

National Water-Quality Assessment Program

Design and Evaluation of a Field Study on the Contamination of Selected Volatile Organic Compounds and Wastewater-Indicator Compounds in Blanks and Groundwater Samples



Scientific Investigations Report 2011–5027

Front cover. Upper right: Sample-collection setup at the Utah site. Photograph by Steven Gerner.
Lower left: Field apparatus for purging volatile pesticide-grade blank water. Photograph by Deborah Parlman.

Design and Evaluation of a Field Study on the Contamination of Selected Volatile Organic Compounds and Wastewater-Indicator Compounds in Blanks and Groundwater Samples

By Susan A. Thiros, David A. Bender, David K. Mueller, Donna L. Rose, Lisa D. Olsen, Jeffrey D. Martin, Bruce Bernard, and John S. Zogorski

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Foreword

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

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

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

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

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

William H. Werkheiser
USGS Associate Director for Water

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Conversion Factors and Datum

Multiply	By	To obtain
Length		
inch (in.)	25.4	millimeter (mm)
inch (in.)	25,400	micrometer (μm)
foot (ft)	0.3048	meter (m)
Volume		
gallon (gal)	3.785	liter (L)
ounce, fluid (fl. oz)	29.57	milliliter (mL)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
Pressure		
pound per square inch (psi or lb/in ²)	6.895	kilopascal (kPa)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:
 $^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32$

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

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

Microgram per liter is equivalent to part per billion (ppb).

Acronyms and Symbols

<	less than
AHTN	acetyl hexamethyl tetrahydronaphthalene
BTEX	benzene, toluene, ethylbenzene, and xylenes
DEET	<i>N,N</i> -diethyl- <i>meta</i> -toluamide
FCS	Field Contamination Study
GC/MS	gas chromatography/mass spectrometry
HHCB	hexahydrohexamethylcyclopentabenzopyran
LRL	laboratory reporting level
LT-MDL	long-term method-detection level
NAWQA	National Water-Quality Assessment
NFM	National Field Manual for the Collection of Water-Quality Data
NWIS	National Water Information System
NWQL	National Water Quality Laboratory
OWQ	Office of Water Quality
PVC	polyvinyl chloride
QC	quality control
USGS	U.S. Geological Survey
VOC	volatile organic compound
VPBW	volatile pesticide-grade blank water
WIC	wastewater-indicator compound
WSC	Water Science Center

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Abstract

The Field Contamination Study (FCS) was designed to determine the field processes that tend to result in clean field blanks and to identify potential sources of contamination to blanks collected in the field from selected volatile organic compounds (VOCs) and wastewater-indicator compounds (WICs). The VOCs and WICs analyzed in the FCS were detected in blanks collected by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program during 1996–2008 and 2002–08, respectively. To minimize the number of variables, the study required ordering of supplies just before sampling, storage of supplies and equipment in clean areas, and use of adequate amounts of purge-and-trap volatile-grade methanol and volatile pesticide-grade blank water (VPBW) to clean sampling equipment and to collect field blanks.

Blanks and groundwater samples were collected during 2008–09 at 16 sites, which were a mix of water-supply and monitoring wells, located in 9 States. Five different sample types were collected for the FCS at each site: (1) a source-solution blank collected at the USGS National Water Quality Laboratory (NWQL) using laboratory-purged VPBW, (2) source-solution blanks collected in the field using laboratory-purged VPBW, (3) source-solution blanks collected in the field using field-purged VPBW, (4) a field blank collected using field-purged VPBW, and (5) a groundwater sample collected from a well. The source-solution blank and field-blank analyses were used to identify, quantify, and document extrinsic contamination and to help determine the sources and causes of data-quality problems that can affect groundwater samples.

Concentrations of compounds detected in FCS analyses were quantified and results were stored in the USGS National Water Information System database after meeting rigorous identification and quantification criteria. The study also utilized information provided by laboratory analysts about

evidence indicating the presence of selected compounds, using less rigorous identification criteria than is required for reporting data to the National Water Information System database. For the FCS, these data are considered adequate to indicate “evidence of presence,” and were used only for diagnostic purposes. Evidence of VOCs and WICs at low concentrations near or less than the long-term method detection level can indicate a contamination problem that could affect future datasets if method detection levels were ever to be lowered.

None of the 13 VOCs and 16 WICs included in this study were quantified in the VPBW collected and analyzed at the NWQL. This finding indicates that the VPBW was “contaminant free” when it was shipped from the laboratory to each of the field offices, although some compounds were present in some of the samples at concentrations less than minimum detection levels based on evidence-of-presence data.

Toluene, *m*- and *p*-xylene, benzene, and carbon disulfide were each quantified in an FCS field-blank analysis, but not in the associated groundwater sample. The native-water rinse of the sampling equipment conducted just before collection of the groundwater sample likely reduced low-level contamination with respect to these compounds.

VOCs had lower detection frequencies in source-solution blanks and field blanks collected during the FCS than in the historical dataset collected by the NAWQA Program during 1996–2008. The detection frequency of toluene in field blanks was reduced about an order of magnitude from about 38 percent in the historical NAWQA dataset to 3.1 percent in the FCS dataset. Other VOCs quantified in 5 percent or more of the field blanks in the NAWQA dataset, but not quantified in the FCS field-blank analyses, were ethylbenzene, *o*-xylene, styrene, 1,2,4-trimethylbenzene, chloroform, dichloromethane, acetone, 2-butanone, and tetrahydrofuran. The lower detection frequencies of most VOCs for the FCS, compared to historical NAWQA data, can most likely be attributed to the use of fresh supplies and rigorous adherence to the protocols for cleaning equipment and collecting samples.

Chloroform, a disinfection by-product that is commonly present in tap water used to clean sampling equipment, was not quantified and had no evidence of presence in the FCS field-blank analyses. It is probable that the relatively high detection frequency of chloroform in historical NAWQA field blanks (about 20 percent) is the result of inadequate rinsing with sufficient volumes of VPBW following cleaning.

The WIC phenol had a high detection frequency in source-solution and field blanks (70 and 64 percent, respectively) collected by the NAWQA Program during 2002–08, compared to a detection frequency of about 3 percent in the FCS source-solution and field blanks. The detection frequency of benzophenone and *N,N*-diethyl-*meta*-toluamide (DEET) in field blanks also was substantially less in the FCS dataset (no detections) compared to historical NAWQA data (about 29 and 36 percent, respectively). Evidence of presence of benzophenone, caffeine, camphor, DEET, and methyl salicylate in FCS source-solution blanks, field-purged source-solution blanks, and field blanks could be attributed to products containing these compounds being used by sampling personnel.

The lower detection frequencies of selected compounds in the FCS field blanks, compared to historical NAWQA data, indicate that careful attention to field protocols will result in higher-quality field blanks. Extrinsic contamination introduced to source-solution blanks and field blanks can make it more difficult to understand the quality of groundwater-sample data and can cause detections of compounds to be questioned. Following the prescribed field procedures will minimize the potential for introduction of VOCs and WICs to blanks and groundwater samples.

Introduction

A **field blank** is a quality-control (QC) sample collected in the field in the same manner as a groundwater sample, except for the native-water rinsing, and is used to identify possible contamination not from the groundwater (the first use of selected terms listed in the Glossary are in boldface type). Members of the U.S. Geological Survey (USGS) Office of Water Quality's Field Quality Control Work Group for Organics designed the Field Contamination Study (FCS) to determine the field processes that tend to result in clean field blanks and to identify sources of contamination from selected **volatile organic compounds** (VOCs) and **waste-water-indicator compounds** (WICs) to the field blanks that hinder their utility in interpreting the quality of corresponding groundwater samples. Source-solution (organic-free) water is used to collect **source-solution blanks** and field blanks, and is presumed to be free of contaminants of interest when it leaves the USGS National Water Quality Laboratory (NWQL) as documented with a certificate of analyses. Historically, some source-solution water, source-solution blanks, and field blanks have become contaminated during shipment to or from

USGS Water Science Centers (WSCs), in storage, in transit to sampling sites, during sample collection, or a combination of these steps. The FCS focused on the quality of freshly purged source-solution (blank) water and the quality of source-solution blanks and field blanks collected in the field. The study evaluated the occurrence of selected VOCs and WICs that have been detected historically in NAWQA source-solution blanks, field blanks, and trip blanks, in a series of diagnostic blanks collected during a carefully controlled experiment.

Objective of the Field Contamination Study

The primary objective of the FCS was to determine the potential source(s) of contamination for selected VOCs and WICs in source-solution and field blanks collected in the field. The study attempted to determine how **blank water** that is certified to not have concentrations of VOCs and WICs greater than reporting levels can contain some of these compounds following its collection as source-solution and field blanks.

Extrinsic contamination, which was the focus of the FCS, is contamination that originates from a process or source that is external to the medium being sampled. Extrinsic contamination of a blank or sample can be caused by the following:

1. contaminant sources within the sampling environment, such as airborne emissions, aerosols, dust, or particulate input;
2. sample-collection equipment, such as pumps and sample tubing;
3. sample-processing equipment and supplies, such as filtration devices, bottles, chemical preservatives, and blank water that can become contaminated through improper storage;
4. sample-cleaning processes and supplies, such as rinse water and cleaning solutions;
5. factors related to sample transport, such as the field vehicle and transportation used during commercial shipment;
6. exposure to contaminants during storage, such as in a cooler or office/laboratory refrigerator; and
7. exposure to contaminants introduced by sampling personnel, such as exposure to food and drinks, personal-care products, and compounds used in (or adhering to) the disposable gloves used during sampling.

A recent review (2008) (David Bender, U.S. Geological Survey, written commun., 2010) of field quality-control data collected during 1996–2008 by the USGS National Water-Quality Assessment (NAWQA) Program indicated that some VOCs were detected more frequently in source-solution and field blanks than in groundwater samples. VOCs are rarely

identified during laboratory analysis of the nitrogen-purged volatile pesticide-grade blank water (VPBW) before shipment from the NWQL. Furthermore, VOC detections in the source-solution and field blanks cannot be attributed to laboratory contamination during sample analysis because **laboratory blanks** historically had VOC concentrations less than reporting levels, with few exceptions. Even when sources of contamination are evident in the source-solution blanks or field blanks, this contamination does not necessarily result in detections of extrinsic contamination in the corresponding groundwater samples because of additional rinsing of the sampling equipment with well water (native-water rinse) before sample collection (Taglioli and others, 2001).

Purpose and Scope

The purposes of this report are to (1) document the study design for the FCS, (2) evaluate the analytical results for blanks and groundwater samples, (3) describe these results in relation to historical NAWQA blank and groundwater data, and (4) emphasize implications of sampling procedures that can make a substantial difference in the quality of blanks.

The FCS evaluated the occurrence of extrinsic contamination of VOCs and WICs to source-solution blanks and field blanks by using freshly purged VPBW, certified to be free of VOCs and WICs before shipment, using fresh sampling supplies, purging the VPBW in the field, evaluating laboratory blanks, and interpreting groundwater-sample data. The study plan emphasized the potential contamination of VPBW, blanks, and groundwater samples during collection in the field and during shipment from the sample-collection site (field) to the NWQL. Blanks and groundwater samples were collected during 2008–09 from 16 sites, which were a mix of water-supply and monitoring wells, located in 9 States (fig. 1).

