounds

Positive or negative bias for individual VOC recoveries is masked when examining recoveries of all compounds combined. Therefore, recoveries from FMSs, FMSRs, LMSs, and LRSs for individual VOCs are statistically examined by spike type. Also, comparisons between the different spike types for individual VOC recoveries are made to characterize variability, degradation, and matrix affects (fig. 1). For example, variability is characterized by comparing FMSs with LMSs; degradation is characterized by comparing FMSs with LMSs; and matrix effects are characterized by comparing LMSs with LRSs. In addition, degradation also is characterized by examining recoveries from FMSs and by examining calculated recoveries from a previously published VOC stability study by Love and others (1998).

Percent recovery was calculated for each of the 85 VOCs and statistically summarized in table 5 for each spike type. Additionally, boxplots for individual VOC recoveries for FMSs, FMSRs, and LMSs are illustrated in Appendix 2.



EXPLANATION

N_a Number of analytical determinations

N_s Number of samples

○ Outlier data value greater than 3 times the interquartile range outside the quartile

× Outlier data value less than or equal to 3 and more than 1.5 times the interquartile range outside the quartile

Data value less than or equal to 1.5 times the interquartile range outside the quartile

75th percentile
Median
25th percentile
Interquartile range

——— One-hundred percent recovery

····· Boundaries of plus or minus 40 percent of complete recovery

Figure 5. Volatile organic compound percent recoveries for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined. Samples were spiked using a 25-microliter syringe with a spike solution of 85 VOCs designed to achieve a concentration of 0.5 microgram per liter.

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
55 analytes included in NAWQA's National VOC Assessment																								
Benzene	10.8	63.3	79.7	91.4	127.4	149	20.0	67.4	84.1	94.4	129.0	107	99.5	108.0	115.4	118.8	153.6	20	79.4	96.5	102.0	107.9	121.3	152
Bromodichloro-methane	21.2	71.1	85.9	96.9	129.8	149	26.0	73.5	87.5	104.0	133.2	107	101.1	110.1	117.9	126.9	162.8	20	89.9	101.1	106.3	115.2	131.9	152
Bromoethene	7.5	60.1	80.0	93.8	481.7	149	19.1	66.6	80.8	98.9	468.5	107	89.4	113.2	121.1	131.1	154.1	20	61.1	95.5	103.1	110.7	145.0	152
Bromomethane	10.2	61.4	98.0	197.7	528.9	149	13.2	57.4	85.9	146.8	456.9	107	55.2	92.2	108.3	134.7	377.0	20	43.6	68.0	91.0	108.7	210.8	152
n-Butylbenzene	8.3	55.9	70.7	84.4	123.0	148	19.5	58.0	75.3	87.5	136.4	107	55.9	98.7	111.3	131.6	158.8	20	77.0	96.7	104.1	113.2	145.4	152
Chlorobenzene	13.1	62.0	76.2	88.0	121.6	149	24.4	64.4	79.7	92.5	129.0	107	101.0	107.2	110.0	120.2	133.7	20	82.5	95.3	101.1	108.4	123.3	152
Chloroethane	7.6	59.3	77.6	89.2	155.6	149	20.7	62.7	74.4	93.4	153.0	107	41.3	100.1	109.9	119.9	159.4	20	32.0	89.1	96.0	102.0	134.5	152
Chloroethene	7.0	57.4	78.1	95.0	196.1	149	11.6	58.2	71.2	95.4	185.5	107	77.3	99.1	121.3	128.8	168.1	20	45.9	90.0	99.0	106.0	169.0	152
Chloromethane	8.7	58.8	83.3	102.3	210.4	149	13.7	56.4	75.6	98.6	165.8	107	58.6	93.6	109.3	136.7	157.2	20	33.9	85.5	97.3	125.7	262.2	152
1,2-Dibromo-3-chloropropane	31.6	73.6	83.0	92.4	137.6	149	28.2	74.9	87.3	96.3	152.3	107	86.5	99.6	105.3	112.4	149.3	20	62.0	89.5	95.2	101.0	127.5	152
Dibromochloro-methane	22.2	71.9	84.4	94.4	139.3	149	24.7	74.0	87.4	99.0	147.6	107	100.3	106.7	111.4	120.5	154.7	20	85.0	97.1	103.8	110.6	134.6	152
1,2-Dibromo-ethane	28.5	73.2	82.3	93.3	123.7	149	29.7	76.0	85.1	96.4	126.2	107	95.4	103.9	111.5	118.3	139.6	20	80.6	95.7	102.0	106.6	123.4	152
1,2-Dichloro-benzene	16.2	67.3	81.4	91.9	133.0	149	27.6	71.3	86.0	97.8	138.1	107	88.4	109.6	114.1	124.1	157.7	20	72.0	97.6	102.8	109.9	130.6	152
1,3-Dichloro-benzene	13.7	63.4	76.7	90.1	127.5	149	24.4	66.7	81.9	94.2	134.9	107	85.3	105.8	109.8	121.3	151.3	20	72.0	96.0	100.9	106.7	126.9	152
1,4-Dichloro-benzene	14.7	64.9	76.8	89.9	130.0	149	26.0	68.1	81.4	94.4	132.0	107	85.9	106.0	111.5	120.2	147.5	20	71.0	96.9	101.5	106.4	150.7	152
Dichlorodifluoro-methane	4.9	61.3	87.6	112.6	313.4	149	3.9	46.9	76.6	108.2	316.2	106	32.8	114.0	135.0	186.3	286.9	20	44.3	82.7	103.5	117.5	249.0	152

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.—Continued

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
55 analytes included in NAWQA's National VOC Assessment—Continued																								
1,1-Dichloroethane	11.2	64.4	80.9	94.7	127.0	149	23.3	68.1	84.7	98.3	133.7	107	100.6	107.6	116.9	124.2	163.9	20	80.3	97.3	102.9	109.0	126.0	152
1,2-Dichloroethane	23.4	74.1	86.8	98.0	129.3	149	29.0	76.5	89.1	104.3	142.8	107	99.9	108.1	114.0	126.5	170.0	20	84.0	98.3	106.0	112.6	130.8	152
1,1-Dichloroethene	6.7	54.0	78.9	93.4	140.2	149	17.2	61.9	79.5	91.5	152.4	107	90.6	101.7	108.7	135.4	157.7	20	68.5	90.9	98.1	109.7	138.4	152
cis-1,2-Dichloroethene	12.0	63.0	78.6	92.6	126.0	149	21.8	65.6	81.6	94.9	130.3	107	100.4	107.0	115.8	120.2	150.5	20	83.4	100.1	105.0	107.9	122.0	152
trans-1,2-Dichloroethene	10.4	59.8	78.2	93.9	131.6	149	21.9	64.5	83.0	95.7	134.9	107	95.6	107.6	120.8	123.9	164.3	20	72.5	97.4	103.3	111.0	126.0	152
Dichloromethane	20.1	52.0	70.7	95.4	186.3	149	23.6	60.2	80.3	104.5	157.8	107	76.9	102.7	112.6	126.8	176.4	20	83.9	100.3	108.0	113.0	147.0	152
1,2-Dichloropropane	17.7	64.3	80.0	93.5	129.9	149	26.9	68.2	84.7	95.2	129.9	107	103.5	109.1	117.6	123.1	150.4	20	79.0	95.8	103.0	112.2	126.2	152
cis-1,3-Dichloropropene	24.2	62.7	73.6	87.2	118.1	149	22.3	65.0	79.4	93.6	122.8	107	90.7	100.4	110.8	123.7	140.5	20	85.5	97.7	105.4	111.2	141.7	152
trans-1,3-Dichloropropene	18.4	63.3	75.8	86.8	125.1	149	23.1	67.3	77.4	88.8	123.6	107	86.8	97.5	109.0	119.9	137.7	20	76.6	96.3	101.8	107.0	123.0	152
1,2-Dimethylbenzene	13.2	57.0	73.9	87.3	134.1	149	27.4	61.9	79.5	93.4	139.0	107	95.2	107.1	117.9	128.5	156.5	20	81.0	97.6	102.7	113.9	136.4	152
1,3- and 1,4-Dimethylbenzene	10.5	72.6	94.2	128.9	223.3	149	26.3	70.0	93.0	120.8	215.2	107	96.3	110.2	122.6	134.7	229.7	20	84.0	99.2	107.0	113.5	132.5	152
Ethenylbenzene	5.0	57.4	72.6	87.6	124.5	148	5.4	61.4	80.7	94.3	130.0	107	91.7	103.8	118.2	126.7	163.8	20	82.0	98.6	108.0	112.9	136.8	152
2-Ethoxy-2-methylpropane (ETBE)	20.7	64.0	76.3	91.6	126.2	149	27.9	68.9	80.5	91.8	121.6	107	81.2	106.2	115.0	122.3	143.2	20	74.0	97.0	102.1	111.4	136.6	152
Ethylbenzene	9.6	57.3	73.0	87.5	123.1	149	23.7	60.6	79.3	92.1	126.6	107	94.9	105.3	113.3	121.9	142.3	20	83.0	97.3	102.7	109.9	121.5	152

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.—Continued

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
55 analytes included in NAWQA's National VOC Assessment—Continued																								
1,1,2,3,4,4-Hexachloro-1,3-butadiene	5.8	60.2	75.1	90.5	128.3	149	20.6	63.5	81.1	96.0	133.6	107	90.2	97.1	114.4	125.1	154.8	20	73.2	99.6	106.4	114.8	136.8	152
1,1,1,2,2,2-Hexachloroethane	11.0	59.4	76.1	89.1	213.3	149	18.5	64.5	81.4	94.7	172.8	107	84.3	104.8	109.7	123.6	189.3	20	71.5	94.0	100.0	106.3	129.6	152
2-Methoxy-2-methylbutane (TAME)	24.5	65.4	79.2	89.4	124.6	149	30.2	70.1	81.7	93.4	135.3	107	88.3	106.8	114.5	123.8	143.8	20	73.0	92.8	101.6	113.1	134.1	152
2-Methoxy-2-methylpropane (MTBE)	23.8	68.2	80.1	91.6	117.5	149	32.1	71.7	83.8	93.2	117.0	107	84.2	104.9	116.2	118.9	144.9	20	71.0	93.2	100.0	109.2	127.3	152
Methylbenzene	10.6	62.7	78.4	89.9	165.2	148	24.5	66.5	82.1	96.0	130.9	106	97.5	109.4	113.5	121.5	150.6	19	82.7	96.2	102.4	108.6	121.7	152
(1-Methylethyl)benzene	9.6	56.9	71.0	87.3	131.5	149	19.8	57.7	82.0	91.4	137.1	107	93.5	103.9	112.1	122.9	150.2	20	78.7	96.4	104.0	111.0	128.0	152
Naphthalene	21.5	65.9	76.9	91.3	178.9	149	29.7	69.8	82.7	94.4	157.5	107	78.2	98.7	110.4	123.3	166.6	20	61.0	88.9	97.0	106.4	148.0	152
2,2′-Oxybispropane (DIPE)	10.2	62.3	76.6	89.9	121.1	149	24.4	68.2	79.9	90.7	126.4	107	92.1	101.7	112.1	116.3	146.6	20	80.8	93.7	100.0	105.4	125.7	152
2-Propenenitrile	33.6	85.2	93.9	102.9	253.3	149	30.8	87.7	96.0	105.1	245.6	107	97.8	104.7	111.9	117.1	210.1	20	61.0	97.2	103.1	109.4	136.0	152
n-Propylbenzene	9.5	55.6	70.6	84.3	131.5	149	21.7	56.2	77.4	91.4	140.0	107	89.0	97.9	107.3	120.1	154.7	20	75.8	94.0	100.0	107.5	127.0	152
Tetrachloroethene	8.6	62.3	80.0	96.4	140.1	149	25.5	66.7	86.2	102.1	140.1	106	96.8	107.8	116.0	131.7	164.5	20	66.0	101.2	107.2	117.2	144.0	152
Tetrachloromethane	6.8	58.6	80.7	93.1	139.0	149	20.4	64.9	85.0	95.3	122.8	107	85.4	103.4	113.4	126.4	165.3	20	78.9	94.4	101.3	109.0	137.2	152
Tribromomethane	27.1	71.3	80.2	91.2	146.6	149	27.3	74.3	84.1	94.1	146.6	107	88.0	101.1	105.4	114.7	132.8	20	78.0	91.6	99.6	105.1	132.2	152
1,1,2-Trichloro-1,2,2-trifluoroethane	4.7	54.7	75.6	89.7	129.1	149	17.2	61.1	75.4	91.4	133.4	107	71.4	101.5	108.4	120.4	138.8	20	67.8	91.0	98.8	107.2	123.4	152

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.—Continued

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
55 analytes included in NAWQA's National VOC Assessment—Continued																								
1,2,3-Trichloro-benzene	15.3	67.8	78.1	89.4	170.9	149	26.8	69.2	80.3	92.8	178.4	107	84.6	101.6	108.9	127.8	197.9	20	70.0	92.0	98.0	107.1	147.0	152
1,2,4-Trichloro-benzene	13.0	61.6	69.9	84.0	129.7	149	21.2	64.1	74.9	87.0	138.1	107	55.9	99.7	107.3	118.8	170.6	20	70.0	91.1	99.0	107.6	132.0	152
1,1,1-Trichloro-ethane	10.1	51.0	69.7	87.3	139.8	149	18.0	57.3	74.4	92.0	128.8	107	78.8	91.7	106.2	117.6	166.4	20	78.1	95.9	101.3	108.7	123.0	152
1,1,2-Trichloro-ethane	27.2	75.3	87.9	99.9	144.0	149	31.6	78.9	90.3	104.1	149.9	107	104.3	114.0	121.2	129.2	156.2	20	74.0	100.0	106.6	115.9	137.6	152
Trichloroethene	9.5	63.1	78.7	93.6	128.0	148	24.0	66.5	85.0	96.8	131.3	106	99.1	110.8	116.0	119.5	164.7	19	83.6	97.9	103.0	109.3	123.0	152
Trichlorofluoro-methane	6.1	60.8	80.4	95.4	139.3	149	16.2	65.6	82.2	97.1	140.5	107	76.8	107.8	115.2	131.2	171.2	20	68.1	91.0	99.7	105.8	138.9	152
Trichloromethane	19.0	66.7	83.0	94.5	144.5	149	23.1	70.4	85.6	101.0	138.8	107	99.7	110.3	114.2	119.6	158.3	20	84.5	98.3	103.1	110.3	123.9	152
1,2,3-Trichloro-propane	26.9	75.3	85.0	95.4	136.0	149	32.6	76.7	89.0	98.9	136.2	107	90.3	111.8	119.2	124.9	145.4	20	69.9	87.9	94.1	101.5	116.4	152
1,2,4-Trimethyl-benzene	11.8	64.2	78.4	94.6	141.5	149	26.4	66.2	86.1	99.4	157.1	107	90.8	111.6	120.9	136.3	170.5	20	76.0	100.5	107.1	118.7	134.6	151
Other NWQL analytes																								
Bromobenzene	17.4	62.9	74.7	87.1	120.7	149	23.4	62.8	79.0	93.2	125.0	107	90.8	104.4	110.3	115.8	134.7	20	72.0	93.2	99.6	104.6	123.9	152
Bromochloro-methane	21.6	68.8	84.5	92.8	154.8	149	25.2	70.2	86.0	98.5	146.3	107	53.1	104.5	112.3	117.2	143.0	20	79.6	98.0	102.6	107.4	121.4	152
2-Butanone	40.1	91.3	101.5	110.1	278.6	148	35.9	90.9	101.4	110.7	275.0	106	100.1	109.9	116.8	122.2	146.2	20	81.0	99.0	105.8	113.8	134.6	152
Carbon disulfide	12.9	55.6	78.2	95.0	157.2	148	21.6	60.5	78.7	95.3	142.4	106	68.0	103.9	121.0	134.0	165.2	20	45.8	95.4	102.2	110.3	154.0	152
1-Chloro-2-methylbenzene	13.8	58.4	72.1	88.7	126.0	149	21.1	60.8	79.2	93.8	134.9	107	84.8	105.2	111.3	121.0	141.3	20	74.8	97.1	101.0	106.5	121.9	152
1-Chloro-4-methylbenzene	11.8	60.7	73.0	87.1	125.0	149	22.5	63.6	78.8	92.4	129.4	107	82.2	105.4	111.1	117.2	147.3	20	75.0	95.9	100.8	107.3	122.0	152

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.—Continued

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
Other NWQL analytes—Continued																								
3-Chloro-1-propene	9.2	56.9	73.6	88.9	142.8	149	18.8	62.2	79.0	89.6	145.2	107	85.7	103.0	114.1	120.6	168.8	19	71.7	97.0	103.7	109.0	136.0	152
Dibromomethane	16.1	24.5	69.2	89.2	134.3	149	17.6	26.4	76.7	96.7	143.7	107	29.4	100.2	109.7	118.2	150.2	20	78.0	96.3	100.8	106.0	127.8	152
trans-1,4-Dichloro-2-butene	25.2	74.7	86.3	97.9	141.2	149	27.7	76.6	88.0	102.4	147.2	107	99.1	102.9	117.0	132.4	157.9	20	74.0	97.4	109.0	119.2	172.0	152
1,3-Dichloropropane	24.3	73.7	86.0	96.0	132.8	149	30.4	74.0	89.8	100.1	135.5	107	102.4	107.9	116.3	123.4	154.1	20	76.0	99.2	105.2	111.2	127.0	152
2,2-Dichloropropane	6.7	49.9	63.7	74.8	95.5	149	15.7	53.0	63.1	79.2	112.4	107	80.7	95.0	101.7	116.9	167.6	20	76.8	91.2	98.5	105.3	133.1	152
1,1-Dichloropropene	6.3	58.6	78.5	92.5	132.0	149	20.6	63.1	81.0	96.6	131.8	107	88.5	103.8	114.1	121.8	166.4	20	78.2	98.1	105.3	110.2	137.5	152
(1,1-Dimethylethyl)benzene	8.5	59.8	77.5	91.4	130.7	149	22.1	65.0	85.7	97.3	138.1	107	94.9	104.4	114.4	121.2	171.1	20	76.0	99.0	105.7	111.6	127.8	152
1,4-Epoxybutane	34.0	80.0	90.4	97.1	124.4	146	33.3	82.9	89.4	98.1	130.8	105	100.1	102.5	106.1	114.4	132.5	20	78.0	95.0	102.1	108.0	169.0	152
1-Ethyl-2-methylbenzene	11.0	59.0	74.9	87.2	133.9	149	20.9	61.4	79.2	95.4	141.3	107	87.2	99.9	113.1	121.9	158.3	20	73.0	95.8	101.2	107.7	129.0	152
Ethyl 2-methyl-2-propenoate	22.7	65.3	77.4	86.1	121.4	149	26.3	70.6	79.3	89.5	125.2	107	89.1	98.6	105.3	111.4	128.6	20	73.0	97.7	106.0	119.0	141.0	152
2-Hexanone	31.3	74.6	87.4	98.0	158.7	149	31.2	79.3	89.4	98.6	171.4	107	92.4	102.5	110.9	118.0	151.6	20	71.0	95.5	100.9	106.9	127.0	152
Iodomethane	3.9	56.6	75.0	98.6	152.7	149	9.2	58.9	82.0	96.3	152.3	107	57.1	115.0	127.1	136.2	221.8	20	50.0	95.4	111.9	135.0	235.8	152
1-Isopropyl-4-methylbenzene	7.1	55.7	70.9	84.8	133.3	149	19.4	58.0	78.4	89.3	143.9	107	84.5	100.6	109.5	116.2	170.0	20	71.1	94.7	100.0	105.5	151.0	152
Methyl-2-methyl-2-propenoate	25.9	73.3	88.4	97.4	125.2	149	32.3	77.4	88.2	98.0	131.2	107	98.9	107.3	112.0	124.1	136.1	20	73.0	97.7	106.0	119.0	141.0	152
4-Methyl-2-pentanone	25.8	72.4	84.3	96.3	137.8	148	36.5	76.5	86.7	97.0	139.0	106	79.4	108.4	113.2	119.6	129.8	20	66.0	88.8	98.3	107.2	129.8	152

Table 5. Summary of statistical information on percent recovery of 85 volatile organic compounds for field matrix spikes, field matrix spike replicates, laboratory matrix spikes, and laboratory reagent spikes for ground- and surface-water samples combined.—Continued

[Spiking procedures utilized a 25-microliter syringe with a spike solution designed to achieve a concentration of 0.5 microgram per liter. Min, minimum; Max, maximum; n, number of samples analyzed; NWQL, National Water Quality Laboratory]

Compound	Field matrix spikes						Field matrix spike replicates						Laboratory matrix spikes						Laboratory reagent spikes					
		Percentile[1]						Percentile[1]						Percentile[1]						Percentile[1]				
	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n	Min	25	50	75	Max	n
Other NWQL analytes—Continued																								
2-Methyl-2-propenenitrile	32.3	81.5	92.4	100.3	206.0	149	32.0	84.6	93.6	102.3	201.8	107	98.7	107.0	113.2	121.8	155.0	20	84.0	96.8	103.3	109.4	134.1	152
Methyl-2-propenoate	33.4	79.6	89.1	99.1	196.2	149	30.7	81.5	91.5	101.7	189.8	107	98.4	108.4	114.0	121.5	151.4	20	0.0	97.4	103.0	110.0	124.4	152
(1-Methyl-propyl)benzene	4.0	57.8	74.5	90.1	133.9	149	22.6	59.4	83.2	96.0	144.5	107	92.1	106.0	116.8	125.6	170.4	20	75.0	99.1	105.5	115.1	138.7	152
1,1′-Oxybisethane	21.2	66.1	78.3	91.2	194.1	149	28.7	72.0	82.6	92.7	167.7	107	90.6	100.6	113.4	120.7	137.6	20	63.1	93.0	100.7	108.8	136.0	152
2-Propanone	26.2	87.2	96.0	108.1	168.9	148	35.0	86.1	98.2	109.6	164.2	106	80.6	96.3	105.7	124.6	167.9	20	64.1	90.9	98.0	108.2	139.0	152
1,1,1,2-Tetrachloroethane	17.0	65.4	77.9	89.3	126.6	149	22.1	69.3	79.8	94.2	122.6	107	92.2	103.8	107.1	114.8	137.7	20	78.8	94.0	99.8	104.6	119.6	152
1,1,2,2-Tetrachloroethane	28.9	76.2	86.1	95.8	138.9	149	30.3	77.3	89.8	100.6	138.9	107	95.6	106.4	112.0	120.6	171.6	20	77.0	95.3	101.7	107.2	123.6	152
1,2,3,4-Tetramethylbenzene	15.0	69.2	83.7	101.6	161.7	130	23.3	70.4	86.2	102.7	164.1	89	94.4	109.7	118.8	136.3	165.4	15	0.0	107.2	118.7	128.2	178.9	152
1,2,3,5-Tetramethylbenzene	12.8	57.9	71.3	89.4	130.6	149	19.4	59.2	75.1	91.7	131.0	107	68.2	101.7	111.8	124.6	163.9	20	75.0	91.3	99.6	108.5	136.1	152
1,2,3-Trimethylbenzene	13.4	66.4	83.8	99.0	150.5	149	25.6	68.7	88.2	104.3	159.4	107	98.3	114.8	126.3	139.3	178.9	20	80.0	104.2	112.2	119.8	147.0	152
1,3,5-Trimethylbenzene	10.3	57.5	74.5	90.1	150.7	149	23.3	59.6	79.8	95.5	162.4	107	88.8	106.7	120.4	130.1	163.6	20	76.0	98.2	105.2	114.7	137.0	152

[1]The 75th, 50th (median), and 25th percentiles split the data into four equal-sized quarters. The 75th percentile, also called the upper quartile, is a value that exceeds no more than 75 percent of the data and is exceeded by no more than 25 percent of the data. The 25th percentile, or lower quartile, is a value that exceeds no more than 25 percent of the data and is exceeded by no more than 75 percent of the data. The median, or 50th percentile, is the central value of the distribution when the data are ranked in order of the magnitude. For an odd number of observations, the median is the data point that has an equal number of observations both above and below it. For an even number of observations, the median is represented by the average of the two central observations (Helsel and Hirsch, 1992).

For all spike types, 87 percent of the individual VOC recoveries were within the range of 60 to 140 percent, which is considered acceptable by the U.S. Environmental Protection Agency's (USEPA) established analytical method (Slater, 1986; Rose and Schroeder, 1995). The range of 60 to 140 percent is designated on the individual VOC recoveries presented in Appendix 2. The ranges of median recovery for 85 individual VOCs for spike types are as follows: (1) FMSs, 63.7 percent (2,2-dichloropropane) to 101.5 percent (2-butanone); (2) FMSRs, 63.1 percent (2,2-dichloropropane) to 101.4 percent (2-butanone); (3) LMSs, 101.7 percent (2,2-dichloropropane) to 135.0 percent (dichlorodifluoromethane); and (4) LRSs, 91.0 percent (bromomethane) to 118.7 percent (1,2,3,4-tetramethylbenzene).

In general, the median percent recoveries determined from each spike type for individual VOCs followed the same pattern as for all VOCs combined. The median percent recovery for all individual VOCs was greater for LRSs than for FMSs. Median recoveries of about 100 percent for LRSs indicate that laboratory performance was good, and therefore, the analytical laboratory method is probably not the reason for the relatively low VOC recoveries associated with FMSs. The reason for the lower VOC recoveries from FMSs than from LRSs may be associated with the spike solution, environmental conditions in the field, spiking technique, and/or loss of VOCs during transport and storage. The median percent recoveries for individual VOCs were greatest for LMSs. Median recoveries from LMSs were greater than LRSs with the exception of two VOCs, iodomethane and 1,2,3,4-tetramethylbenzene. The reason for greater VOC recovery from LMSs than from LRSs is not known, but may be attributed to matrix effects (discussed in the Matrix Effects section in more detail).

Variability

Variability associated with the field spiking procedure is primarily characterized by comparing the recoveries from FMSs to those from FMSRs on an individual VOC basis (fig. 1). Overall, recoveries from 107 paired FMSs and FMSRs were evaluated for each of the 85 VOCs (table 1). The median percent recovery of individual VOCs from FMSs and FMSRs can be compared visually on figure 6. The FMSR recoveries are greater than the FMS recoveries for most VOCs. Statistical analyses (Wilcoxon Rank Sum Test) indicate that the difference in individual VOC recoveries between FMSs and FMSRs are statistically significant at a 95-percent confidence interval for 75 of the 85 VOCs analyzed. Only 1,2,3,4-tetramethylbenzene, 1,3- and 1,4-dimethylbenzene, 2-butanone, 2-propanone, bromomethane, chloroethene, chloromethane, dichlorodifluoromethane, ethenylbenzene, and *trans*-1,2-dichloroethene had FMS and FMSR recoveries that were not statistically different indicating similar recoveries for these VOCs.

Permanently E-coded compounds (bromomethane, chloromethane, dichlorodifluoromethane, and iodomethane) also had variability in recovery (table 5 and Appendix 2). The recoveries associated with these compounds had IQRs that exceeded 40 percent in one or more of the spike types. The recoveries associated with dibromomethane, dichloromethane, and 1,3- and 1,4-dimethylbenzene also had IQRs greater than 40 percent in one or more of the spike types. It is unknown why there is a larger variation in recoveries for the latter three compounds.

Because the FMS sample is processed before the FMSR in the field, there is a greater opportunity for VOC losses from the spiking solution used to spike the samples when the FMSR is processed than when the FMS is processed. This would have resulted in lower recoveries in FMSRs than in FMSs. However, this was not observed. It is possible that the routine established by processing the FMS sample results in a more fluid and efficient technique that is employed when processing the FMSR. The increased efficiency in spiking the FMSR may explain the higher recoveries obtained in these samples. Recoveries from FMSRs generally are greater and statistically different for most VOCs in comparison to FMSs indicating that variability may be associated with the spiking procedure.

Degradation

Degradation of VOCs in ground-water and surface-water samples is not expected because samples were preserved with a 1:1 solution of HCl:H_2O to a pH of 2.0 to inhibit microbiological activity; chilled at 4°C (39.2°F); and analyzed within a maximum holding period of 14 days. However, documenting the extent of degradation, if any, is important to understand if specific compounds of interest are being correctly qualified in ground- and surface-water samples and if concentrations may be underestimated. Degradation is characterized by examining recoveries from FMSs and by comparing recoveries from FMSs to LMSs (fig. 1). In addition, degradation is characterized by calculating recoveries from data previously published in a stability study.

The most fundamental mechanism to characterize all facets of degradation (losses incurred during transport, storage, and analyses) is through the evaluation of FMSs. One-hundred forty-nine FMSs were processed and evaluated. The median recoveries ranged from 63.7 percent (2,2-dichloropropane) to 101.5 percent (2-butanone) (table 5), with an overall median of 79.9 percent for all VOCs.

Comparison between FMS and LMS recoveries can provide additional information on degradation, specifically losses incurred during shipping to and storage at the laboratory. Recoveries for 20 pairs of FMS and LMS samples were compared for each of the 85 individual VOCs (table 1). Median recoveries were greater for LMSs than FMSs (fig. 6).

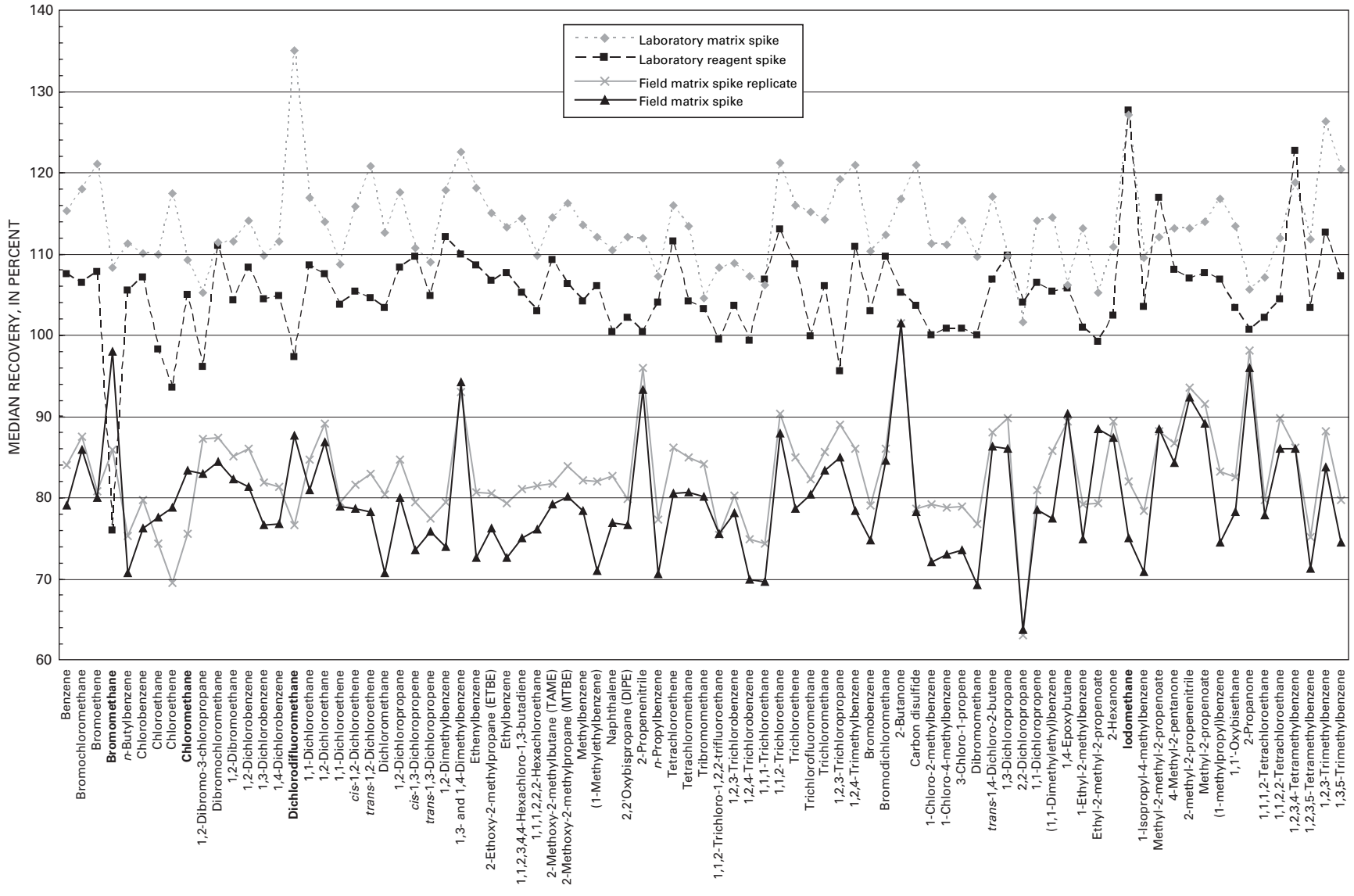


Figure 6. Median percent recoveries of individual volatile organic compounds for field matrix spikes, field matrix spike replicates, and laboratory matrix spikes for ground- and surface-water samples combined; and for laboratory reagent spikes (alphabetized by 55 NAWQA analytes and by 33 additional compounds; recoveries for bolded compounds are reported as estimated concentrations by the U.S. Geological Survey's National Water Quality Laboratory).