The FCS included a 2-hour long field purge of VPBW with nitrogen gas immediately before sampling in an attempt to reduce contamination if any had been inadvertently introduced to the blank water during shipment from the NWQL's National Field Supply Service to the WSCs that participated in the study or during transportation from the WSCs to the field sites. This allowed a comprehensive understanding of the contamination associated with the collection of field blanks and from the shipment of samples. **Quantified** concentrations for VOCs and WICs stored in the USGS National

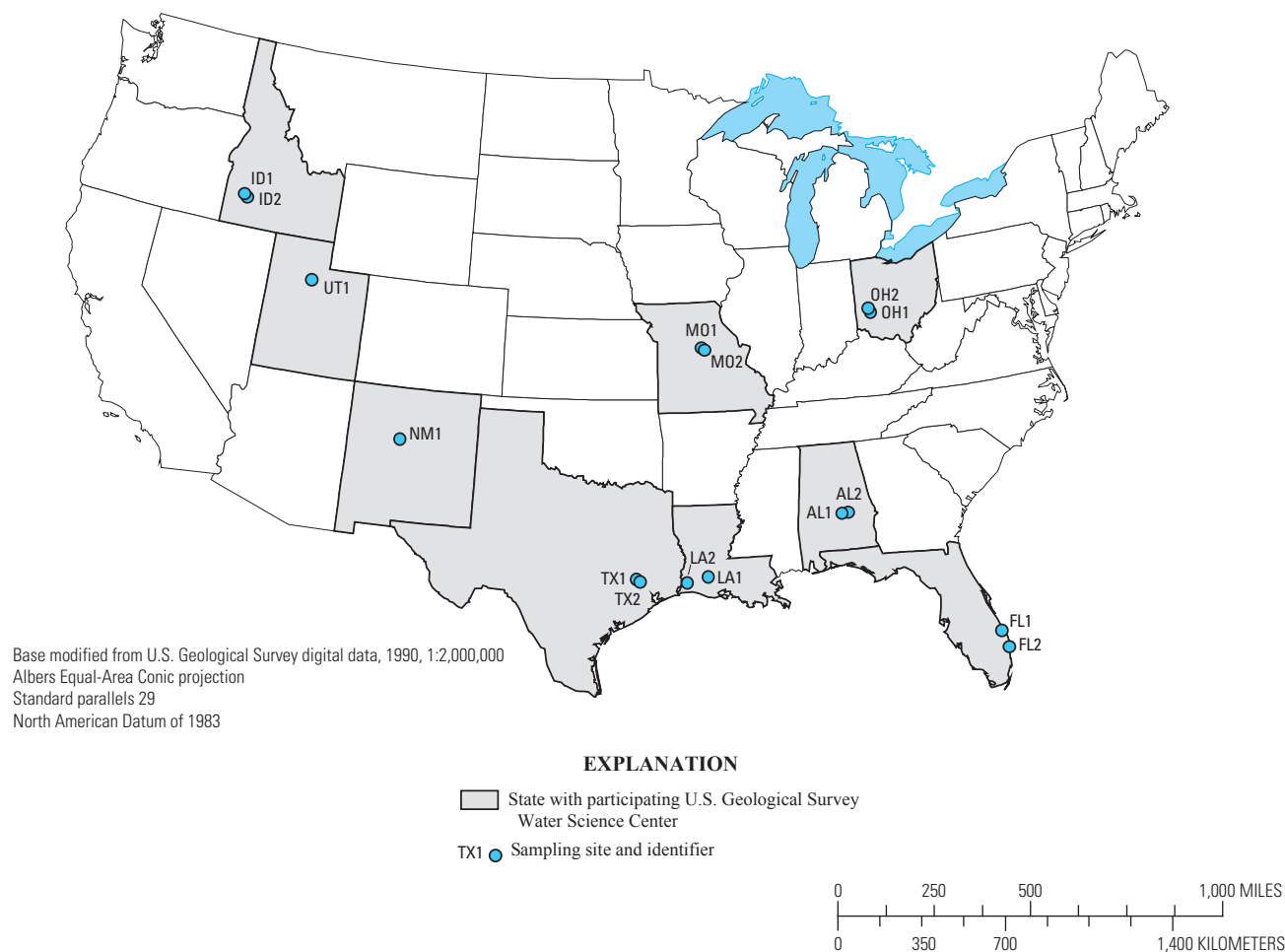


Figure 1. Sites sampled in the Field Contamination Study.

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Water Information System (NWIS) database are included in the “Supplemental Information” section of this report. Also included are the laboratory analysts’ determinations of **evidence of presence** for compounds using less rigorous identification criteria (not stored in the NWIS database); this information provided insights about the potential presence of a compound whose concentration normally would be reported as less than the reporting level.

Study Design and Methods

The sampling methods used in the FCS followed National Field Manual (NFM; U.S. Geological Survey, variously dated) guidelines, but with some modifications to typical protocols for sampling VOCs and WICs. Modifications specific to the FCS included (1) sample bottles, filters, preservative, purge and trap volatile-grade methanol for cleaning, and VPBW were ordered and received only a few days before sampling at each site so that storage time of supplies at the WSCs was short; (2) in addition to the certificate of analysis that is provided by the NWQL after testing the lot of source solution received from the manufacturer, a sample of the VPBW ordered for each FCS site was collected immediately after purging and analyzed at the NWQL to assess the quality of the VPBW before shipment to the WSC (typically, a sample of VPBW is not collected and analyzed after being purged); (3) the VPBW was purged in the field for 2 hours using prepurified grade nitrogen gas before collecting source-solution and field blanks (as opposed to not being purged

in the field at all); (4) the sample-collection chamber was set up outside (rather than inside) of the sampling vehicle; (5) the volume of field-purged VPBW used in the last step of equipment cleaning and in the field-blank sample collection (as described in the “Sequence of Field Sample Collection, Purging, and Equipment Cleaning” section of this report) was specified, and was constant between sampling sites (these volumes vary with the diameter and length of sample lines in the NFM); and (6) the section of sample tubing between the flow manifold and the sample-collection chamber was rinsed before a sample was collected using a larger volume of field-purged VPBW for the field blank and a larger volume of native water for the groundwater sample than the volumes indicated in the NFM.

Selection of Compounds

Selected VOCs and WICs of interest for this study were analyzed by the NWQL using custom schedules. Normally, 86 VOCs are analyzed in samples collected by the NAWQA Program as part of NWQL Schedule 2020. These VOCs are categorized into use groups, including disinfection by-products that are formed during chlorination of drinking water and wastewater, fumigant-related compounds, **gasoline hydrocarbons** and oxygenates and their degradates, organic synthesis compounds, refrigerants, propellants, and solvents. For this study, 13 VOCs or VOC pairs were included (table 1) because of their frequency of detection (greater than 5 percent) in field blanks collected by NAWQA during about the last 10 years, because of their potential presence in methanol used in the

Table 1. Volatile organic compounds included in the Field Contamination Study.

[USGS, U.S. Geological Survey; --, not applicable]

Compound name (ordered by use group)	Chemical Abstract Service Registry Number ¹	USGS parameter code	Primary use or source group	Alternate name or abbreviation
Benzene	71–43–2	34030	Gasoline hydrocarbon	--
Toluene	108–88–3	34010	Gasoline hydrocarbon	Methylbenzene
Ethylbenzene	100–41–4	34371	Gasoline hydrocarbon	--
<i>m</i> - and <i>p</i> -Xylene	<i>m</i> : 108–38–3 <i>p</i> : 106–42–3	85795	Gasoline hydrocarbon	1,3- and 1,4-Dimethylbenzene
<i>o</i> -Xylene	95–47–6	77135	Gasoline hydrocarbon	1,2-Dimethylbenzene
Styrene	100–42–5	77128	Gasoline hydrocarbon	Ethenylbenzene
1,2,4-Trimethylbenzene	95–63–6	77222	Gasoline hydrocarbon	1,2,4-TMB
Carbon disulfide	75–15–0	77041	Organic synthesis compound	--
Chloroform	67–66–3	32106	Disinfection by-product	Trichloromethane
Dichloromethane	75–09–2	34423	Solvent	Methylene chloride
Acetone	67–64–1	81552	Solvent	2-Propanone
2-Butanone	78–93–3	81595	Solvent	Methyl ethyl ketone (MEK)
Tetrahydrofuran	109–99–9	81607	Solvent	--

¹The Chemical Abstract Service Registry Number (CASRN)[®] is a Registered Trademark of the American Chemical Society. The Chemical Abstracts Services (CAS) recommends the verification of the CASRNs through CAS Client ServicesSM.

equipment cleaning process (acetone, 2-butanone, and tetrahydrofuran), or because of a tendency to co-occur with other frequently detected compounds. The VOCs analyzed for the FCS consist of 7 individual or pairs of gasoline hydrocarbons, 1 organic synthesis compound, 1 disinfection by-product, and 4 solvents.

The WICs have not been analyzed as extensively as VOCs by the NAWQA Program, but have been analyzed since 2002 as part of Source Water-Quality Assessment studies of groundwater and surface water used for public supply; WICs are referred to as anthropogenic organic compounds in groundwater Source Water-Quality Assessment studies (Hopple and others, 2009). Normally, 66 WICs are analyzed as part of NWQL Schedule 1433 and include personal-care and domestic-use products, such as triclosan (an anti-bacterial agent in many hand soaps), detergent metabolites, and fragrance compounds; manufacturing additives, such as plasticizers and fire retardants; pavement- and combustion-derived compounds, which are predominantly polynuclear aromatic hydrocarbons; and plant- and animal-derived biochemicals, such as cholesterol. For the FCS, 16 WICs were originally included (table 2), mainly because of their frequency of detection in field and source-solution blanks collected by NAWQA. These 16 compounds included 10 personal-care and domestic-use products, 3 manufacturing additives, 1 solvent, 1 gasoline hydrocarbon, and 1 pavement- and combustion-derived compound. However, laboratory quality-control data for bisphenol A, which is a manufacturing

additive, did not meet quality-assurance criteria, and therefore, results for this compound were not reported to the NWIS database (Steven Smith, National Water Quality Laboratory, written commun., 2010) and are not included in the FCS evaluation.

Selection of Sampling Sites

The FCS included personnel from nine WSCs who had already planned to sample wells during October 2008 to January 2009, and who were willing to participate in the study. A total of 16 wells were sampled in 9 States (fig. 1), and the FCS intentionally avoided known highly contaminated sites, such as sites regulated by the U.S. Environmental Protection Agency. Typical monitoring or water-supply wells that are part of a NAWQA network were sampled by personnel from six WSCs. Monitoring, domestic, or public-supply wells that are not part of NAWQA studies were sampled by personnel in three WSCs.

The wells sampled for the FCS varied from 2-inch diameter polyvinyl chloride (PVC)-cased wells used for monitoring to large-diameter steel-cased wells used for public supply. Monitoring wells typically were sampled with a portable stainless-steel submersible pump connected to fluorocarbon polymer (Teflon®) tubing supplied by each WSC, whereas the water-supply wells generally were equipped with a dedicated downhole pump, such as a submersible or turbine

Table 2. Wastewater-indicator compounds included in the Field Contamination Study.

[USGS, U.S. Geological Survey; --, not applicable]

Compound name (ordered by use group)	Chemical Abstract Service Registry Number ¹	USGS parameter code	Primary use or source group	Alternate name or abbreviation
Acetyl hexamethyl tetrahydro-naphthalene	21145-77-7	62065	Personal-care and domestic-use products	AHTN
Benzophenone	119-61-9	62067	Personal-care and domestic-use products	--
Caffeine	58-08-2	50305	Personal-care and domestic-use products	--
Camphor	76-22-2	62070	Personal-care and domestic-use products	--
<i>N,N</i> -Diethyl- <i>meta</i> -toluamide	134-62-3	62082	Personal-care and domestic-use products	DEET
Hexahydrohexamethylcyclo-pentabenzopyran	1222-05-5	62075	Personal-care and domestic-use products	HHCB
Menthol	89-78-1	62080	Personal-care and domestic-use products	--
Methyl salicylate	119-36-8	62081	Personal-care and domestic-use products	--
4-Nonylphenol (total, branched)	84852-15-3	62085	Personal-care and domestic-use products	--
Phenol	108-95-2	34466	Personal-care and domestic-use products	--
Bisphenol A	80-05-7	62069	Manufacturing additives	--
Tributyl phosphate	126-73-8	62089	Manufacturing additives	--
Triphenyl phosphate	115-86-6	62092	Manufacturing additives	--
Isophorone	78-59-1	34409	Solvents	--
Naphthalene	91-20-3	34443	Gasoline hydrocarbon	--
Phenanthrene	85-01-8	34462	Pavement- and combustion-derived compounds	--

¹The Chemical Abstract Service Registry Number (CASRN)[®] is a Registered Trademark of the American Chemical Society. The Chemical Abstracts Services (CAS) recommends the verification of the CASRNs through CAS Client ServicesSM.

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pump, connected to a discharge line to which the sampling personnel attached Teflon® sample tubing near the wellhead. Water samples from supply wells were collected from an access point near the wellhead, positioned before the water passes into pressure or holding tanks and before any chemical treatment. Additional information about the groundwater sites is included in table 3.

Field Methods

The experimental design of the FCS consisted of ordering supplies and gathering and cleaning sampling equipment, transporting sampling supplies and equipment to the field, purging the VPBW in the field with nitrogen gas, setting up the sampling equipment at the site, purging the well, cleaning the sampling equipment in the field before collecting samples, collecting the source-solution blanks and field blank, collecting the groundwater sample, cleaning the equipment in the field before transport to the next site, and finally, shipping the samples to the NWQL.

Supplies and Equipment

Field supplies were ordered for each site and were shipped together to arrive just before sampling in order to minimize potential contamination that may occur during

storage. Most of the field supplies, including 1:1 hydrochloric acid for preserving the VOC samples; precleaned 40-milliliter amber borosilicate vials with Teflon®-faced silicone septa for VOC samples (VOC vials); 1-liter amber glass bottles for the WIC samples; 142-millimeter diameter, 0.7-micrometer nominal pore size glass-fiber filters baked at 450 degrees Celsius for the WIC samples; foam sleeves to cushion the filled sample vials and bottles; and 4-liter bottles of VPBW, were ordered through the One-Stop Shopping system of the NWQL, where quality-control testing is done on most supplies (certificate of analyses of supplies are available to WSCs). The VPBW used for the FCS was NWIS Lot Number 80302 and had a NWQL certificate of analysis date of December 12, 2008. Each order of VPBW that was placed for an FCS sampling site consisted of six 4-liter bottles, each of which was purged with nitrogen gas by staff of the National Field Supply Service at the NWQL. A separate aliquot was collected from one of the six VPBW bottles in each sampling-site set after NWQL purging and was analyzed and certified to be free of the VOCs and WICs of interest to this study, just before shipment (sample 1). The VPBW is to be used within 14 days of the purge date listed on the bottle label. Office of Water Quality (OWQ) Technical Memorandum 2009.04 (Mohrman, 2009) states that holding VPBW longer than 14 days (even in unopened bottles) increases the likelihood that the water will become contaminated with VOCs. The VPBW is not to be used for collecting blanks in the field or

Table 3. Information about groundwater sites sampled for the Field Contamination Study.

[USGS, U.S. Geological Survey]

USGS Water Science Center	Site name	Well type	Use of water	Well depth (feet)	Pump type used to collect groundwater sample/ pump type used to collect field blank	Length of sample tubing used to collect field blank (feet)
Alabama	AL1	Monitoring	None	31.5	Fultz submersible/same	120
Alabama	AL2	Monitoring	None	40	Fultz submersible/same	120
Florida	FL1	Supply	Domestic	30	Dedicated jet pump/Fultz submersible	185
Florida	FL2	Supply	Domestic	115	Dedicated jet pump/Fultz submersible	145
Idaho	ID1	Monitoring	None	485	Dedicated submersible/metering pump	10
Idaho	ID2	Supply	Public	610	Dedicated submersible/metering pump	10
Louisiana	LA1	Supply	Domestic	260	Dedicated submersible/Fultz submersible	65
Louisiana	LA2	Supply	Domestic	170	Dedicated submersible/Fultz submersible	65
Missouri	MO1	Supply	Public	104	Dedicated turbine/metering pump	23
Missouri	MO2	Monitoring	None	60	Fultz submersible/same	35
New Mexico	NM1	Supply	Public	960	Dedicated turbine/metering pump	60
Ohio	OH1	Monitoring	None	28.5	Fultz submersible/same	40
Ohio	OH2	Monitoring	None	22	Fultz submersible/same	40
Texas	TX1	Monitoring	None	33.5	Fultz submersible/same	125
Texas	TX2	Monitoring	None	53.5	Fultz submersible/same	125
Utah	UT1	Supply	Irrigation	176	Dedicated submersible/metering pump	25

for the final rinse of the equipment cleaning procedure if the 14-day use period has elapsed. NWQL supplies were delivered to the WSCs within 1 to 3 days after ordering and used for sampling within a maximum of 12 days after arrival at the WSCs.

Methanol is an organic solvent used by the NAWQA Program to clean sampling equipment when samples are collected for analysis of most organic compounds. Purge-and-trap volatile-grade methanol was used in this study to reduce the likelihood of contamination from compounds possibly present in the methanol. This is a higher grade than the American Chemical Society pesticide-grade methanol that is specified in chapter A3 of the NFM (Wilde, 2004). The methanol was ordered by field personnel in each WSC from various vendors and was scheduled to arrive no earlier than 1 week before sampling. This precaution was taken to minimize the potential for contamination from carryover of older methanol that could have acquired contaminants during long-term storage at WSCs.

A large tank of prepurified grade nitrogen gas (99.998 percent minimum purity or better) was ordered by field personnel in each WSC from local vendors about 1 week before sampling. The tank contained about 250 cubic feet of nitrogen gas that was used to purge the VPBW at the sampling site. The field-purge apparatus was provided to WSC field personnel by the Field QC Workgroup for Organics. Sampling equipment, such as submersible pumps, sample tubing, instruments to monitor field measurements, flowthrough chambers, flow manifolds, plate-filter assemblies, and sample-collection chambers were supplied by each WSC.

Sampling supplies and equipment were stored away from possible sources of contamination, such as gasoline-related hydrocarbons, solvents, disinfection by-products, and other chemicals, during storage and transport to the field. Potential sources of VOCs and WICs in the storage area, field vehicle, and in the vicinity of the sampled well were documented, if present. Loading, transit, sampling, and shipping times were recorded for the sampling equipment, supplies, and samples.

Equipment Cleaning

U.S. Geological Survey clean-sampling procedures (sometimes called parts-per-billion protocol) require that sampling equipment is constructed of noncontaminating materials and cleaned rigorously before field work and between field sites, that the equipment and samples are handled in a manner that prevents contamination, and that quality-control samples are collected. Equipment cleaning for the FCS followed the protocols for organic compounds or for inorganic and organic analytes described in chapter A3 of the NFM (Wilde, 2004), except where modified for this study. The following briefly describes the cleaning steps used in the FCS (additional details are provided in the “Sequence of Field Sample Collection, Purging, and Equipment Cleaning” section of this report):

1. Wear disposable, powderless, nitrile gloves and change gloves with each change in cleaning solution.
2. Scrub equipment using a brush and 0.1- to 0.2-percent solution of nonphosphate laboratory-grade detergent (Liquinox[®] solution), and rinse thoroughly with tap water to remove any detergent residue. For Teflon[®] sample tubing, use about 1 liter of Liquinox[®] solution for every 100 feet of tubing and circulate the solution through the tubing and pump, followed by sufficient tap water to remove detergent residue. If also sampling for inorganic constituents, follow the tap-water rinse with a deionized-water rinse.
3. Rinse the sampling equipment with purge-and-trap volatile-grade methanol. The methanol rinse is used to remove organic contaminants from the equipment and is standard procedure for equipment used by NAWQA to collect organic samples (not including dissolved organic carbon samples). Pump about 2 liters of methanol through the submersible pump and sample tubing as specified in the NFM (Wilde, 2004, chap. A3.3.10.B). Rinse only the interior of the tubing with methanol, not the exterior. Place methanol-rinsed equipment, such as the plate-filter assembly, on a clean aluminum foil surface to air dry, if practical. Store the used methanol in a waste container for later disposal.
4. Rinse the sampling equipment that was not allowed to air dry with VPBW to remove any residual methanol. Methanol can serve as a sink for VOCs with time, such as while in storage. To rinse the sampling line (that is, the last step in the cleaning protocol) use about 8 liters (two 4-liter bottles) of field-purged VPBW.
5. Wrap exposed plate-filter assembly in aluminum foil and place in sealable plastic bag or other container for storage and transport. Place Teflon[®] tubing in doubled plastic bags and seal for storage and transport.

The length of Teflon[®] sample tubing cleaned by the sampling crews in the field ranged from 10 to 185 feet (table 3), depending on whether or not a portable submersible pump was installed for sampling and on how much tubing was attached to the pump used to collect the field blank. At sites where a dedicated pump was used to sample the well, a submersible pump or a portable metering pump with Teflon[®] tubing was connected to the sample line to collect the field blank. Given the range of tubing lengths, the associated volume of water required to fill the entire length of Teflon[®] sample tubing with an inside diameter of 3/8 inch ranged from about 0.2 to 4.3 liters. Because a constant volume of field-purged VPBW was specified in the FCS for the final rinse of the cleaning procedure, sampling

sites that used short sampling lines received a rinse that exceeded the minimum volume indicated by the NFM. In contrast, sampling sites where long sampling lines were used received a final rinse less than the minimum indicated by the NFM.