Recoveries for individual VOCs were significantly different at the 95-percent confidence interval (Wilcoxon Rank Sum Test) for 83 of the 85 paired VOCs analyzed; statistical differences were not observed for 2-propanone and bromomethane. One possibility for the large difference in recoveries between LMSs and FMSs may be degradation. However, LMSs generally had median recoveries greater than 110 percent (overall median of 113.1 percent), whereas most FMS median recoveries were less than 90 percent (overall median of 79.9 percent). It is unknown why the median recoveries from the LMSs were consistently greater than 110 percent (Donna Rose, U.S. Geological Survey, oral commun., 2004). Regardless, this large difference in median recoveries between LMSs and FMSs renders it impossible to determine if these losses were due to degradation or simply the difference in spiking technique, spiking experience, the number of different individuals involved in processing the FMSs, and/or environmental conditions when the samples were spiked. The results from a separate stability study (Love and others, 1998) performed under controlled conditions does, however, better characterize degradation of VOCs in water samples.

Adjusted LMS recoveries (LMS_{adj}), as explained in the Methods Used for Interpretation of a Stability Study section of this report, are used to further characterize VOC degradation. Interpretation of these data is used to examine the stability of low (0.5 µg/L) concentrations of VOCs in ground- and surface-water samples preserved with hydrochloric acid, chilled at 4°C (39.2°F), and kept in the dark prior to analysis, as is the normal protocol for processing ground- and surface-water samples intended for VOC analysis.

Overall, after 14 days, LMS_{adj} recoveries were very good, with an overall mean for ground- and surface-water recoveries of 100.4 and 103.8 percent, respectively (Appendix 3). Sixty-seven of the 85 VOCs had mean LMS_{adj} recoveries within the range of 90 to 110 percent (table 6). Only 5 VOCs had LMS_{adj} recoveries less than 90 percent, ranging from 80.9 percent (1,2,3,5-tetramethylbenzene) to 86.7 percent (*trans*-1,4-dichloro-2-butene) (table 6). Thirteen VOCs had overall LMS_{adj} recoveries greater than 110 percent, ranging from 110.3 percent (1,1-dichloroethene) to 148.0 percent (dichlorodifluoromethane) (table 6). Four of the 18 VOCs are permanently E-coded by the NWQL including bromomethane, chloromethane, dichlorodifluoromethane, and iodomethane. Overall, the LMS_{adj} recoveries indicate that VOC degradation does not appear to markedly affect the recovery for VOCs monitored by the NAWQA Program.

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Table 6. Volatile organic compounds with laboratory matrix spike adjusted recoveries equal to or less than 90 percent, and equal to or greater than 110 percent based on the volatile organic compound stability study by Love and others (1998).

[Recoveries represent calculations for day 14 of the study]

Compound	Adjusted recoveries of laboratory matrix spikes, in percent[1]
Recoveries equal to or less than 90 percent	
trans-1,4-Dichloro-2-butene	86.7
Ethenylbenzene	84.9
Naphthalene	82.1
1,2,3,4-Tetramethylbenzene	82.4
1,2,3,5-Tetramethylbenzene	80.9
Recoveries equal to or greater than 110 percent	
Bromoethene	113.1
Bromomethane[2]	118.9
Carbon disulfide	115.2
Chloroethane	120.3
Chloroethene	126.7
Chloromethane[2]	139.4
Dichlorodifluoromethane[2]	148.0
1,1-Dichloroethene	110.3
trans-1,2-Dichloroethene	111.8
1,1-Dichloropropene	114.8
Iodomethane[2]	118.3
2-Propenenitrile	111.6
Trichlorfluoromethane	121.2

[1]Adjusted recoveries for both ground- and surface-water samples were calculated. The lower of the two values is listed for adjusted laboratory matrix spike recoveries equal to or less than 90 percent recovery; and the greater of the two values is listed for adjusted laboratory matrix spike recoveries equal to or greater than 110 percent.

[2]Detections of these compounds are reported by the U.S. Geological Survey's National Water-Quality Laboratory as estimated concentrations (E-coded).

Matrix Effects

The efficiency of analytical processes may be adversely affected by matrix effects. Matrix effects are typically associated with VOC analytical interference resulting from organic matter and from salts that are present in briny water samples. That is, high salt content in a sample may affect the purging efficiency of VOC analytical methods. This loss or modification of VOC recoveries due to constituents in the water sample can be assessed by comparing the recoveries from LMS and LRS pairs

LMS samples consist of surface water or ground water that contains naturally occurring constituents that may negatively affect VOC recoveries. In contrast, LRSs consist of deionized water that is continuously purged with ultrapure nitrogen at the NWQL. Recoveries from LRSs are not considered to be affected by matrix effects because LRSs do not contain significant organic matter or other constituents that may be present in ground water and surface water. LMSs and LRSs are prepared by trained analytical chemists in a controlled environment, and as such, the variability of VOC recoveries associated with spiking is small. Therefore, any differences between LMS and LRS recoveries primarily characterize the effects, if any, from matrix interference.

To characterize the matrix effects of spiked samples, the recoveries of 20 pairs of LMS and LRS samples were compared. The median recoveries of LMSs (overall median of 113.1 percent) were greater than median recoveries of LRSs (overall median of 103.5 percent) (fig. 6 and table 5). However, individual VOC recoveries were not significantly different between LMSs and LRSs at a 95-percent confidence level (Wilcoxon Rank Sum Test) with the exception of 2-propenenitrile and dichloromethane.

LMS recoveries (table 5) indicate minimal effects of organic matter on purging efficiency associated with the NWQL analytical processes. In addition, LRS recoveries used to assess the method performance indicate minimal bias in the analytical method. The excellent and statistically significant comparison between LMS and LRS recoveries demonstrates that low VOC concentrations routinely and accurately can be measured by the analytical methods used by the NWQL and indicates that VOC recoveries are not affected by matrix effects. This was to be expected, however. Matrix effects should be negligible to non-existent due to the analytical technique (P&T GC/MS) used for VOC samples at the NWQL, which should account for 99.9 percent of the true concentration, especially considering that the NAWQA Program does not monitor briny or brackish waters (James F. Pankow, Oregon Health & Science University, written commun., 2002).

Summary

The data-quality objectives of the U.S. Geological Survey's (USGS) National Water-Quality Assessment (NAWQA) Program include estimating the extent to which measurement variability, degradation, and matrix effects, if any, may affect the interpretation of chemical analyses of ground- and surface-water samples. In order to help meet these objectives, a known mass of volatile organic compounds (VOCs) are added (spiked) to water samples. These spiked VOC samples were used to assess the quality of VOC data from samples collected and processed by 25 Study Units. The 276 ground- and surface-water samples included in this report were spiked using a 25-microliter gas-tight syringe with a spike solution containing 85 VOCs designed to achieve a concentration of 0.5 microgram per liter. Water samples spiked in the field include field matrix spikes (FMSs) and field matrix spike replicates (FMSRs). Water samples spiked at the USGS National Water-Quality Laboratory (NWQL) include laboratory matrix spikes (LMSs) and laboratory reagent spikes (LRSs). These four different types of spiked samples were used to evaluate variability, degradation, and matrix effects associated with measuring low-level concentrations of 85 VOCs in ground- and surface-water samples.

Combined recoveries for 85 VOCs from 149 FMSs, 107 FMSRs, 20 LMSs, and 152 LRSs were used to broadly characterize general patterns and central tendencies of VOC recoveries. FMSs had the lowest median recovery of the spike types, 79.9 percent; FMSRs had a median recovery of 83.3 percent; LMSs had a median recovery of 113.1 percent; and LRSs had a median recovery of 103.5 percent.

The recovery pattern for individual VOCs by spike type was similar to recovery for all 85 VOCs combined. Most of the individual VOC recoveries from FMSRs, in general, were slightly greater than recoveries from FMSs. Individual VOCs from LMSs had the greatest percent recoveries, and those from LRSs had median recoveries of about 100 percent. The median recoveries for individual VOCs ranged from 63.7 percent (2,2-dichloropropane) to 101.5 percent (2-butanone) in FMSs, 63.1 percent (2,2-dichloropropane) to 101.4 percent (2-butanone) in FMSRs, 101.7 percent (2,2-dichloropropane) to 135.0 percent (dichlorodifluoromethane) in LMSs, and 91.0 percent (bromomethane) to 118.7 percent (1,2,3,4-tetramethylbenzene) in LRSs. Two of these compounds, dichlorodifluoromethane and bromomethane, are always reported with estimated concentrations (E-coded) and do not perform as well as other VOCs in the purge and trap gas chromatography/mass spectrometry (P&T GC/MS) methodology used by the NWQL.

Individual VOC recoveries were compared among paired spike types and used to evaluate variability, degradation, and matrix effects that may affect the interpretation of chemical analyses of ground- and surface-water samples. Variability associated with the field spiking procedure primarily was characterized by comparing the recoveries from 107 pairs of FMS and FMSR samples on an individual VOC basis. The FMSR recoveries were slightly greater than the FMS recoveries for most VOCs. It is possible that the routine established by processing the FMS sample first resulted in a more fluid and efficient technique that is employed when processing the FMSR. This increased efficiency in spiking the replicates may explain the greater FMSR recoveries than FMS recoveries.

Degradation was characterized by evaluating FMS recoveries and by comparing recoveries from 20 pairs of FMS and LMS samples. As previously described, FMS recoveries were between about 63 and 101 percent, and all individual recoveries were greater for LMSs than for the paired FMSs. The cause of the large difference in median recoveries between LMSs and FMSs is unknown. This difference in median recoveries may be due to degradation, environmental conditions, and/or the difference in spiking technique and spiking experience. Degradation also was characterized by interpretation of data from a previously published VOC stability study in which ground- and surface-water samples were spiked with VOCs and analyzed after 14 days. Data from this study yielded an overall mean for ground- and surface-water samples of 100.4 and 103.8 percent, respectively. This comprehensive study indicates that low concentrations of VOCs in samples are stable when preserved with hydrochloric acid, chilled at 4°C (39.2°F), kept in the dark prior to analysis, and analyzed within 14 days; as is the case with ground- and surface-water samples analyzed for the NAWQA Program.

LRSs when paired to LMSs were used to assess matrix effects, if any, caused by organic matter or other factors in the ground and surface water that may potentially affect analytical purging efficiency. With the exception of 2-propenenitrile and dichloromethane, individual VOC recoveries were not significantly different between LMSs and LRSs. Additionally, matrix effects should be negligible due to the analytical technique (P&T GC/MS) used for VOC analysis from ground- and surface-water samples at the NWQL.

The reason for the lower VOC recoveries from FMSs and FMSRs than from LMSs and LRSs may be associated with differences in technique and spiking experience, and to varying environmental conditions at the time of spiking. However, for all spike types, 87 percent of the individual VOC recoveries were within the range of 60 to 140 percent, a range that is considered acceptable by the U.S. Environmental Protection Agency's established analytical method. Additionally, the median recovery for each spike type was within the range of 60 to 140 percent. The excellent VOC recoveries from LMSs and LRSs demonstrate that low VOC concentrations routinely and accurately can be measured by the analytical methods used by the NWQL.

References

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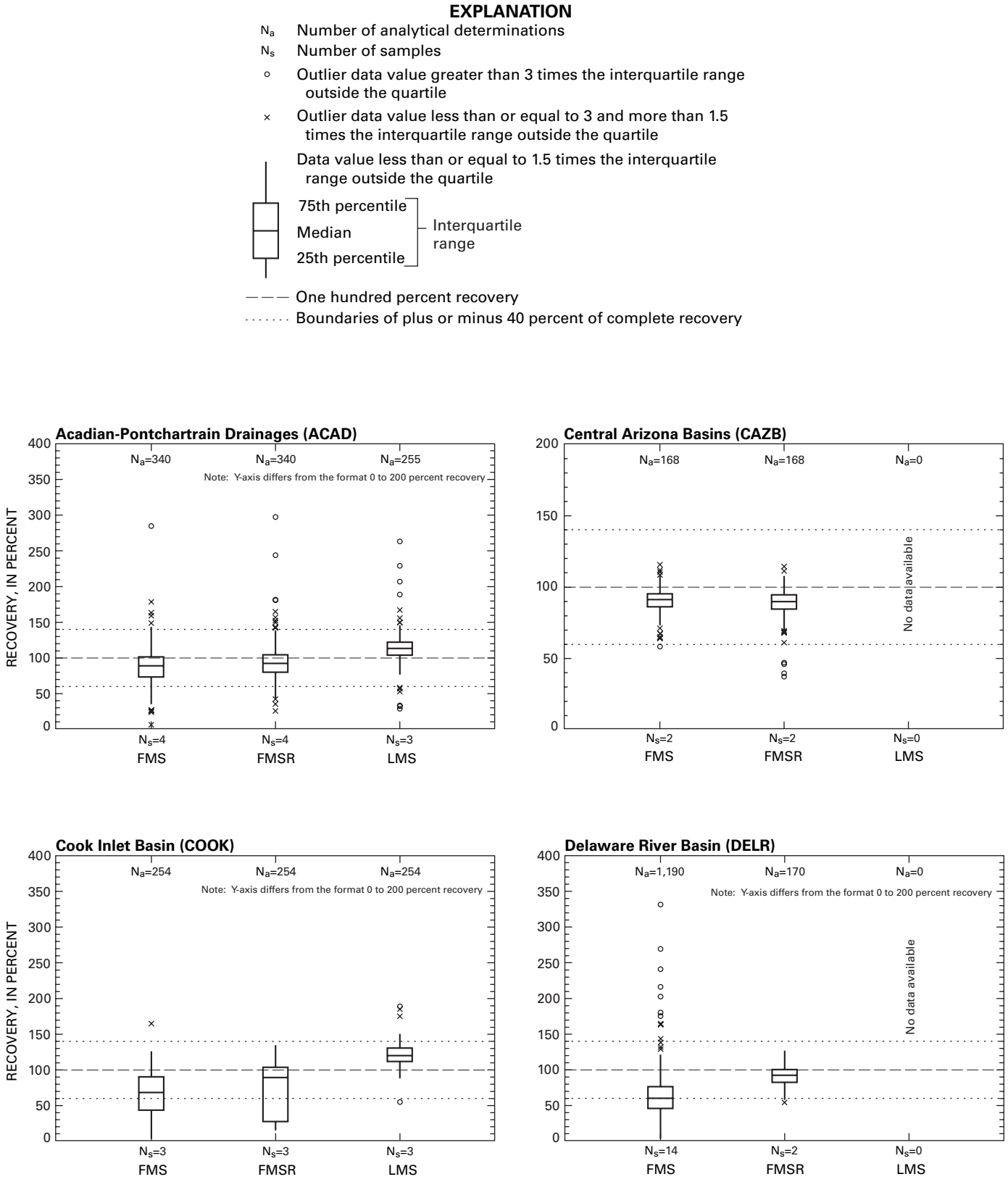
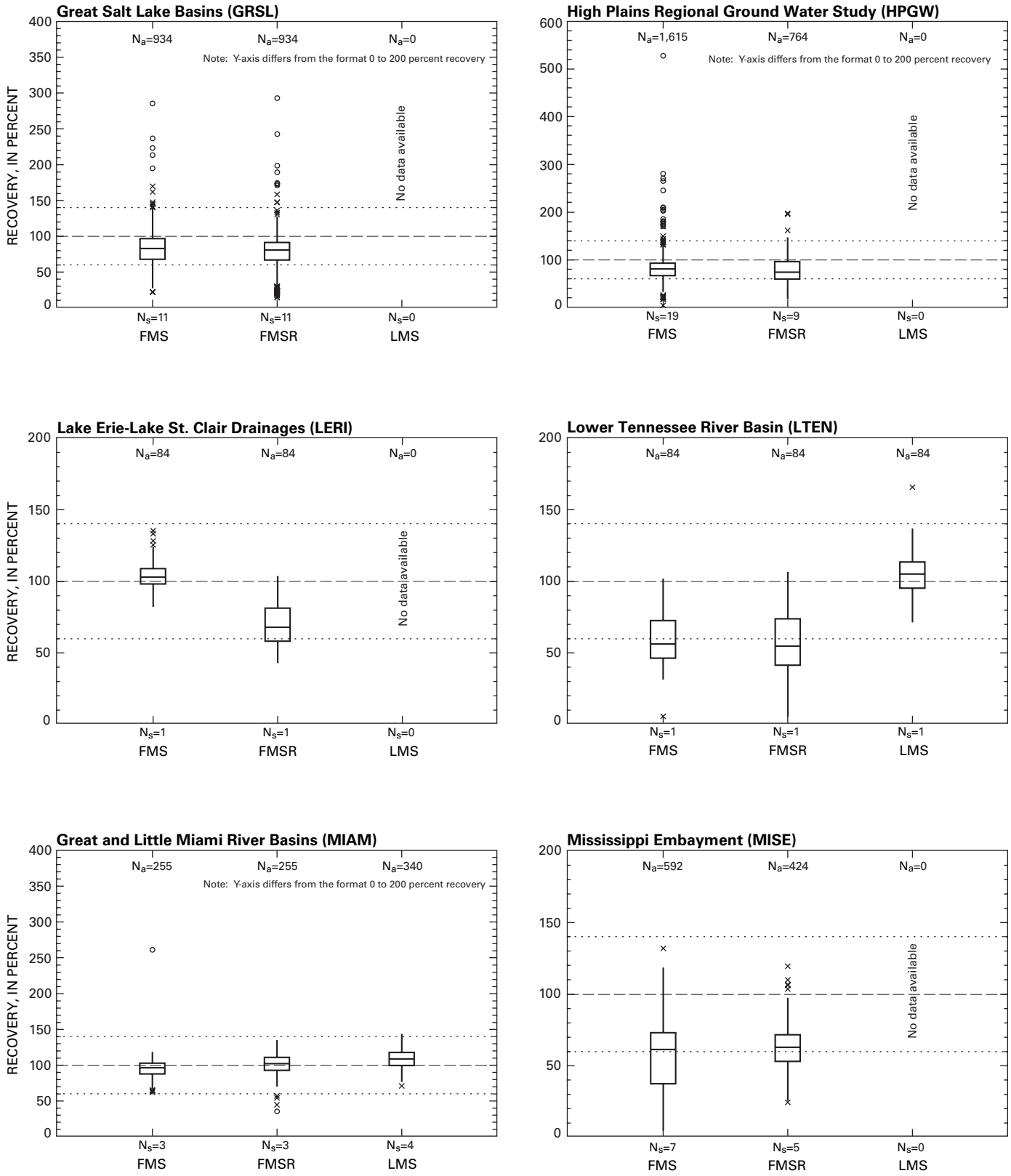
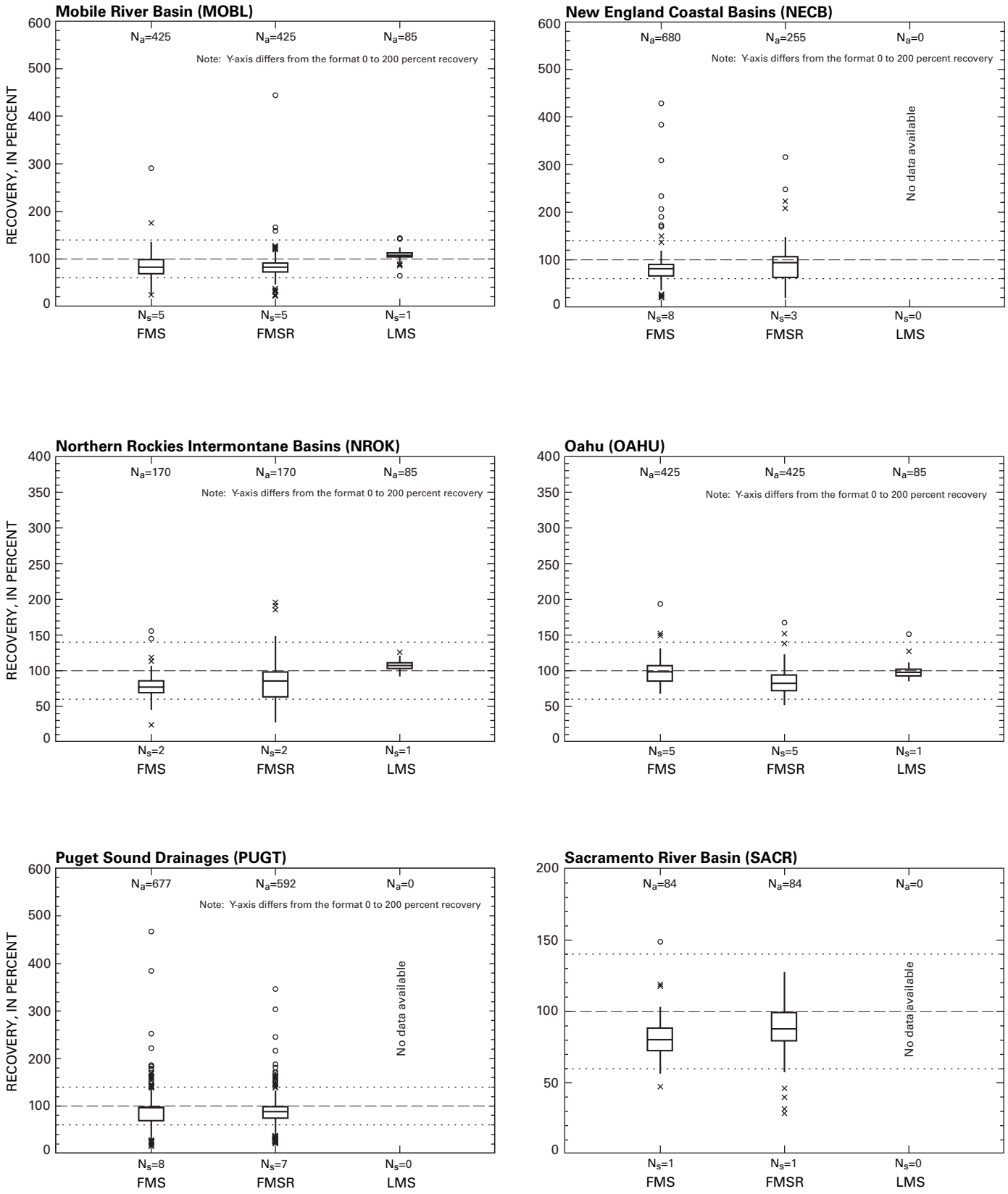
Appendixes