Field Purge of the Volatile Pesticide-Grade Blank Water

A unique aspect of the FCS was the field purge of VPBW with prepurified nitrogen gas, primarily to remove VOCs that may have contaminated the blank water after leaving the NWQL. An experiment was conducted by the Colorado WSC in September 2008 to test the logistics of field purging and to evaluate the efficacy of this step in removing VOCs and some of the WICs. The experiment consisted of spiking known volumes of VOCs and WICs into the VPBW to result in concentrations that are typical of those observed in contaminated environmental samples (0.2 to 30 micrograms per liter ($\mu\text{g/L}$), depending on the compound) (Zogorski and others, 2006; Kingsbury and others, 2008; Bender and others, 2009; Hopple and others, 2009) and then purging the spiked VPBW with nitrogen gas in the field. Analyses from the Colorado field-purge experiment indicated that most VOCs included in this study were not detected in the spiked VPBW sample after the field purge, and therefore, these compounds were removed by the purging test. However, the VOCs acetone and 2-butanone were exceptions. Only about 40 percent of the acetone and about 60 percent of the 2-butanone was removed from the spiked VPBW sample by the nitrogen-gas field purge (David Bender, U.S. Geological Survey, written commun., 2008).

Less than 50 percent of the WICs phenol, isophorone, camphor, menthol, methyl salicylate, *N,N*-diethyl-*meta*-toluamide (DEET), tributyl phosphate, benzophenone, 4-nonylphenol, phenanthrene, caffeine, and triphenol phosphate was removed from the spiked VPBW sample by the nitrogen-gas field purge, whereas more than 80 percent of the naphthalene, hexahydrohexamethylcyclopentabenzopyran (HHCB), and acetyl hexamethyl tetrahydronaphthalene (AHTN) was removed (Steven Smith, U.S. Geological Survey National Water Quality Laboratory, written commun., May 7, 2010). In summary, the Colorado experiment determined that purging the spiked VPBW in the field with nitrogen gas removed (that is, reduced the concentration to less than the analytical detection limit) all of the VOCs of interest, except for acetone and 2-butanone, but did not remove the WICs of interest because of their lower vapor pressure. Vapor pressure determines, to a large extent, the tendency of a compound to transfer to and from gaseous phases (Schwarzenbach and others, 1993). This property is critical for prediction of the equilibrium distribution or the rates of exchange to and from natural waters (Schwarzenbach and others, 1993).

For the FCS, the field-purge apparatus (figs. A1–A4 in the “Supplemental Information” section at the back of this report) was assembled at each sampling site in accordance with instructions provided with the equipment. Details on the field purge are presented in the “Supplemental Information” section of this report. Briefly, the six 4-liter bottles of VPBW that were sent for each sampling site were purged by placing Teflon[®] tubing connected to the nitrogen-gas tank into each bottle and slowly bubbling a steady amount of nitrogen gas through the VPBW for 2 hours. The purging was done outside of a mobile laboratory, vehicle, or trailer, but inside of a plastic-covered chamber. This loosely enclosed chamber allowed the nitrogen to escape while minimizing exposure of the purging bottles of VPBW to dust and airborne contaminants (fig. A4 in the “Supplemental Information” section).

Sample Types

Field blanks and source-solution blanks were collected as part of the FCS to identify, quantify, and document extrinsic contamination (positive bias) in the VOC and WIC analytical data for these types of samples. These QC samples also are used to help determine the sources and causes of data-quality problems that can affect groundwater samples. A source-solution blank is collected by pouring VPBW directly into the sample vial or bottle in the field and is used to determine if the VPBW is contaminated. A field blank consists of VPBW that has been processed through the sampling system (after cleaning) and is used to determine if there is a source of contamination from equipment cleaning, sample collection, sample processing, or sample storage/transport.

Sample collection for analysis of VOCs consists of sequentially filling three vials. Printed labels for the VOC vials were provided to sampling personnel that contained the site identification number, sample type, and vial sequence number. The vials were filled in the sequence that they were numbered and were analyzed by the NWQL starting with vial 3 (the last vial filled). The intent of this numbering and analysis scheme as described in OWQ Technical Memorandum 2009.04 (Mohrman, 2009) is to reduce the potential for contamination from the small diameter Teflon[®] tube that channels the water sample into the VOC vials. As part of the FCS, vials 2 and 3 of the blanks collected in the field were analyzed for VOCs to (1) assess the precision between two analyses of a sample, and (2) to increase the number of analyses to better estimate the occurrence or non-occurrence of each compound. Vial 1 of each sample was an extra vial collected in case of breakage or if reruns during analysis were needed. Vial 1 typically was not analyzed.

Sample collection for analysis of WICs consists of filling 1-liter baked amber glass bottles. Only the field blank and groundwater samples were filtered. Printed labels for the 1-liter WIC bottles were provided to sampling personnel that contained the site identification number and sample type.

The following five different sample types were collected for the FCS (fig. 2) and were analyzed for VOCs and WICs:

1. **Sample 1** (source-solution analysis performed at NWQL): a source-solution blank collected at the NWQL using laboratory nitrogen-purged VPBW. One blank was collected for each set of six VPBW bottles used in the FCS and analyzed for VOCs and WICs.
2. **Samples 2A and 2B** (source-solution blanks): source-solution blanks collected in the field using laboratory-purged VPBW from two different bottles and analyzed for VOCs and WICs. Sequential intra-sample vials (vials 2 and 3) of each sample were analyzed for VOCs.
3. **Samples 3A and 3B** (field-purged source-solution blanks): source-solution blanks collected in the field using field-purged VPBW from two different bottles and analyzed for VOCs and WICs. Sequential intra-sample vials (vials 2 and 3) were analyzed for VOCs.
4. **Sample 4** (field blank): a field blank collected using field-purged VPBW and analyzed for VOCs and WICs. Sequential intra-sample vials (vials 2 and 3) were analyzed for VOCs.
5. **Sample 5** (groundwater sample): a groundwater sample from the well and analyzed for VOCs and WICs.

The source-solution blanks collected in the field sequentially tested two different bottles of VPBW (samples 2A and 2B) and field-purged VPBW (samples 3A and 3B). Each VPBW bottle was considered a separate experiment. Sequential, intra-sample vials (vials 2 and 3) from the source-solution blanks and the field blank were analyzed for VOCs, resulting in 4 VOC analyses from source-solution blanks, 4 VOC analyses from field-purged source-solution blanks, and 2 VOC analyses from the field blank collected at each site. Analytical results from the comparison samples of VPBW bottles (sample A in comparison to sample B) and sequential intra-sample (vial 2 in comparison to vial 3) for the applicable blanks provided information on the reproducibility and variability in bottles of VPBW and in the VOC vials, and provided a greater number of analyses for the study.

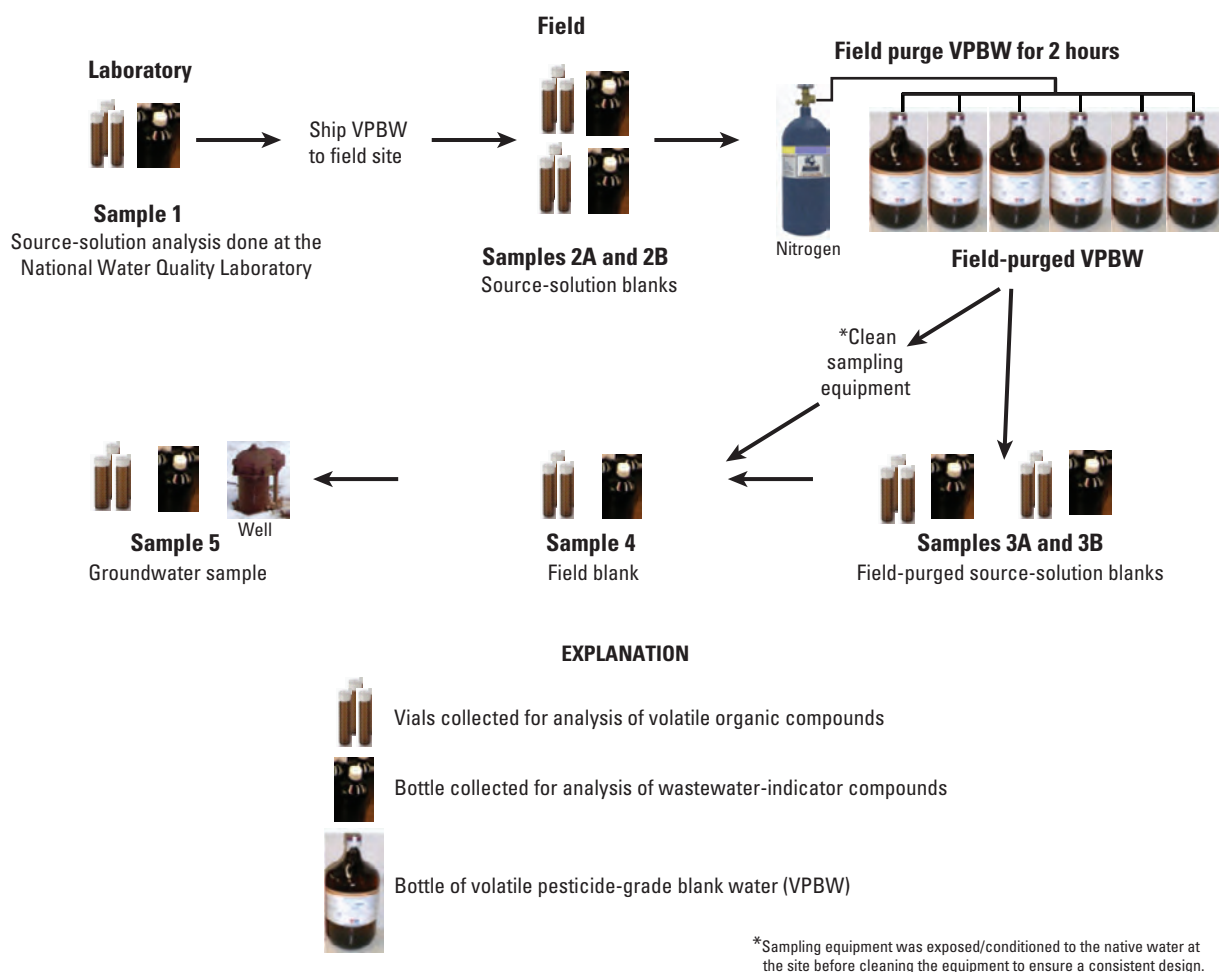


Figure 2. Sample types and order of sample collection used in the Field Contamination Study.

Information about the possible sources of contamination can be gained by comparing different QC samples from a single site. Comparison of results from the source-solution blanks collected in the field (samples 2A and 2B) to the source-solution analysis at the NWQL (sample 1) provides information on potential contamination that might occur during shipment from the NWQL to the field and its reproducibility. If VOCs or WICs are detected in sample 2A or 2B, but not in sample 1, contamination is likely occurring during shipment of the VPBW from the NWQL to the WSC, during short-term storage at the WSC, during transportation from the WSC to the field, or during the return trip to the NWQL. On the other hand, the field-purged source-solution blanks (samples 3A and 3B) address potential contamination that might occur during shipment from the field to the NWQL. Comparing analyses for samples 2A and 2B (source-solution blanks) and samples 3A and 3B (field-purged source-solution blanks) can indicate the effectiveness of purging VPBW in the field assuming that the VPBW used in samples 2A and 2B was contaminated during shipment from the NWQL to arrival in the field. Comparing analyses for samples 3A and 3B (field-purged source-solution blanks) to sample 4 (field blank) can indicate contamination during sample

collection or from the sampling equipment. Comparing analyses for sample 4 (field blank) and sample 5 (groundwater sample) can provide information on whether contamination in the field blank could be carried over to the subsequent groundwater sample or if the groundwater sample is unbiased. If a contaminant is present in all of the samples collected in the field, then it is possible that it was introduced by the same contamination process, such as transportation to the NWQL.

Sequence of Field Sample Collection, Purging, and Equipment Cleaning

The sequence of steps specified for the field component of the FCS are shown in figure 3 and are described in this section of the report. In addition, the lower left part of figure 3 illustrates that the sampling equipment (that was cleaned at a prior site) was conditioned by using the groundwater at the FCS sampling site and thereafter re-cleaned before its use. These procedures were added to the FCS to improve the ability to interpret the analytical results for various samples collected as part of the study.

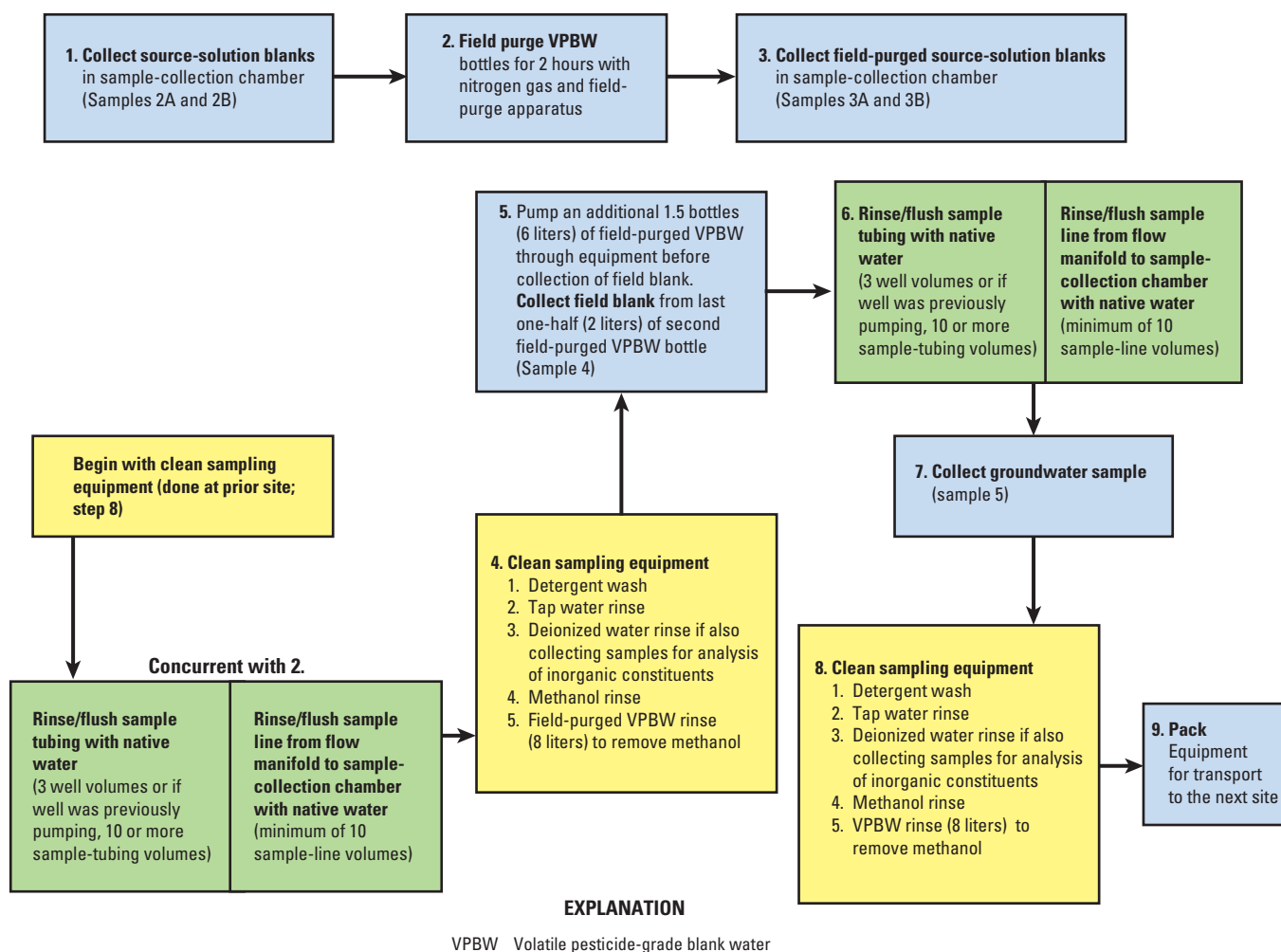


Figure 3. Sample collection steps used by the field crews in the Field Contamination Study.

The first samples collected at the site were source-solution blanks poured from two different bottles of VPBW before the field purge (samples 2A and 2B in fig. 2; step 1 in fig. 3). First, the sample-collection chamber was set up outside of a mobile laboratory or sampling vehicle to remove any associated source of potential contamination. Next, a 4-liter VPBW bottle, three sequentially numbered VOC vials, and hydrochloric acid (for sample preservation) were placed within the plastic-covered sample-collection chamber to minimize contamination from atmospheric sources. The VPBW was then poured into VOC vial 1 to overflowing so that a reverse meniscus was formed. Two drops of preservative were added to the vial to change the pH of the sample to 2 or less. The vial was then capped and checked to see if any air bubbles were present and if so, the vial was discarded and a new vial filled. These steps were repeated with the other two VOC vials for sample 2A, and using a separate VPBW bottle to collect the 3 vials for sample 2B.

After the VOC vials were filled and preserved, the plastic bag covering the sample-collection chamber was replaced and a new VPBW bottle and a 1-liter bottle for WIC analysis were placed inside. The WIC bottle was filled to the shoulder with water poured from the VPBW bottle and then capped. A separate VPBW bottle was used to collect sample 2B. The WIC source-solution blanks were not filtered, but the sample bottles were weighed before and after filling to determine sample volume. The VOC and WIC source-solution blanks

were chilled to about 4 degrees Celsius with ice before shipment to the NWQL, as was done for all subsequent samples collected for the FCS.

The field purge of the six VPBW bottles was started next and lasted for about 2 hours (step 2 in fig. 3). After the VPBW field purge was completed, the Teflon[®] tubing used to transmit the nitrogen gas was removed from the 4-liter bottles of VPBW and the bottles were capped. Source-solution blanks of the field-purged VPBW were collected from two different bottles (samples 3A and 3B in fig. 2; step 3 in fig. 3) in the sample-collection chamber as described previously for the prefield purge source-solution blanks.

While the VPBW was purging, the instruments used to monitor field measurements of pH, water temperature, specific conductance, dissolved oxygen, and turbidity were calibrated, and most instruments were placed in a flowthrough chamber to monitor water pumped from the well to be sampled. A photograph of the sample-collection setup with the VPBW field-purge apparatus next to the trailer in the background and the sample-collection chamber and flowthrough chamber near the well in the foreground is shown in figure 4. The well was purged long enough to remove three or more well volumes if a WSC supplied submersible pump was used, or long enough to move 10 or more sample-line volumes through the Teflon[®] sample tubing if collecting samples from a water-supply well with an existing pump that was already pumping. Field measurements had to meet the stabilization criteria listed in table 6.0–1 of the NFM (Wilde, variously dated).



Figure 4. Sample-collection setup at the Utah site (photograph by Steven Gerner).

After the well purge was completed, the sampling equipment was removed from the well and cleaned using the steps listed in the “Equipment Cleaning” section of this report (step 4 in fig. 3). As noted previously, the final rinse of the cleaning process used about 2 bottles of the field-purged VPBW (about 8 liters) to remove any remaining detergent, tap water, deionized water, or methanol.

The next step in sample collection for the FCS was to collect a field blank (sample 4 in fig. 2; step 5 in fig. 3). The cleaned sampling equipment was connected together as if to collect a groundwater sample, except that the submersible pump used in the monitoring well was placed in a cleaned standpipe, such as a glass or Teflon® cylinder, that could be filled with VPBW; or, in the case of a well with a dedicated pump, the sample tubing was connected to a portable metering pump with the intake tubing placed in a 4-liter bottle of field-purged VPBW, or to a Fultz pump placed in a cleaned standpipe. Referred to in this report as the conditioning

volume, this amount of VPBW mimics the native-water rinse in the sampling process for groundwater samples. The conditioning volume reduces possible carryover from the previous cleaning solutions and rinse water in the sample lines to the field-blank samples and is in addition to the volume of VPBW used in the final rinse of the cleaning procedures. Instructions for the FCS sample collection prescribed a conditioning volume of about 6 liters of field-purged VPBW (1.5 bottles) to be pumped through the sampling equipment, including at least 10 sample-line volumes through the short section of Teflon® tubing between the manifold controlling flow direction and the sample-collection chamber (sample line 2 in fig. 5). Sample line 2 includes a flexible Teflon® tube inserted into the sample-collection chamber for the filling of the VOC vials.