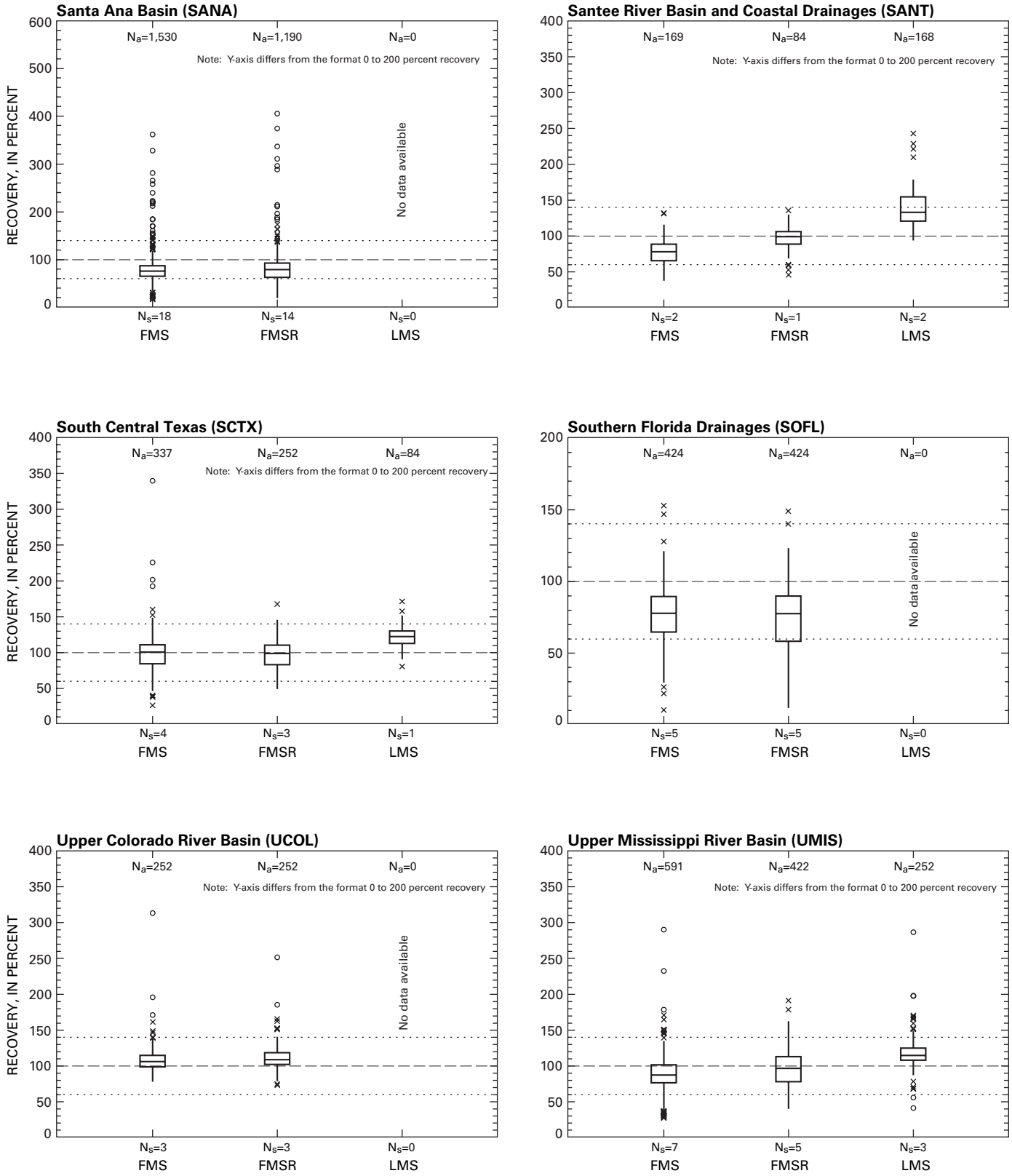
Appendix 1. Volatile organic compound recoveries from field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs) by Study Unit.



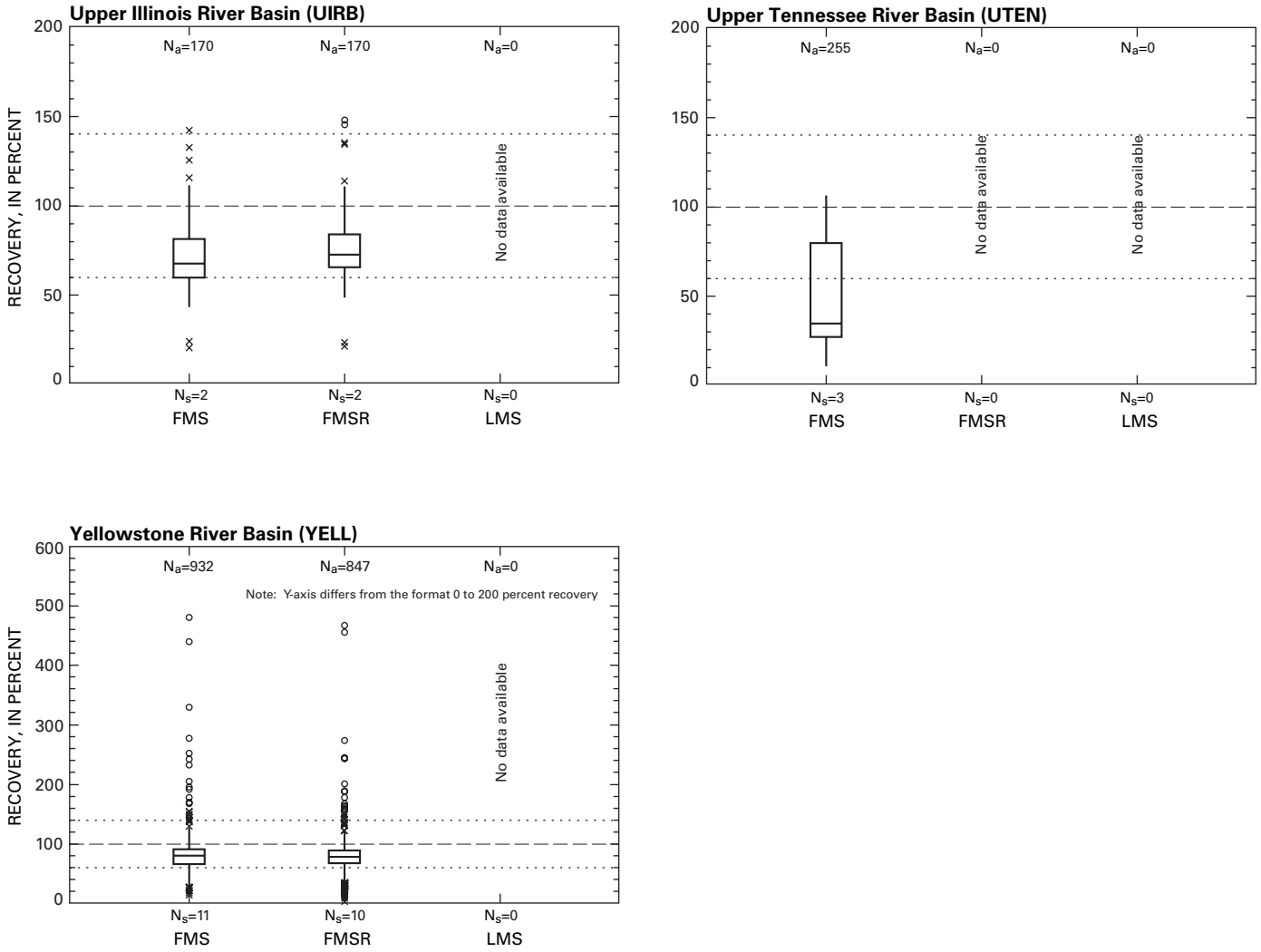
Appendix 1. Volatile organic compound recoveries from field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs) by Study Unit.—Continued



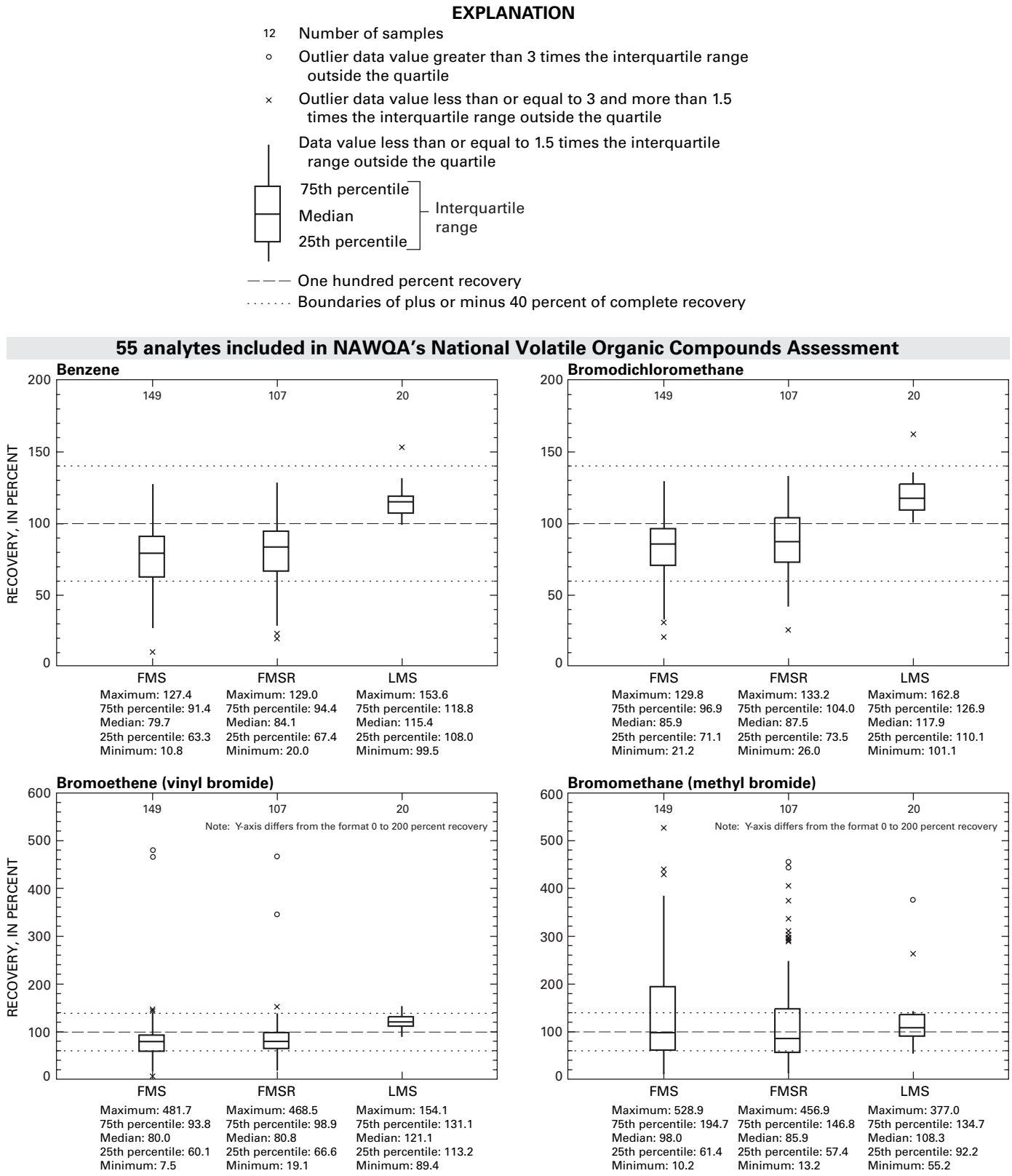
Appendix 1. Volatile organic compound recoveries from field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs) by Study Unit.—Continued



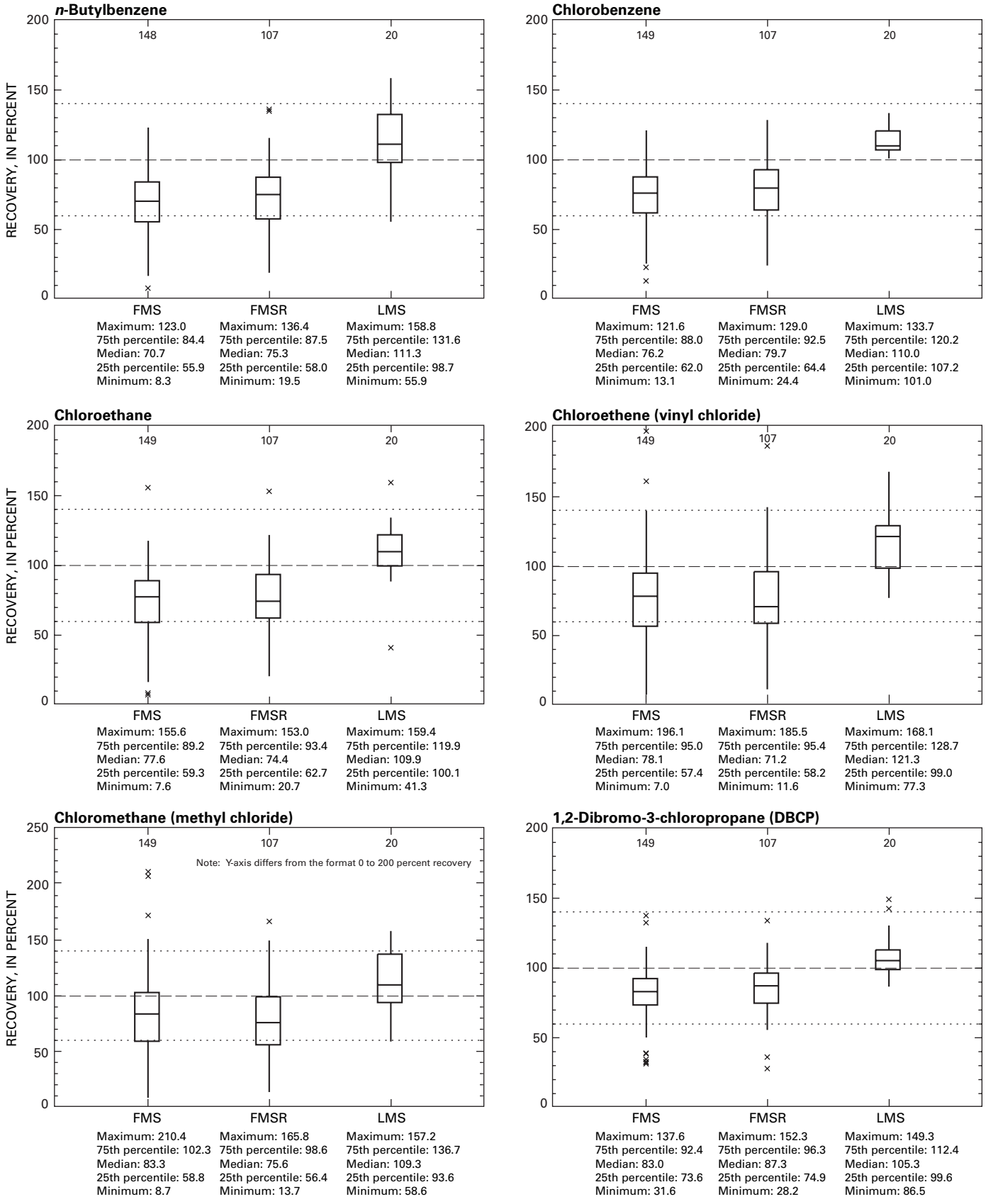
Appendix 1. Volatile organic compound recoveries from field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs) by Study Unit.—Continued



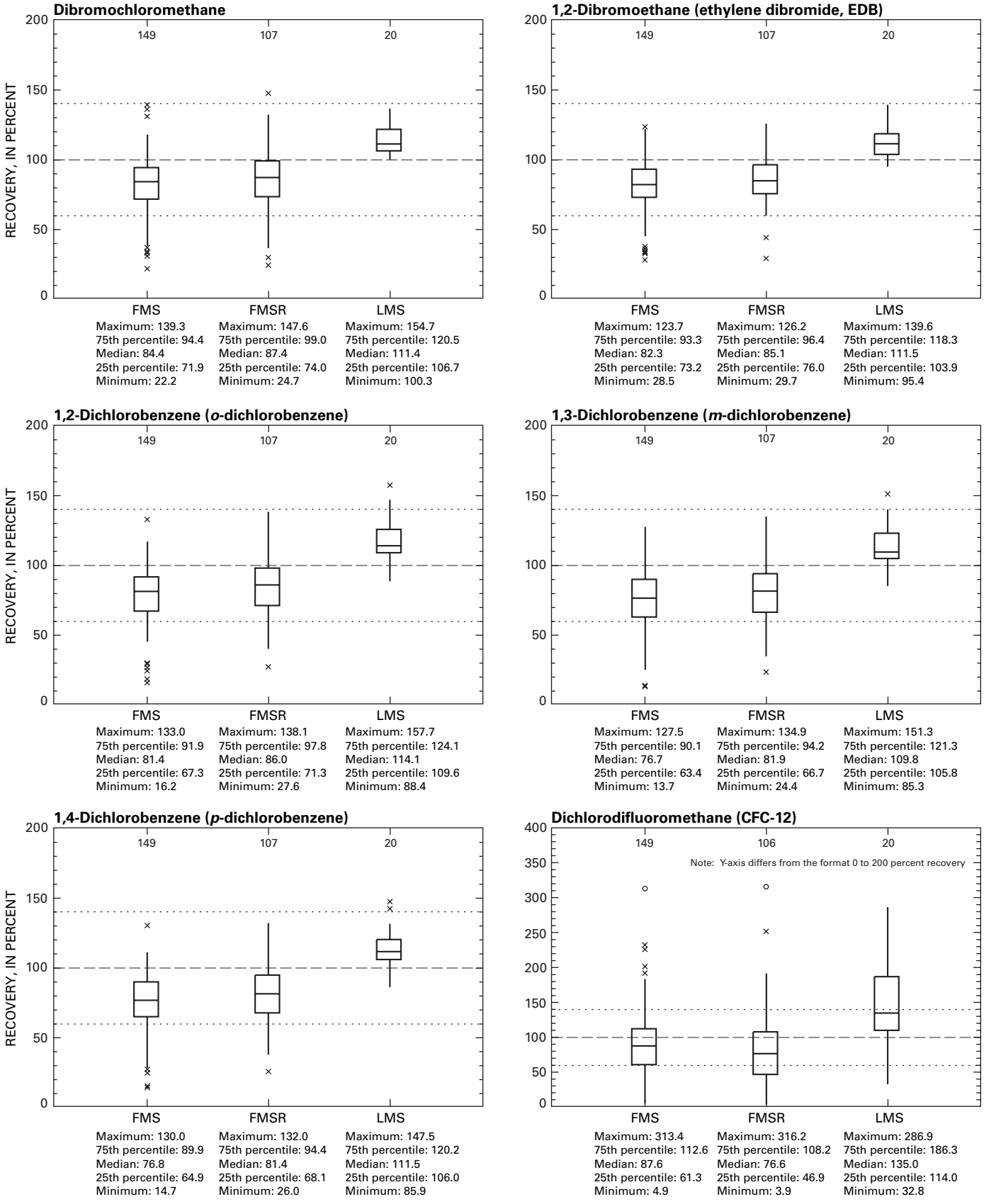
Appendix 1. Volatile organic compound recoveries from field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs) by Study Unit.—Continued



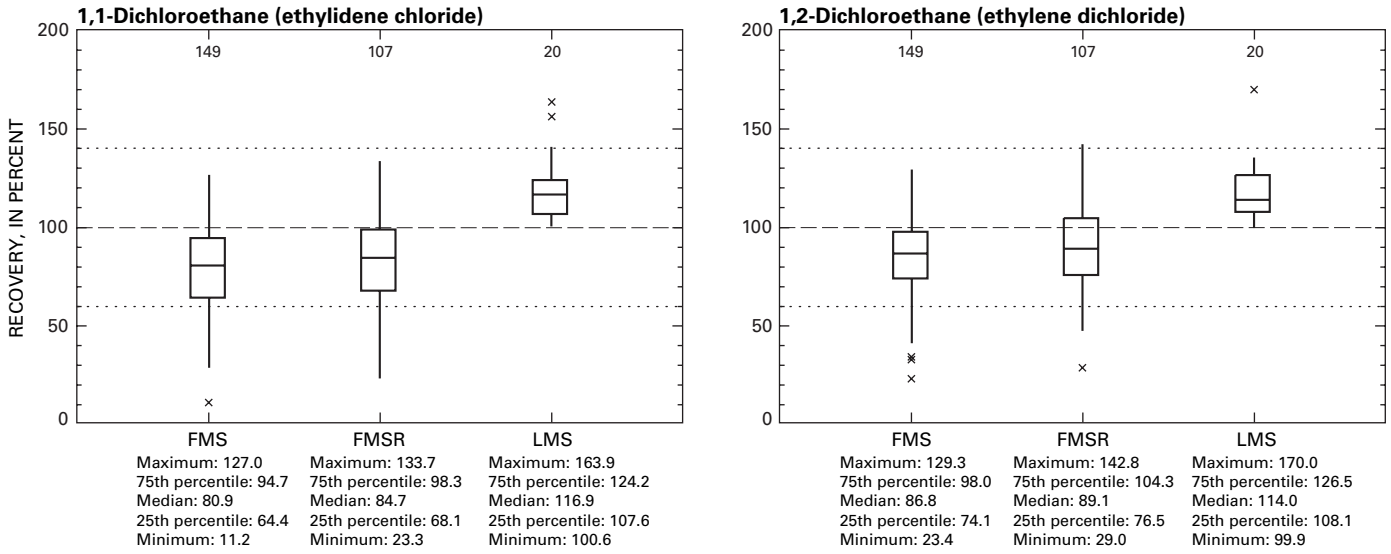
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).

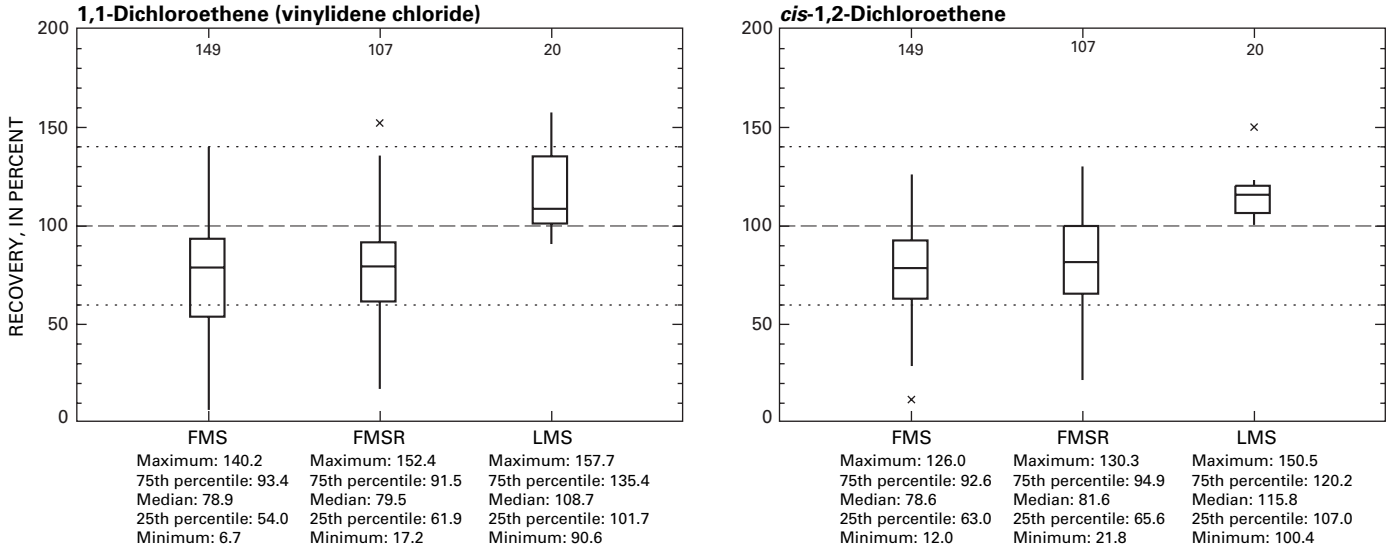


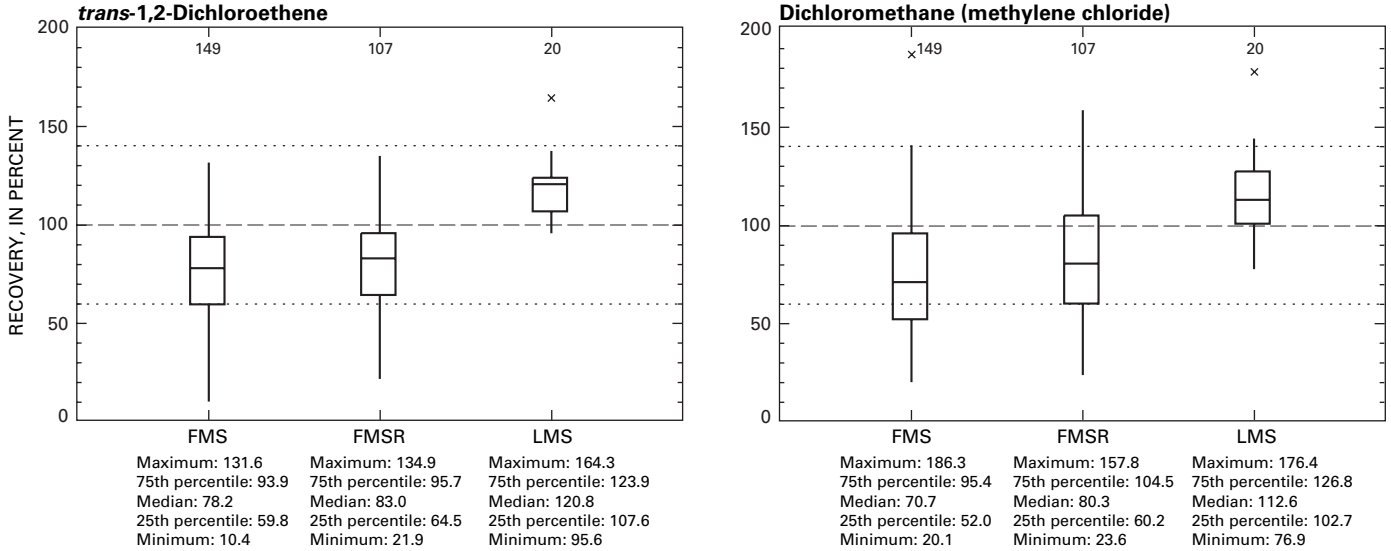
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