Field crews were directed to collect the FCS field blank from about the last 2 liters (or last one-half) of the second bottle of field-purged VPBW. The VOC vials were filled,

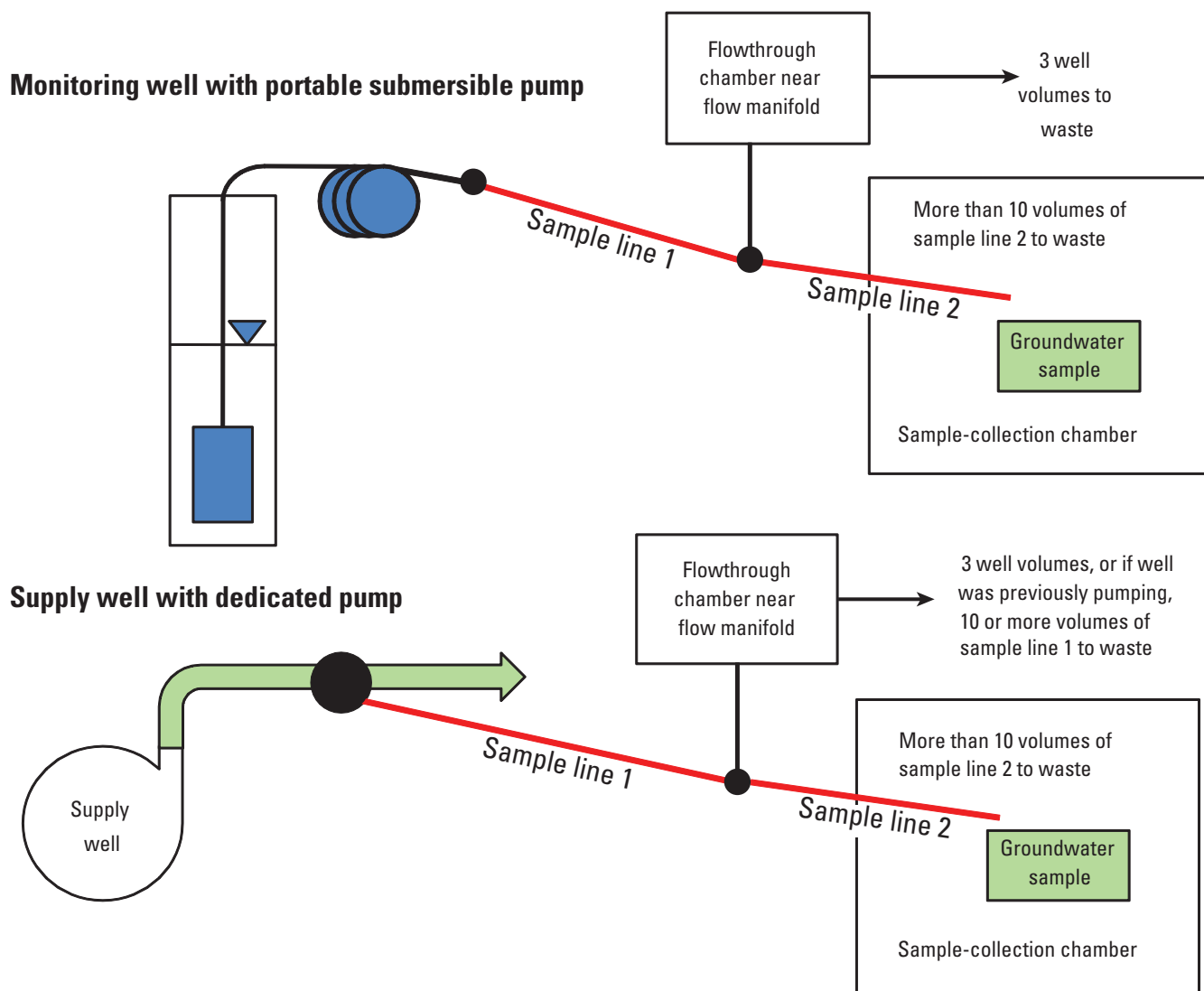


Figure 5. Sampling equipment used to collect samples from wells in the Field Contamination Study.

preserved, and capped in the sample-collection chamber as described for the source-solution blanks. After collecting the VOC field blank, the plastic bag covering the sample-collection chamber was replaced and the sample-collection line was attached to a plate-filter assembly containing a glass-fiber filter through which the WIC field blank was collected.

The volume of field-purged VPBW used in the FCS was specified and was constant for the conditioning of the equipment and the subsequent collection of the field blank. This volume differed from the minimum volume indicated in the NFM, which varies with the diameter and length of sample lines (Wilde, 2004). Six 4-liter bottles of VPBW were shipped to the participating WSC for each site for the FCS. Two 4-liter bottles of VPBW were used in the final rinse of the cleaning protocol and four 4-liter bottles of VPBW were used to condition the equipment and collect the subsequent field blank. These volumes of VPBW were based on a design assumption of 100 feet of 3/8-inch tubing on a pump reel using the volume indicated for that design in the NFM. Because variable tubing lengths were used at the sampling sites, some sites (10) used a larger volume of VPBW than the minimum indicated by the NFM and some sites (6) used less than the minimum indicated in the NFM. Based on the tubing lengths, the ratio of the calculated minimum volume from the NFM to the volume used in the FCS for the conditioning of the equipment and the subsequent collection of the field blank ranged from 1.76 to 0.37. The ratio of 1.76 was for one site in Florida (FL1) with the tubing length of 185 feet and the ratio of 0.37 was for the two sites from Idaho (ID1 and ID2) with sample tubing lengths of 10 feet (table 3).

After collection of the field blank, the submersible pump was placed back in the well or the sample tubing was connected to the well for purging (step 6 in fig. 3). After the well/sample-tubing purge volume and field measurement stabilization criteria were met, flow was redirected from the field-measurement flowthrough chamber to the sample-collection chamber, allowing enough time and volume to rinse the short section of sample tubing downstream from the manifold controlling flow direction (at least 10 volumes of sample line 2) with water from the well. The native-water rinse of the sampling equipment that occurs during the well purge provides additional opportunity for contaminant removal beyond what is provided by the cleaning process and has been documented in a previous study to be effective in minimizing carryover contamination (Taglioli and others, 2001). The groundwater sample (sample 5 in fig. 2; step 7 in fig. 3) was then collected using the same process described for the field blank.

After the groundwater sample was collected for analysis of VOCs and WICs, preserved, and chilled, the sampling equipment was again disconnected from the well and cleaned in the field (step 8 in fig. 3). The sampling equipment was then wrapped for transport to the next sampling site or for storage. The samples were packed on ice, contained in sealed plastic bags within coolers, and shipped overnight to the NWQL.

Documentation of Sampling Activities

Most activities of the FCS were documented to help interpret the study results. Each sampling crew provided documentation on the ordering, receipt, and storage of field supplies; transportation times to and from the sampling site; and possible exposure to VOCs or WICs, such as gasoline at filling stations, solvents or pesticides in the vicinity of the sampling site, and chlorinated tap or deionized water used for equipment cleaning. The equipment used to collect the field blank was described, including the length of Teflon® tubing used as a sample line and the pump used to move the VPBW through the sample line. Information on the VPBW field purge, such as the pressure in the nitrogen-gas tank and at the regulator outlet at the start, intermediate stages, and end of the purge, was noted. Photographs of the VPBW field purge and collection of the field blank and well samples were taken at each sampling site.

Field notes were made for each site and analytical service request (ASR) forms were submitted to the NWQL. The field notes document basic information about the location and construction of the sampled well, quality-control information on the supplies used, and sampling information, such as sample date and time, field measurements, and type of samples. The ASR forms for each sample lists the type of analysis requested (laboratory schedule of compounds) and other sample information that is used by the laboratory.

Laboratory Methods

Groundwater samples and blank samples collected at each site were analyzed at the NWQL. All samples from each site, except the source-solution analysis done at the NWQL (sample 1), were analyzed as part of a single machine run containing 10 to 30 samples. Each VOC run included the following laboratory QC samples: one laboratory **reagent-spike** sample containing known quantities of VOCs and two bracketing **laboratory set blanks** for each group of 10 samples. Each WIC run included a laboratory reagent-spike sample containing known quantities of WICs and one set blank for each group of 10 samples. These QC samples were used to monitor method performance. Set blanks also provide information regarding contamination that might be introduced into samples at the laboratory.

VOC samples collected for the FCS were analyzed with USGS method GCM66 described by Connor and others (1998). This method uses purge-and-trap gas chromatography/mass spectrometry (GC/MS). Sample water is actively purged with helium to extract the VOCs. The VOCs are collected onto a sorbent trap, thermally desorbed and separated by a gas chromatographic capillary column, and measured by a full-scan quadrupole mass spectrometer. Analytical results are reported for 86 VOCs (NWQL Schedule 2020 combines *x*- and *p*-xylene), 13 of which are included in this study (table 1).

WIC samples were analyzed with USGS method GCM37 (Zaugg and others, 2007), using solid phase extraction and GC/MS. The water sample is passed through a solid-phase-extraction cartridge to separate the compounds from the water matrix. The solid-phase-extraction cartridge is eluted with a solvent and the compounds in the extract are analyzed using capillary-column GC/MS. Analytical results are reported for 63 WICs (NWQL Schedule 1433), 16 of which are included in this study (table 2).

Compound Identification and Quantitation

Identification and quantitation of compounds are described by Connor and others (1998) for the VOC analytical method, and by Zaugg and others (2007) for the WIC analytical method. In both analytical methods, compounds are separated using capillary-column gas chromatography, then fragmented and analyzed using electron-impact mass spectrometry. The instrument produces a total-ion chromatogram, an example of which is shown in figure 6. Peaks in the chromatogram are associated with ions from carbon dioxide (CO_2), surrogate compounds, internal standards, and

individual compounds. The x-axis in figure 6 is the amount of time that compounds from the sample have been retained in the column before elution, and the y-axis is the instrument response to ions generated from those compounds. Ions for each individual compound occur at characteristic retention times.

Single-ion chromatograms are displayed at retention times characteristic of each compound. These single-ion chromatograms are evaluated to identify compounds that are in the sample and to measure their concentrations. For each compound, one quantitation ion and one or two associated qualification ions are evaluated. The quantitation ion is used to determine the concentration of the compound; the qualification ions are used to help identify presence of the compound. Identification criteria for each ion include the retention time, the area under the ion peak, the relative abundance of the ion, the height of the peak above the instrument background level, and comparison to a reference mass spectrum.

The process used for identification and quantitation of individual compounds for the FCS can be described as a series of steps, as shown by the flow chart in figure 7. For each compound, the steps are:

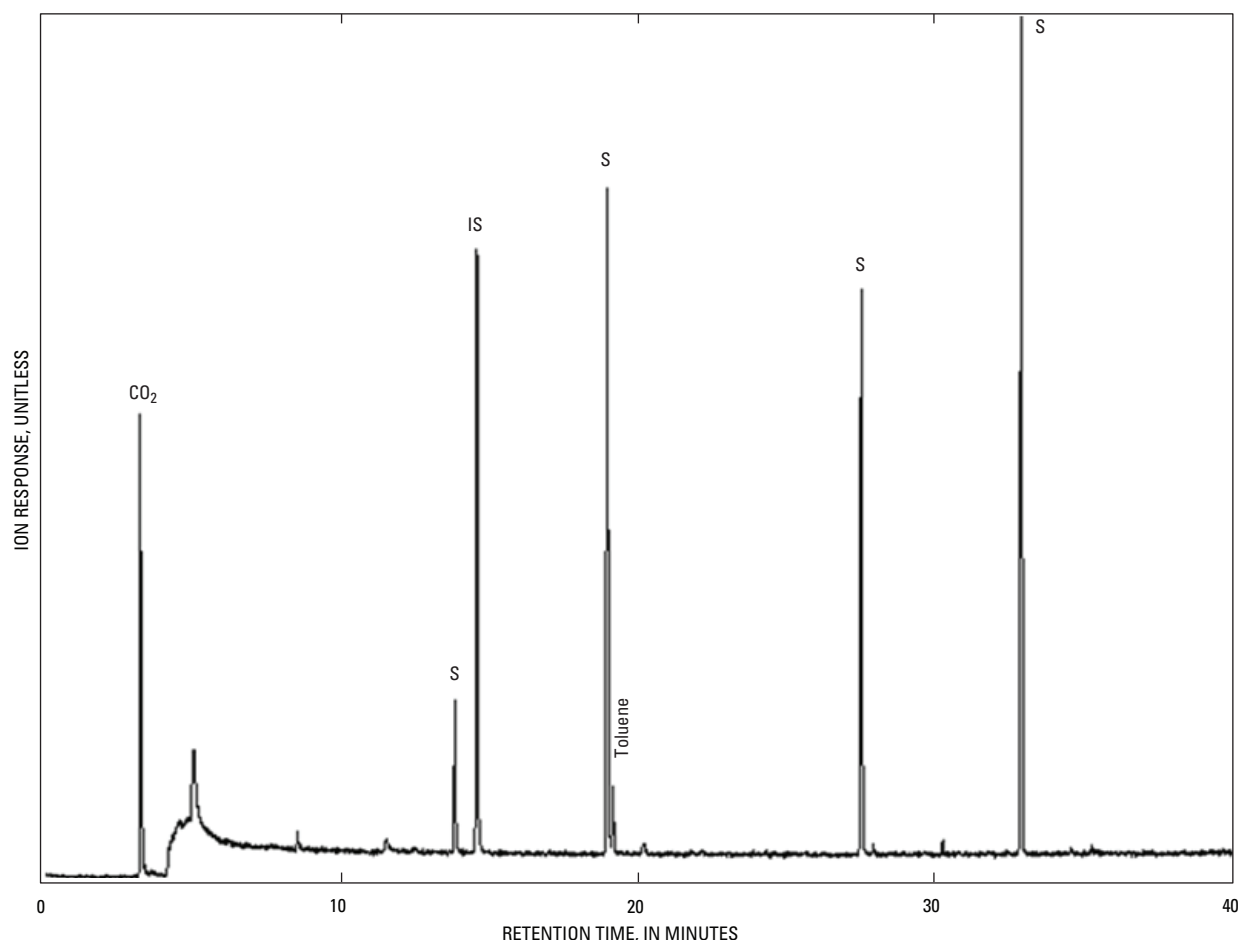


Figure 6. Example of a total-ion chromatogram showing carbon dioxide (CO_2), surrogates (S), an internal standard (IS), and toluene.

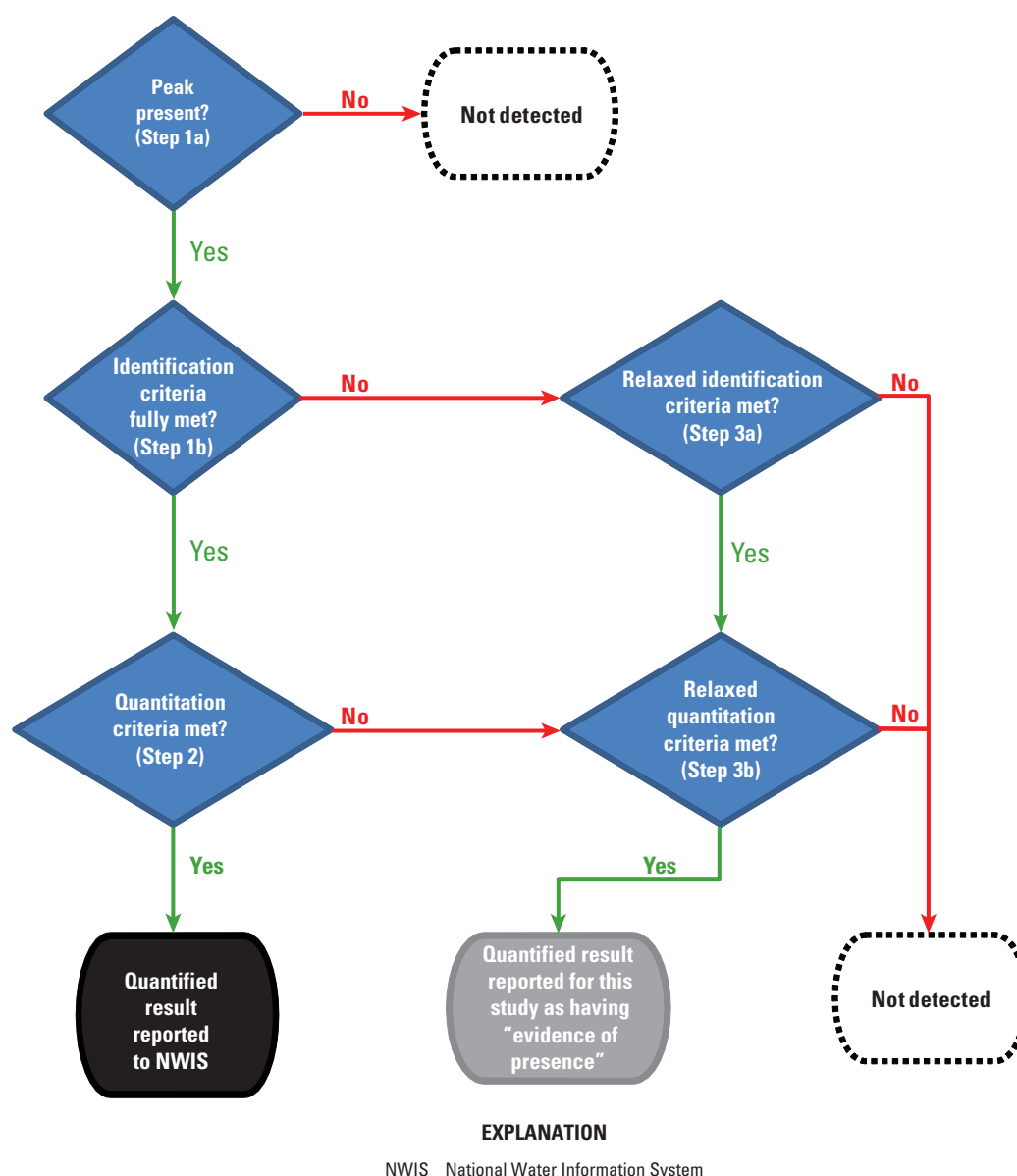


Figure 7. Flow chart of the compound identification and quantitation process used in the Field Contamination Study. The “Steps” referred to in the diamond boxes are described in the “Compound Identification and Quantitation” section of this report.

Step 1—Identification.—

- a. Is there a peak at the expected retention time for the quantitation ion for the compound?
- b. If yes, compare the single-ion chromatograms for the quantitation and qualification ions to a reference standard. Do all the ion-chromatograms meet identification criteria (all peaks’ maxima occur together at the expected retention time, are at least twice the instrument background signal, and are in the expected ratios)? If yes, the compound is identified.

*Step 2—Quantitation.—*If the compound is identified, the concentration of the compound is computed based on the area under the peak of the quantitation-ion chromatogram. Does this concentration exceed laboratory contamination? If yes, the result is quantified. For VOCs, laboratory contamination is defined as equal to five times the higher concentration of the two bracketing laboratory set blanks. For WICs, laboratory contamination is defined as equal to either 3 times the concentration in the laboratory set blank or 3 times the second-highest concentration in the 10 previous laboratory set blanks, whichever is greater.

Step 3—Relaxed Identification and Quantitation.—Multiple criteria must be met to identify and quantify a compound, as described for steps 1 and 2 and shown in figure 7. Normally, a compound is considered “not detected” unless all of these criteria are met; however, for this study, additional steps (3a and 3b in fig. 7) were used by laboratory analysts to determine whether there was evidence that a compound might be present even though it did not meet all the identification criteria. Single-ion chromatograms of toluene that exemplify three different situations are shown in figure 8. In figure 8A, none of the peaks for the ions associated with toluene are present; therefore, toluene is “not detected.” In figure 8B, all of the identification criteria are met, and toluene is identified and can be compared to criteria for quantification. In figure 8C, some but not all of the identification criteria for toluene are met; the quantitation ion and the first qualification ion are present, and the retention times and mass spectrum match those of the standard, but the second qualification ion is not twice the instrument background level. For this study, these data are considered adequate to indicate “evidence of presence,” and were used only for diagnostic purposes within the context of this report. The specific steps in figure 7 used to determine “evidence of presence” are:

- a. Relaxed identification—were most, but not all, of the criteria in step 1b met?
- b. Relaxed quantitation—if yes for relaxed identification, did the concentration exceed the less stringent definition of laboratory contamination of 2 times the concentration in set blanks, rather than 3 to 5 times the concentration in set blanks as required in step 2? If yes, the laboratory analyst reports “evidence of presence,” with an estimated concentration.

Detection and Reporting Levels

Quantified results determined using the criteria shown in figure 7 are reported as concentrations in micrograms per liter ($\mu\text{g/L}$) and are transmitted by the NWQL to the USGS NWIS database. Compounds that are “not detected” (or, in this study, identified as having only “evidence of presence”) are reported to NWIS as censored values. In the database, censored values are indicated by a remark code of “<” (less than) and are assigned a numeric value based on the **laboratory reporting level (LRL)**.

At the NWQL, the LRLs for each compound are determined annually. Reagent-spike samples are prepared that contain low concentrations of each compound. At least 24 spiked samples are analyzed by each method throughout the year. Spike results are used to determine the **long-term method detection level (LT-MDL)** for each compound. The LT-MDL is the minimum concentration of a compound that can be reported with 99-percent confidence that the measured value is greater than zero. The LT-MDL accounts for method variance because of multiple instruments, multiple operators,

and multiple calibrations throughout the year (Connor and others, 1998; Childress and others, 1999). The LRL used by the NWQL is two times the LT-MDL. The LT-MDLs and LRLs for the VOCs and WICs analyzed in this study are listed in table 4.

Quantified results that are measured as being less than the LRL are stored in NWIS with a remark code of “E,” indicating an estimated value. This code indicates that the reported concentration has a greater relative uncertainty than higher concentrations reported for the same compound. The “E” code is used for various other purposes, such as indicating that the reported value is less than the lowest calibration standard. Also, for “information rich” GC/MS methods, the “E” code is used to indicate that a quantified result is less than the LT-MDL. Such results can be reported without censoring if all identification criteria have been met.

Evaluation of Contamination in Blanks and Groundwater Samples

The analytical results from the FCS that were used to evaluate contamination in blanks and groundwater samples were divided into two parts: (1) results that met all of the identification criteria for their laboratory method and, therefore, are quantified, reported, and stored in the NWIS database (this includes concentrations that are less than the LRL) and (2) results that did not meet all of the identification criteria, but had evidence of presence and have concentrations that are stored in NWIS as less than (<) the LRL. Additional information about the evidence-of-presence results was supplied to the FCS investigators by laboratory analysts as described in the “Compound Identification and Quantitation” section of this report and interpreted as part of the study, but was not stored in the NWIS database. Evidence-of-presence results for VOCs and WICs in an FCS analysis include an estimated concentration. The analytical data stored in the NWIS database are listed in table A1 in the “Supplemental Information” section at the back of this report. Compounds determined to have evidence of presence in an analysis are highlighted in table A1.