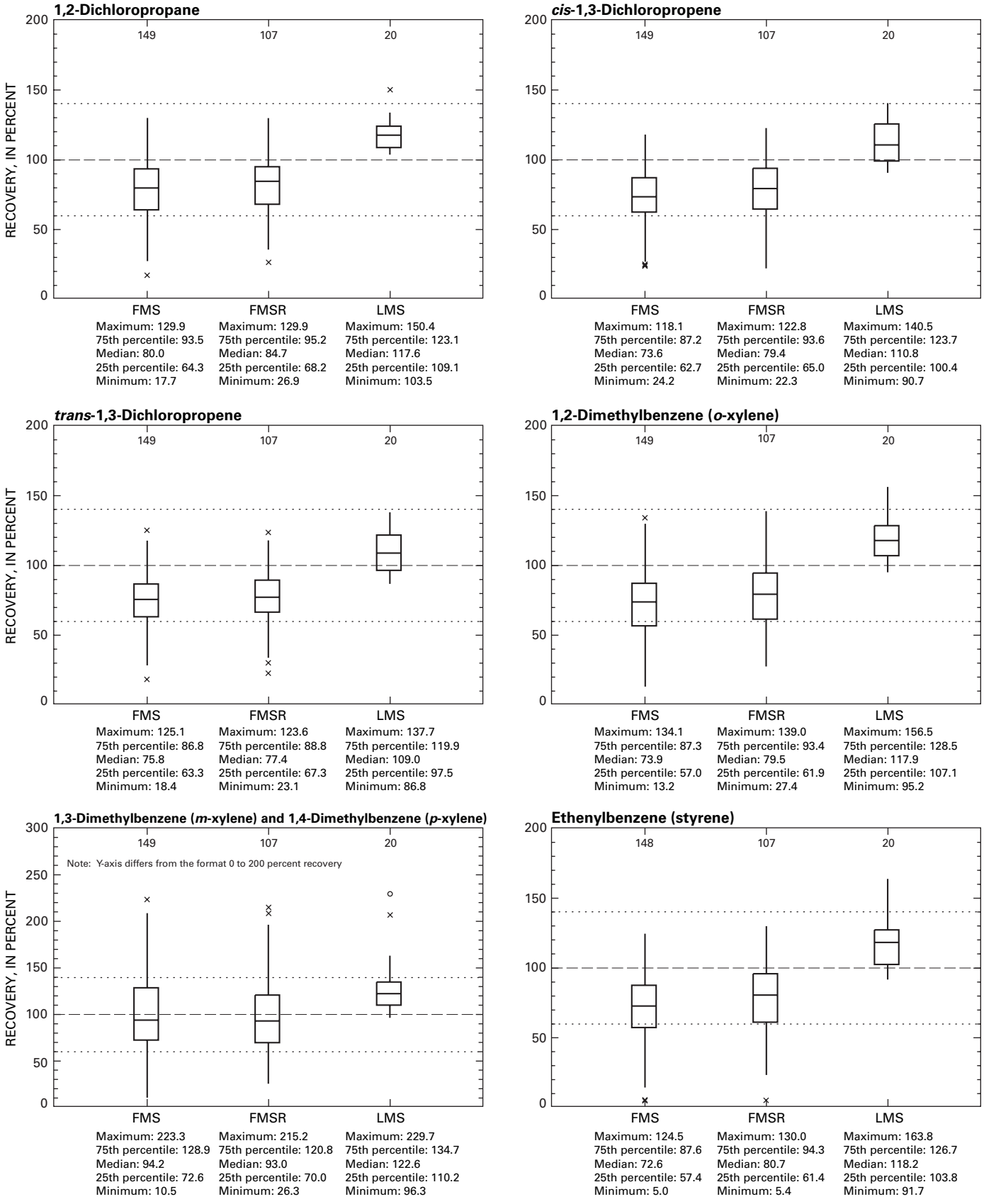
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



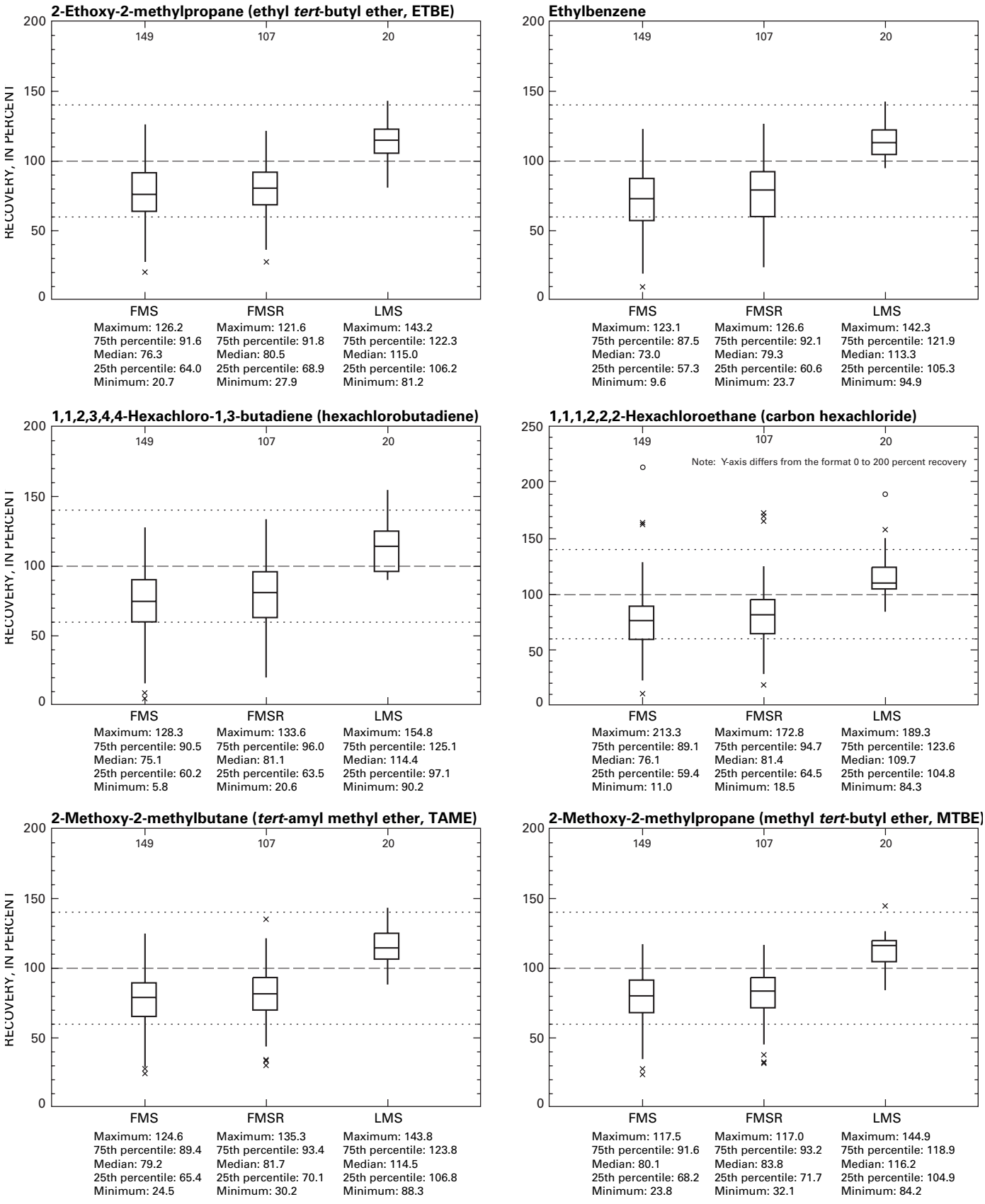




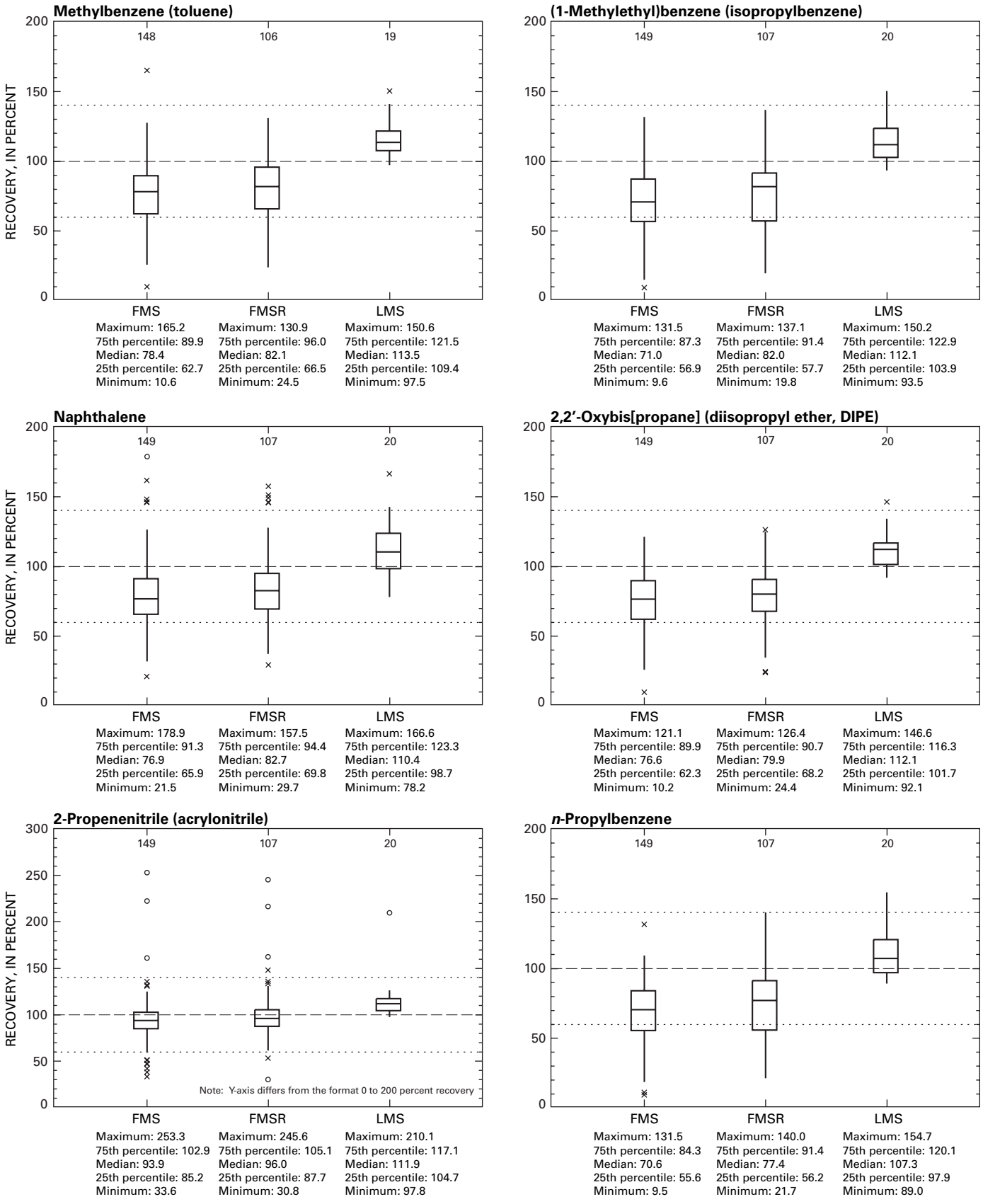
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



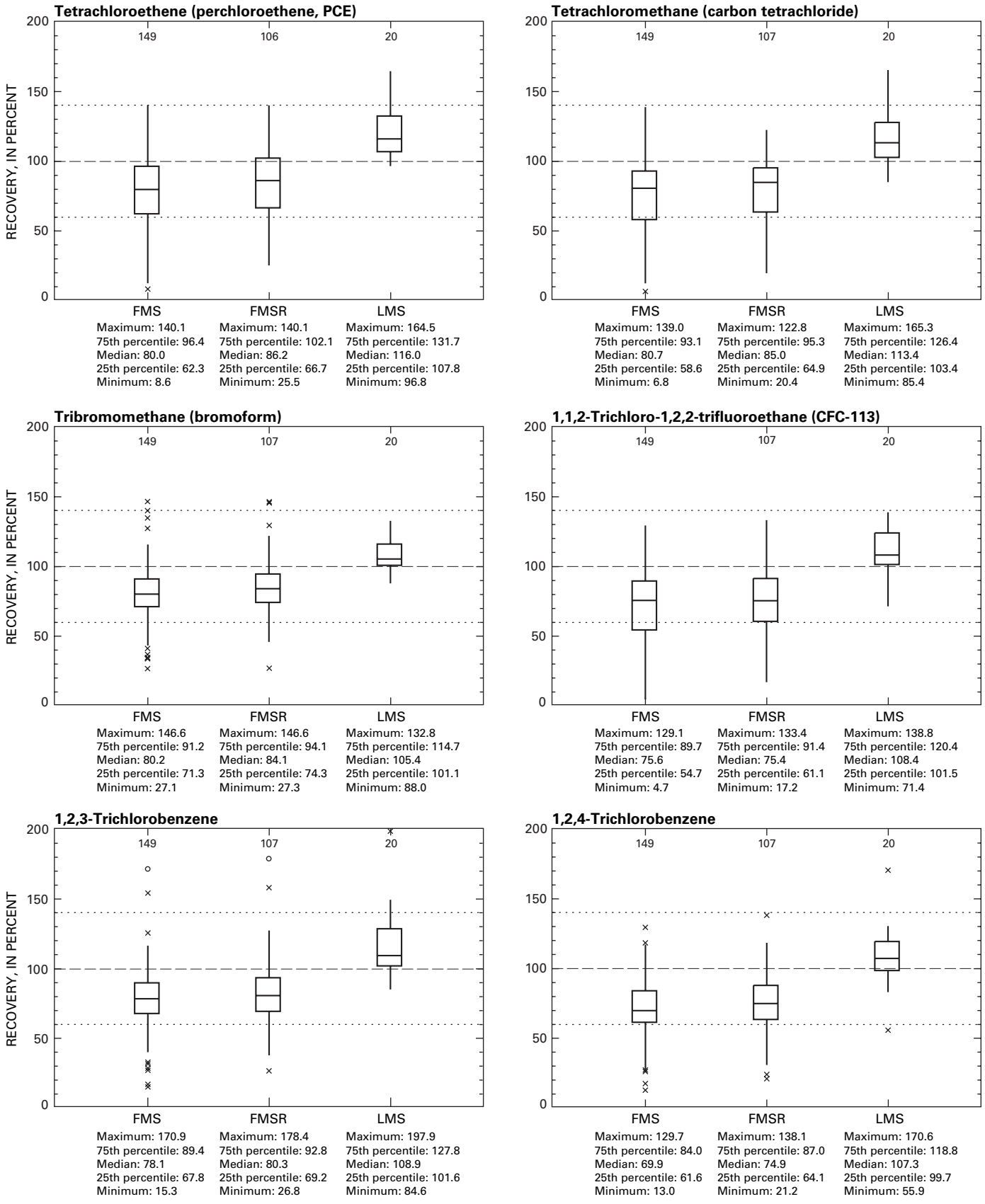
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



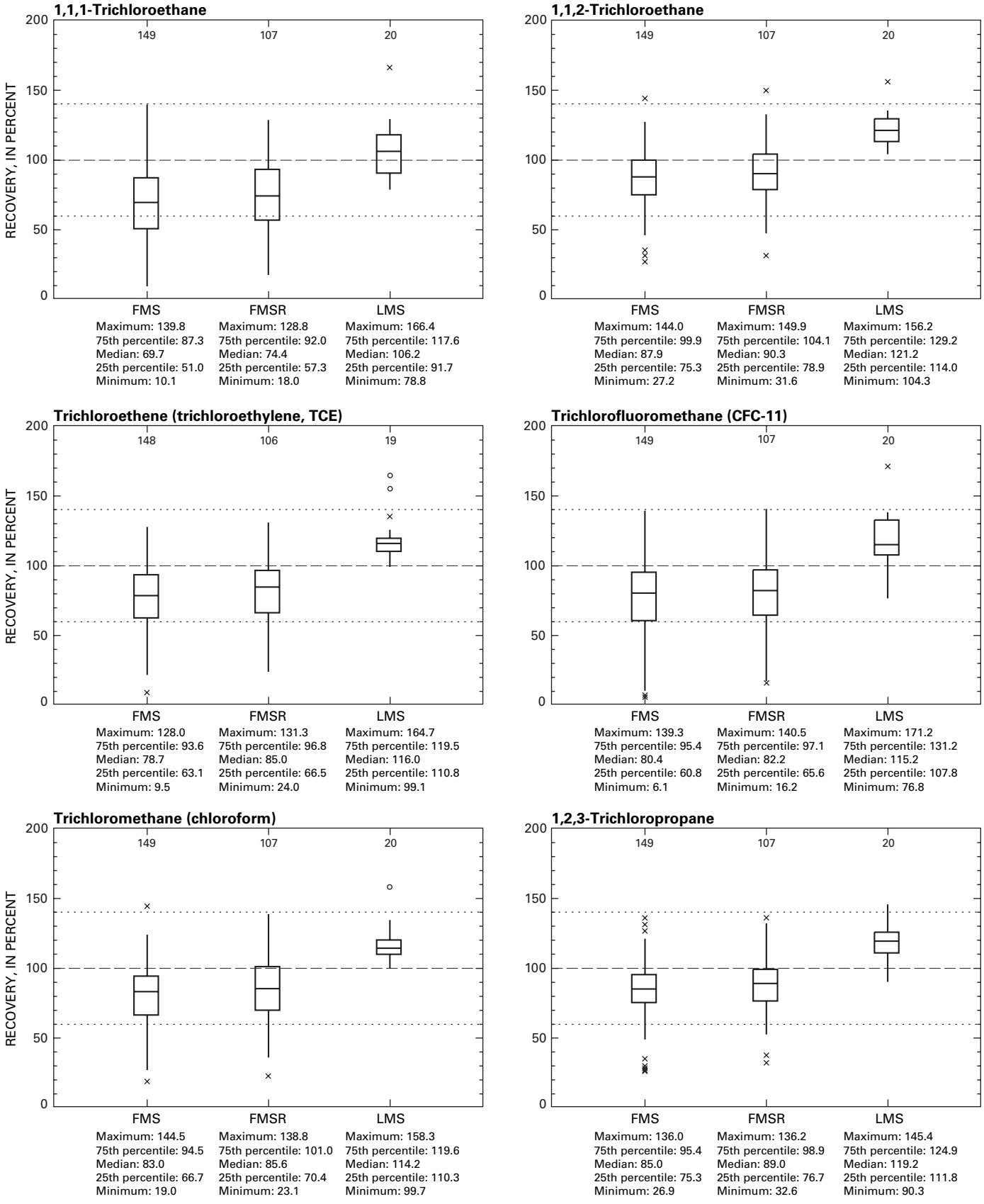
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



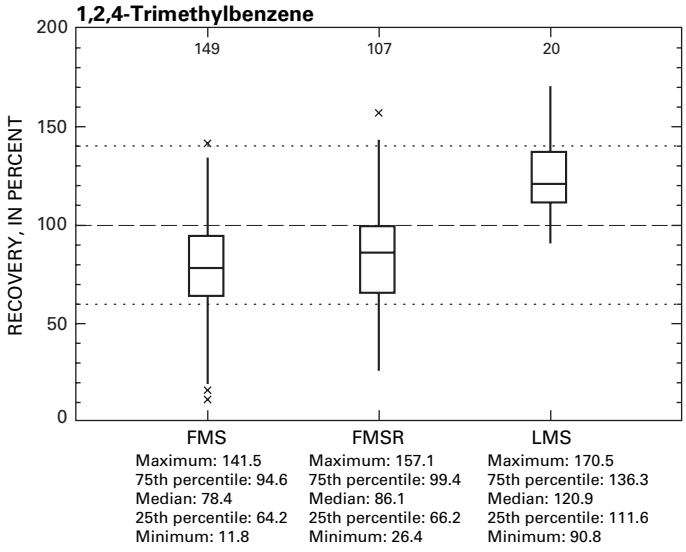
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



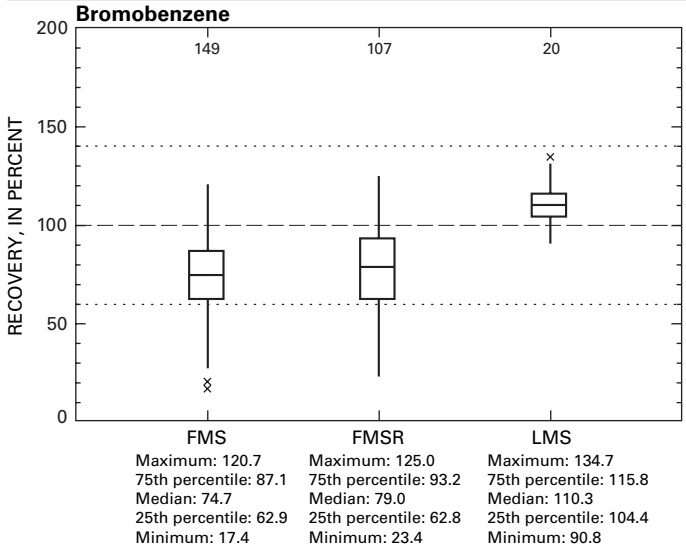
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued

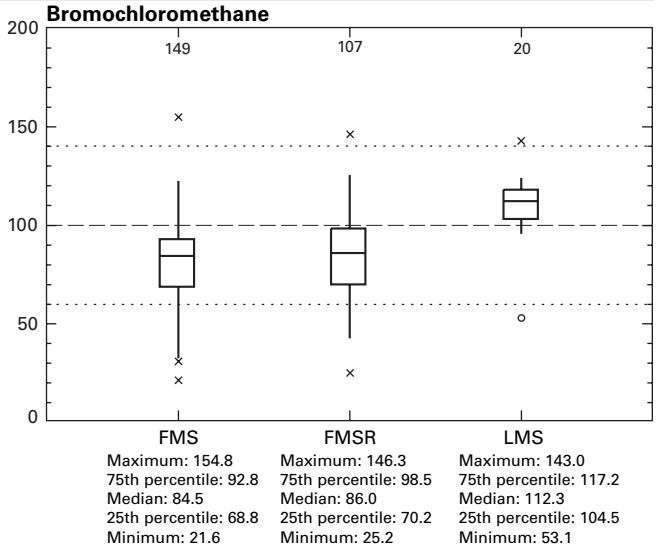


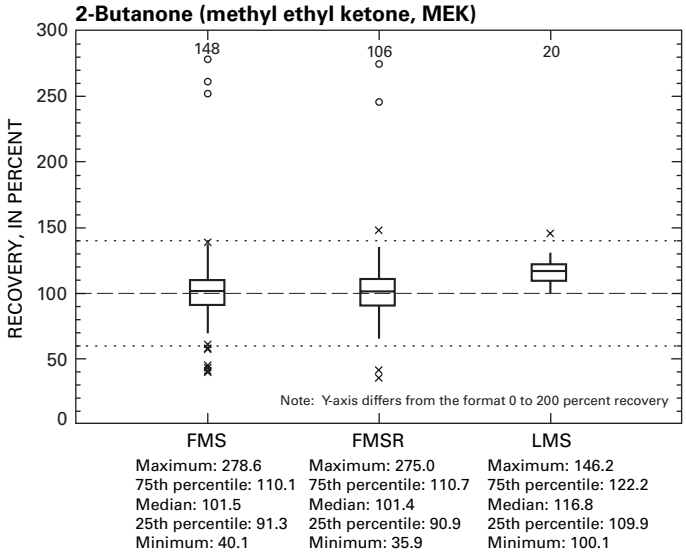
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued

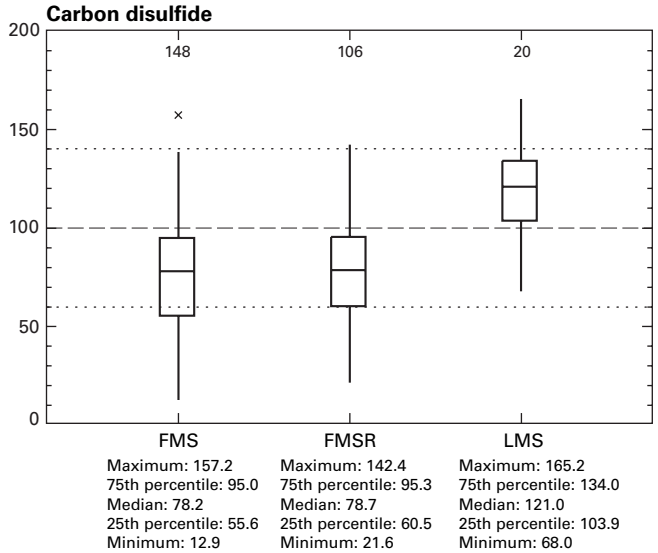


Other National Water Quality Laboratory analytes

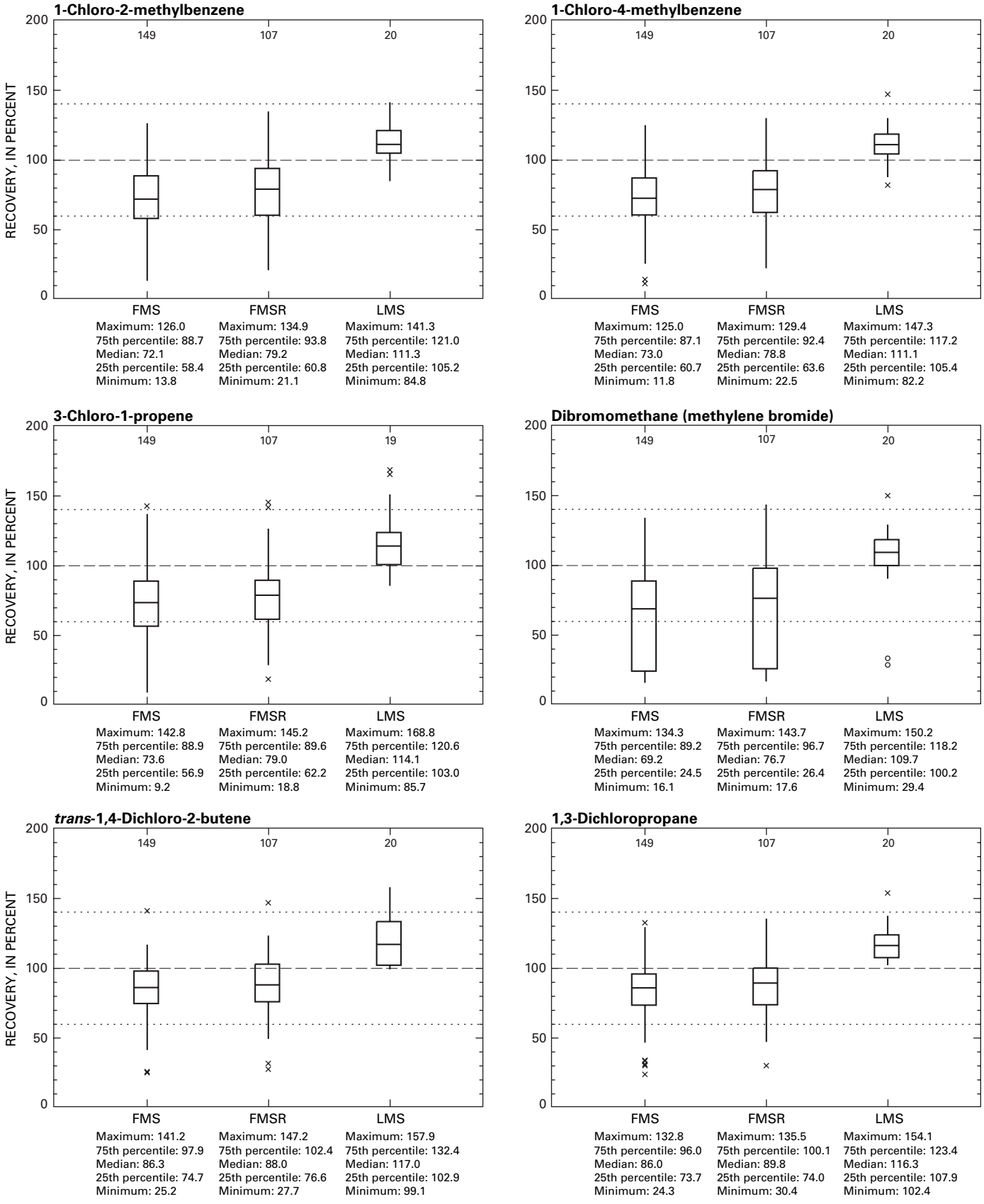




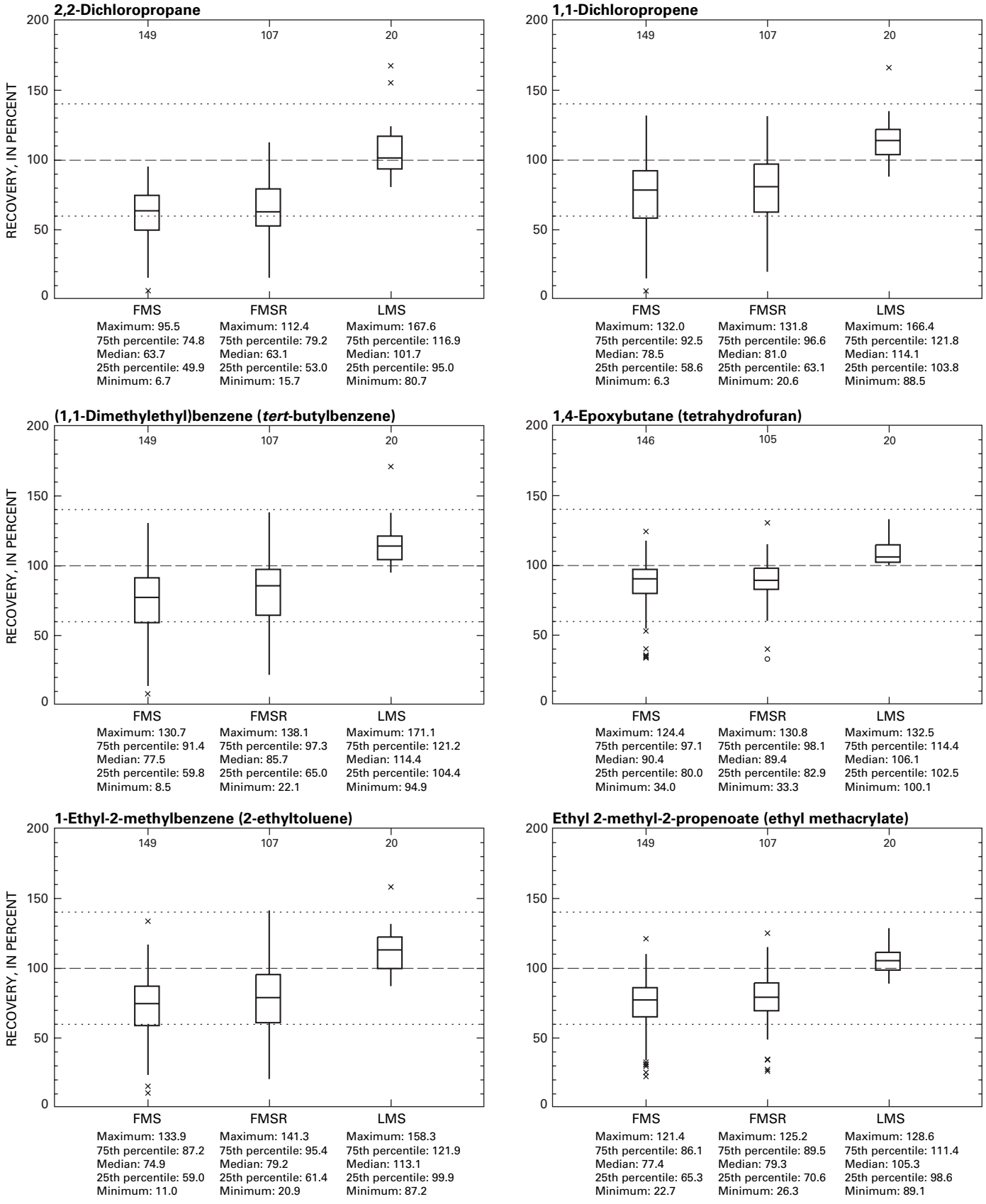




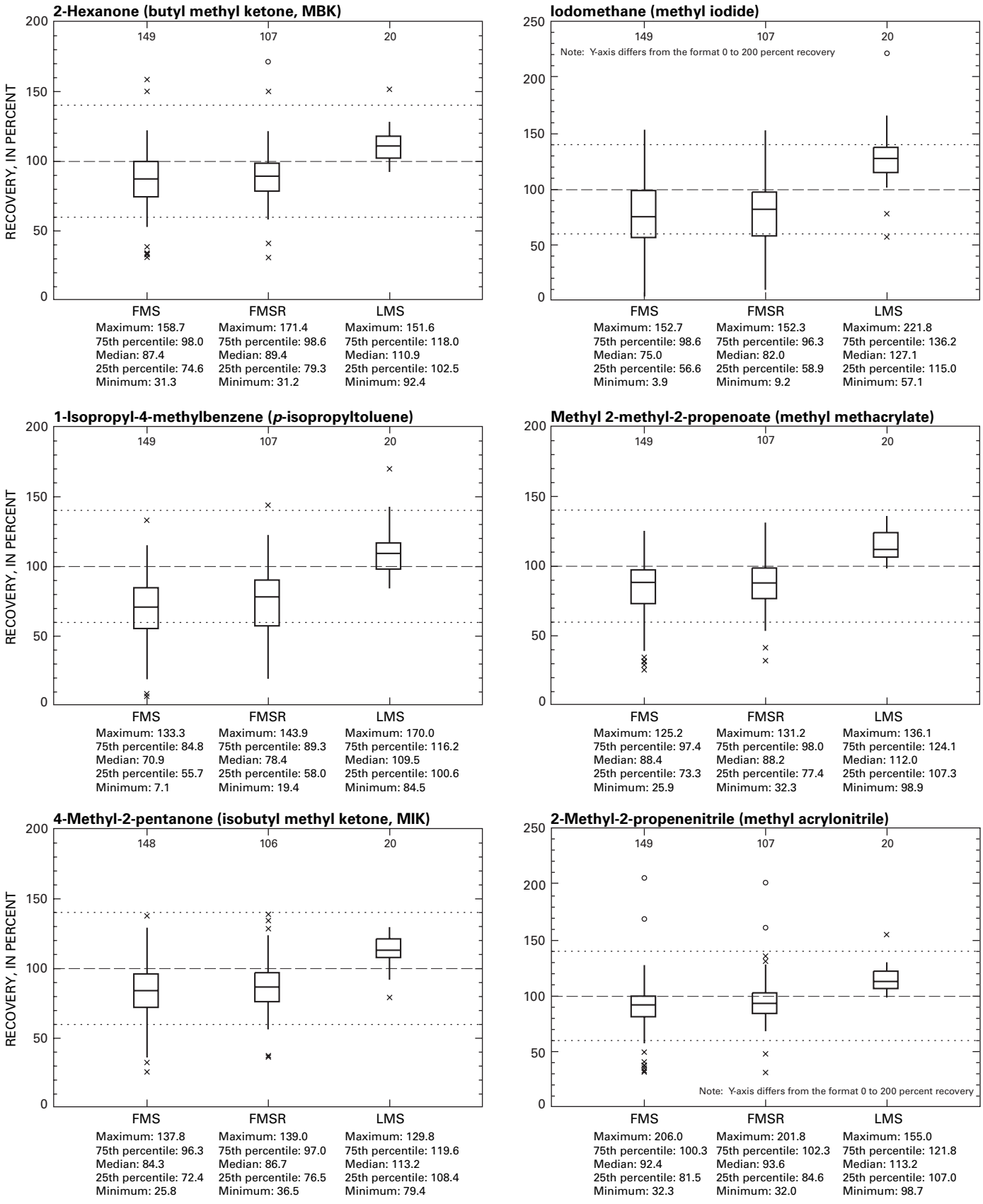
Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



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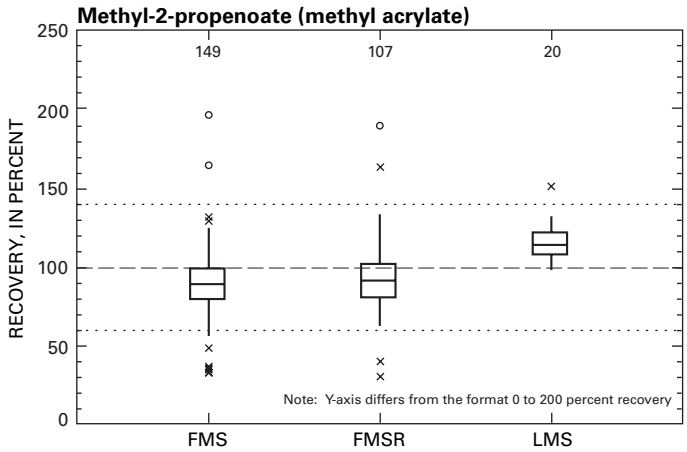
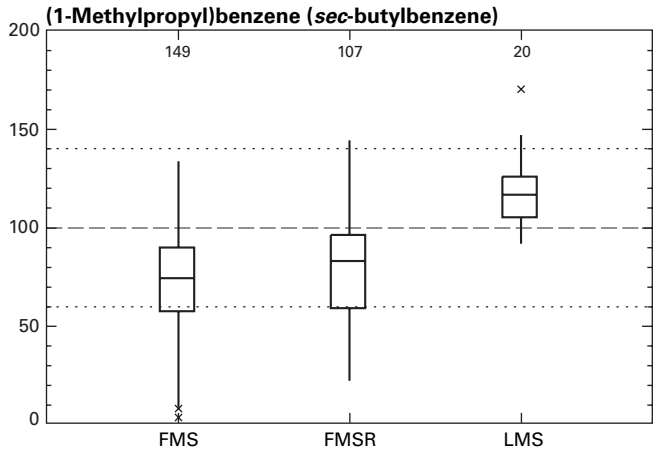
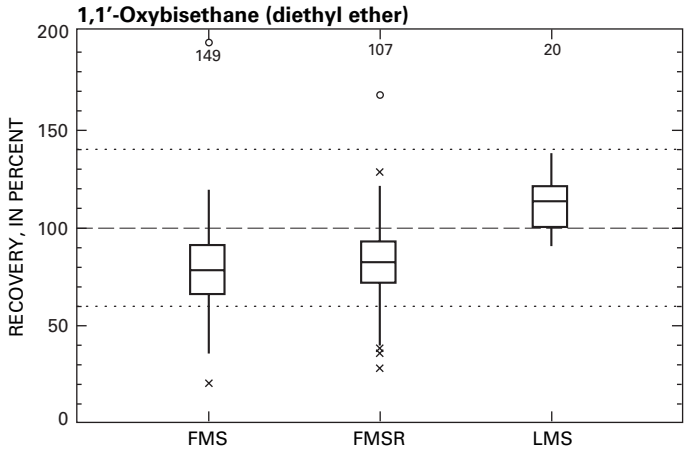
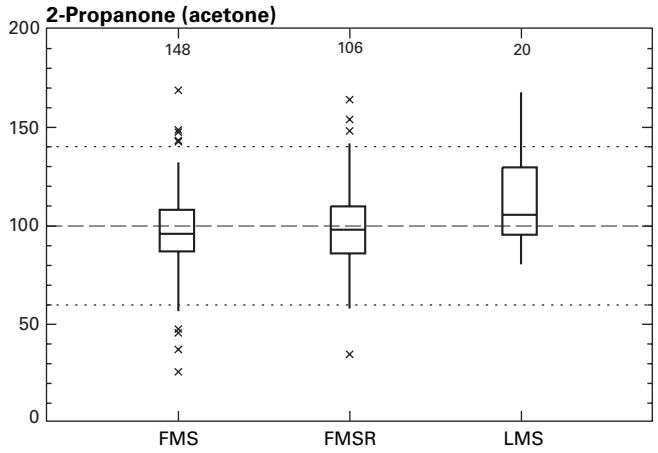
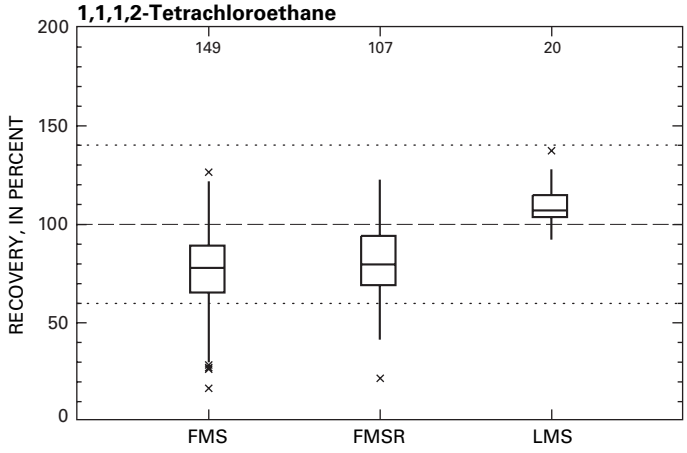
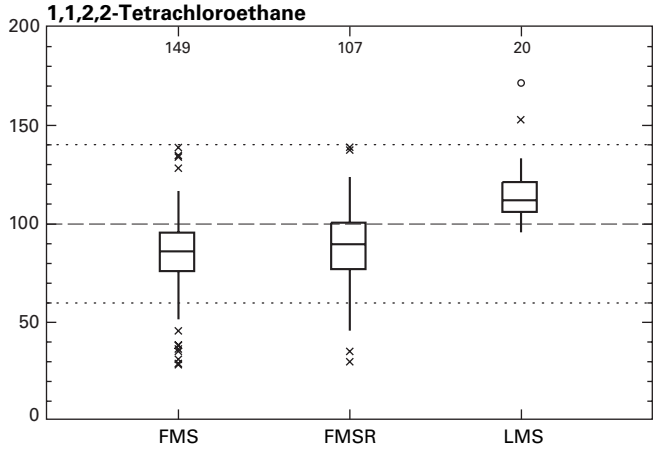




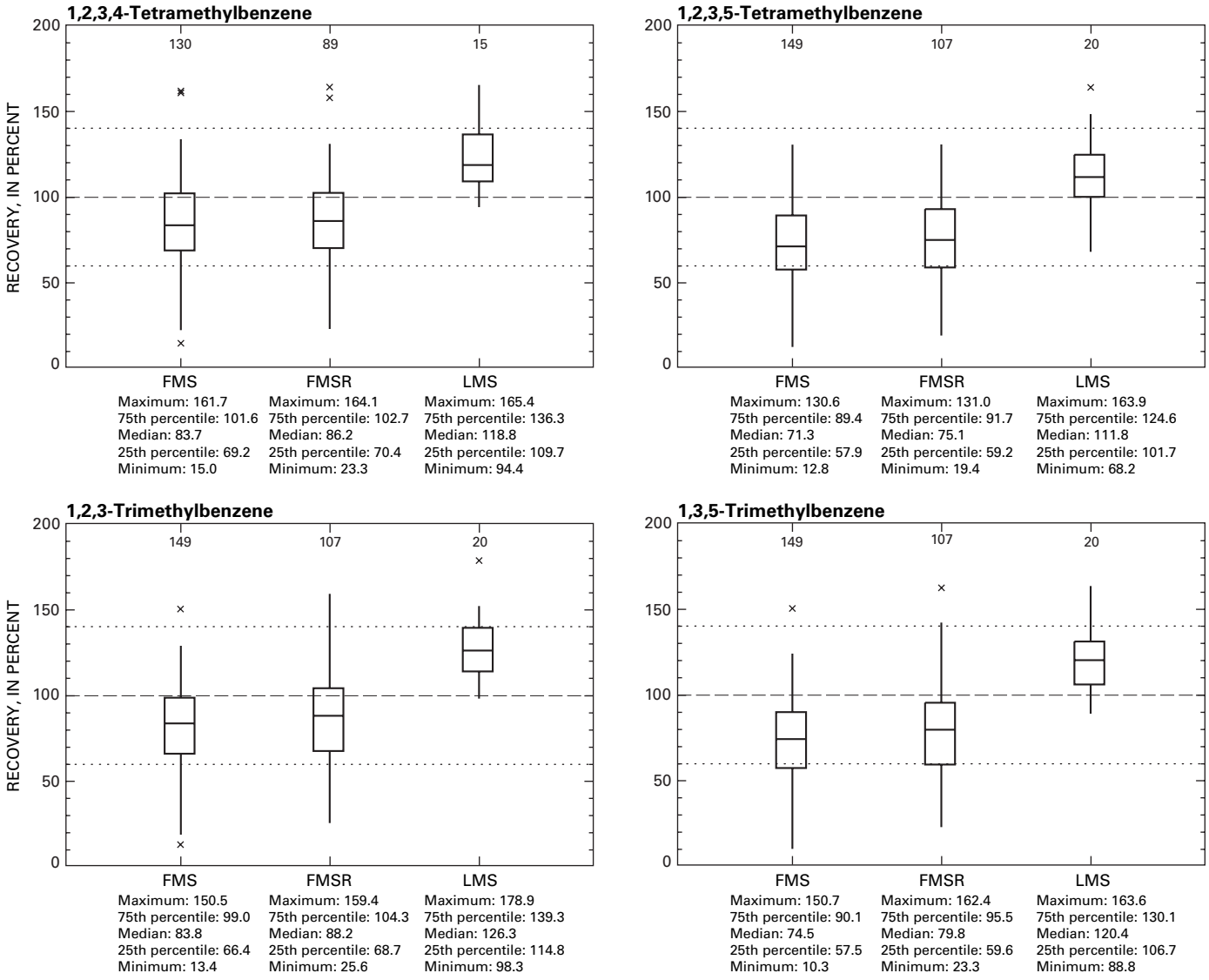








Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued



Appendix 2. Percent recovery of each of the 85 volatile organic compounds for field matrix spikes (FMSs), field matrix spike replicates (FMSRs), and laboratory matrix spikes (LMSs).—Continued

Appendix 3. Laboratory matrix spike adjusted VOC recoveries on day 14 for ground- and surface-water samples. Recoveries were calculated from data in a previously published stability study by Love and others (1998).

[NWQL, National Water Quality Laboratory]

Compound	Laboratory matrix spike adjusted recoveries, in percent	
	Ground water	Surface water
55 analytes included in NAWQA's National VOC Assessment		
Benzene	103.4	103.6
Bromodichloromethane	99.3	101.9
Bromoethene	113.1	113.1
Bromomethane	118.9	113.1
n-Butylbenzene	90.1	92.6
Chlorobenzene	99.1	99.8
Chloroethane	117.1	120.3
Chloroethene	126.3	126.7
Chloromethane	139.4	134.5
1,2-Dibromo-3-chloropropane	96.4	105.1
Dibromochloromethane	97.1	100.6
1,2-Dibromoethane	97.6	103.6
1,2-Dichlorobenzene	97.0	101.5
1,3-Dichlorobenzene	96.7	99.1
1,4-Dichlorobenzene	95.7	97.8
Dichlorodifluoromethane	146.2	148.0
1,1-Dichloroethane	107.0	107.0
1,2-Dichloroethane	100.2	102.7
1,1-Dichloroethene	110.3	109.9
cis-1,2-Dichloroethene	102.7	102.3
trans-1,2-Dichloroethene	110.9	111.8
Dichloromethane	105.0	106.0
1,2-Dichloropropane	102.0	105.3
cis-1,3-Dichloropropene	98.5	102.1
trans-1,3-Dichloropropene	96.1	101.9
1,2-Dimethylbenzene	99.0	100.4
1,3- and 1,4-Dimethylbenzene	100.2	100.2
Ethenylbenzene	84.9	95.0
2-Ethoxy-2-methylpropane	99.5	103.8
Ethylbenzene	100.0	101.1
1,1,2,3,4,4-Hexachloro-1,3-butadiene	93.9	92.7
1,1,1,2,2,2-Hexachloroethane	101.8	99.7

Appendix 3. Laboratory matrix spike adjusted VOC recoveries on day 14 for ground- and surface-water samples. Recoveries were calculated from data in a previously published stability study by Love and others (1998).—Continued

[NWQL, National Water Quality Laboratory]

Compound	Laboratory matrix spike adjusted recoveries, in percent	
	Ground water	Surface water
55 analytes included in NAWQA's National VOC Assessment—Continued		
2-Methoxy-2-methylbutane	97.0	101.8
2-Methoxy-2-methylpropane	97.9	103.0
Methylbenzene	102.2	101.9
(1-Methylethyl)benzene	92.1	91.4
Naphthalene	82.1	104.2
2,2′-Oxybis[propane]	97.6	96.6
2-Propenenitrile	105.4	111.6
n-Propylbenzene	96.6	97.8
Tetrachloroethene	99.0	100.8
Tetrachloromethane	103.5	104.6
Tribromomethane	95.8	100.7
1,1,2-Trichloro-1,2,2-tri-fluoroethane	109.9	109.6
1,2,3-Trichlorobenzene	93.4	99.6
1,2,4-Trichlorobenzene	92.9	96.7
1,1,1-Trichloroethane	105.4	105.0
1,1,2-Trichloroethane	96.3	102.1
Trichloroethene	103.5	104.9
Trichlorofluoromethane	121.2	118.3
Trichloromethane	103.5	104.4
1,2,3-Trichloropropane	101.4	109.3
1,2,4-Trimethylbenzene	90.4	95.9
Other NWQL analytes		
Bromobenzene	98.4	102.7
Bromochloromethane	100.5	104.7
2-Butanone	94.3	100.0
Carbon disulfide	115.2	114.1
1-Chloro-2-methylbenzene	98.7	99.0
1-Chloro-4-methylbenzene	98.0	97.2
3-Chloro-1-propene	101.5	101.5
Dibromomethane	99.2	103.4
trans-1,4-Dichloro-2-butene	86.7	93.5
1,3-Dichloropropane	100.5	103.5

Appendix 3. Laboratory matrix spike adjusted VOC recoveries on day 14 for ground- and surface-water samples. Recoveries were calculated from data in a previously published stability study by Love and others (1998).—Continued

[NWQL, National Water Quality Laboratory]

Compound	Laboratory matrix spike adjusted recoveries, in percent	
	Ground water	Surface water
Other NWQL analytes—Continued		
2,2-Dichloropropane	90.8	92.6
1,1-Dichloropropene	113.1	114.8
(1,1-Dimethylethyl)benzene	102.0	100.1
1,4-Epoxybutane	93.5	104.6
1-Ethyl-2-methylbenzene	97.5	98.5
Ethyl 2-methyl-2-propenoate	90.0	99.3
2-Hexanone	94.2	101.6
Iodomethane	118.3	113.2
1-Isopropyl-4-methylbenzene	95.5	95.9
Methyl 2-methyl-2-propenoate	91.2	103.6
4-Methyl-2-pentanone	92.6	100.8
2-Methyl-2-propenenitrile	93.8	98.6
Methyl-2-propenoate	93.4	99.2
(1-Methylpropyl)benzene	98.1	97.5
1,1′-Oxybisethane	104.0	109.5
2-Propanone	94.7	105.2
1,1,1,2-Tetrachloroethane	99.9	101.0
1,1,2,2-Tetrachloroethane	97.1	102.6
1,2,3,4-Tetramethylbenzene	82.4	100.2
1,2,3,5-Tetramethylbenzene	80.9	97.9
1,2,3-Trimethylbenzene	94.0	99.3
1,3,5-Trimethylbenzene	94.4	97.1

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