Volatile Organic Compounds

A total of 192 VOC analyses were made by the NWQL as part of the FCS (table 5), including 16 source-solution analyses of samples collected at the NWQL (sample 1), 64 analyses of source-solution blanks collected in the field (vials 2 and 3 of samples 2A and 2B), 64 analyses of field-purged source-solution blanks (vials 2 and 3 of samples 3A and 3B), 32 analyses of field blanks (vials 2 and 3 of sample 4), and 16 analyses of groundwater (sample 5). Figures A5–1 to A5–13 in the “Supplemental Information” section at the back of this report show the evidence-of-presence and quantified concentrations for selected VOCs in

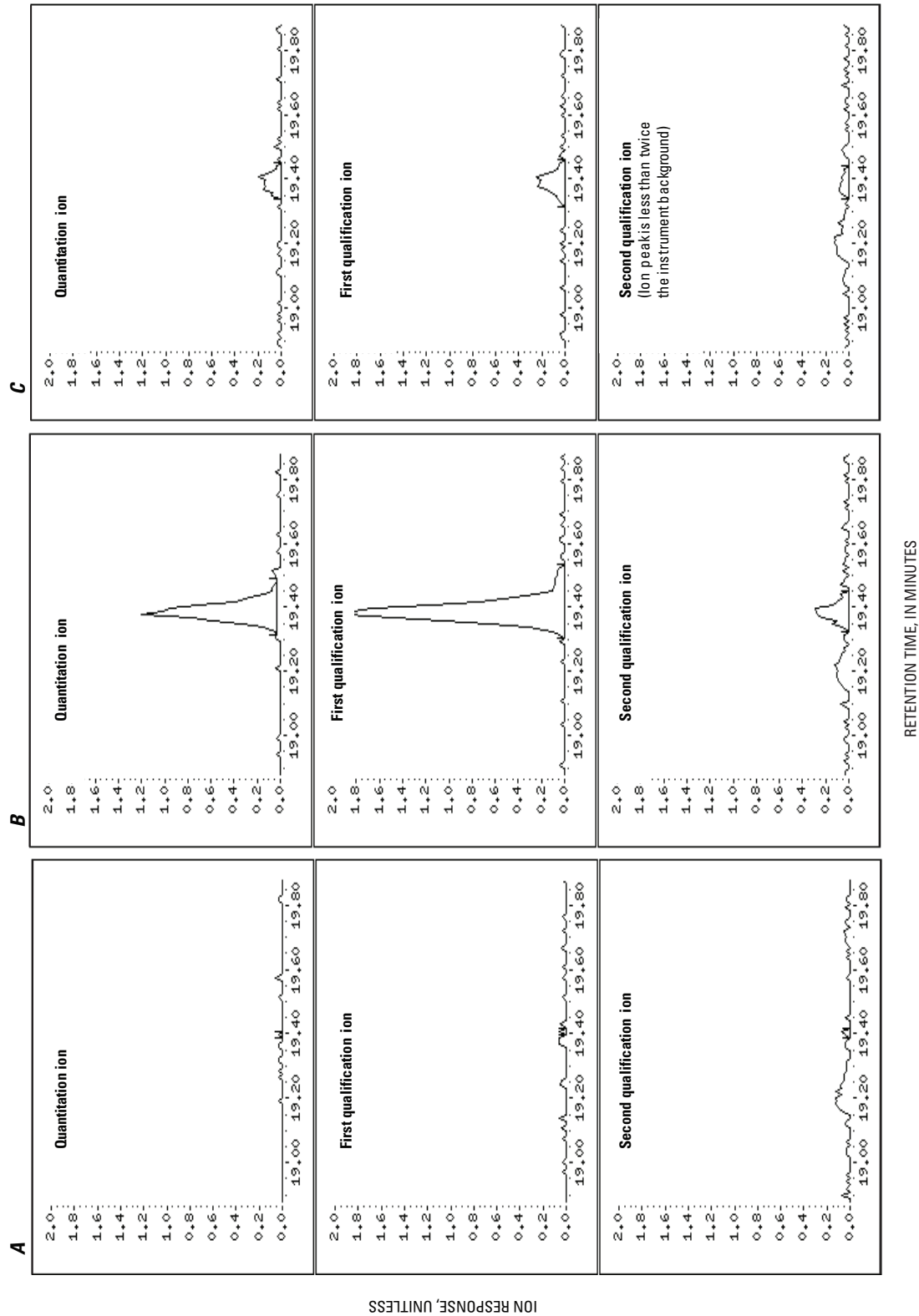


Figure 8. Examples of single-ion chromatograms for toluene in three samples: *A*, identification criteria are not met, toluene is “not detected;” *B*, all identification criteria are met, toluene is identified and quantified; *C*, some but not all identification criteria are met, there is evidence that toluene might be present (reported in the Field Contamination Study as “evidence of presence”).

Table 4. Long-term method detection levels and laboratory reporting levels for volatile organic compounds and wastewater-indicator compounds included in the Field Contamination Study.

Compound (ordered by use group, see tables 1 and 2)	Parameter code	Long-term method detection level (micrograms per liter)	Laboratory reporting level (micrograms per liter)
Volatile organic compounds			
Benzene	34030	0.008	0.016
Toluene	34010	.009	.018
Ethylbenzene	34371	.02	.04
<i>m</i> - and <i>p</i> -Xylene	85795	.04	.08
<i>o</i> -Xylene	77135	.02	.04
Styrene	77128	.02	.04
1,2,4-Trimethylbenzene	77222	.02	.04
Carbon disulfide	77041	.02	.04
Chloroform	32106	.02	.04
Dichloromethane	34423	.02	.04
Acetone	81552	2	4
2-Butanone	81595	.8	1.6
Tetrahydrofuran	81607	.7	1.4
Wastewater-indicator compounds			
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	62065	0.5	¹ 0.5
Benzophenone	62067	.06	.12
Caffeine	50305	.05	.1
Camphor	62070	.03	.06
<i>N,N</i> -Diethyl- <i>meta</i> -toluamide (DEET)	62082	.07	.14
Hexahydrohexamethylcyclopentabenzopyran (HHCB)	62075	.3	.5
Menthol	62080	.2	.4
Methyl salicylate	62081	.05	.1
4-Nonylphenol (total) (branched)	62085	1	2
Phenol	34466	.7	1.4
Tributyl phosphate	62089	.1	.2
Triphenyl phosphate	62092	.06	.12
Isophorone	34409	.04	.08
Naphthalene	34443	.02	.04
Phenanthrene	34462	.02	.04

¹Interim reporting level (IRL) is a temporary reporting level that was determined during original method validation (Zaug and others, 2007).

FCS analyses (upper panel of figures) and the percentage of analyses with a VOC not detected, with evidence of presence, and with quantified concentrations (lower panel of figures).

Quantified Analytical Results Stored in the National Water Information System Database

Concentrations of VOCs that met the rigorous identification criteria to be stored in the NWIS database (quantified analytical results) are described in this section. Concentrations of seven VOCs included in this study,

o-xylene, styrene, 1,2,4-trimethylbenzene, dichloromethane, acetone, 2-butanone, and tetrahydrofuran, were not quantified in any of the samples collected (table 5). Benzene, toluene, ethylbenzene, *m*- and *p*-xylene, carbon disulfide, and chloroform were quantified in analyses of FCS blanks or in groundwater samples and the concentrations are stored in the NWIS database (table A1). Possible sources of VOCs quantified and with evidence of presence in FCS analyses are listed in table 6 and are described in this section of the report. Chloroform and styrene are not included in table 6 because these compounds were not detected in any blank samples; styrene also was not detected in any groundwater samples.

Table 5. Detection frequency of volatile organic compounds (VOCs) in Field Contamination Study analyses having quantified results stored in the National Water Information System (NWIS) database and results of analyses having only evidence of presence reported exclusively to study investigators.

[NWQL, U.S. Geological Survey National Water Quality Laboratory; VPBW, volatile pesticide-grade blank water; N, number of analyses]

Volatile organic compound (ordered by use group, see table 1)	Detection frequency, in percent, of VOCs stored in the NWIS database and <i>as having evidence of presence only</i>									
	NWQL-purged VPBW		NWQL-purged VPBW		Field-purged VPBW		Field-purged VPBW		N = 16 Sample 5	
	N = 16 Sample 1		N = 64 Samples 2A & 2B		N = 64 Samples 3A & 3B		N = 32 Sample 4			
	Source-solution analysis at NWQL		Source-solution blank		Source-solution blank		Field blank		Groundwater sample	
Benzene	0	12	0	16	1.6	27	3.1	28	0	12
Toluene	0	19	3.1	42	0	30	3.1	47	6.2	25
Ethylbenzene	0	12	3.1	0	0	0	0	6.2	0	0
<i>m</i> - and <i>p</i> -Xylene	0	6.2	0	9.4	0	3.1	6.2	19	0	6.2
<i>o</i> -Xylene	0	0	0	1.6	0	0	0	19	0	0
Styrene	0	0	0	0	0	0	0	0	0	0
1,2,4-Trimethylbenzene	0	12	0	4.7	0	0	0	0	0	0
Carbon disulfide	0	0	7.8	9.4	7.8	22	6.2	9.4	12	19
Chloroform	0	0	0	0	0	0	0	0	31	6.2
Dichloromethane	0	0	0	0	0	0	0	3.1	0	0
Acetone	0	0	0	6.2	0	23	0	19	0	0
2-Butanone	0	0	0	25	0	30	0	34	0	25
Tetrahydrofuran	0	0	0	1.6	0	0	0	0	0	6.2

None of the 13 VOCs included in this study were quantified in the source-solution analysis done at the NWQL (sample 1; table A1). This indicates that the VPBW was “VOC free” when it was shipped from the laboratory to each of the field offices. Toluene, ethylbenzene, and carbon disulfide were the only VOCs quantified in analyses of the source-solution blanks (samples 2A and 2B) and possibly were introduced to the VPBW during shipment from the NWQL to the WSC (table 6). Toluene and ethylbenzene were quantified at similar concentrations in both analyses of a source-solution blank (vials 2 and 3 of sample 2B) collected at site AL1, but were not quantified in analyses of the other source-solution blank (vials 2 and 3 of sample 2A) or in analyses of the subsequent field-purged source-solution blanks (vials 2 and 3 of samples 3A and 3B). This likely indicates that the field purge of VPBW using nitrogen gas reduced the concentration of these VOCs in the VPBW to less than the detection limits.

The only VOCs quantified in FCS field-purged source-solution blank analyses were benzene and carbon disulfide. Benzene was quantified in vial 3 of a field-purged source-solution blank (sample 3B) from site TX2, but not in vial 2 of sample 3B or in either vial of sample 3A. Carbon disulfide was quantified in a field-purged source-solution blank analysis

(vial 3 of sample 3B) from site MO2. Because carbon disulfide was not detected in source-solution blank analyses (sample 2) for these two sites, it is possible that the contamination was introduced to the VPBW during the field-purge process. In contrast, carbon disulfide was quantified in all eight of the analyzed vials for the source-solution blanks collected before (samples 2A and 2B) and after the VPBW field purge (samples 3A and 3B) at site MO1.

Benzene, toluene, *m*- and *p*-xylene, and carbon disulfide were each quantified in an FCS field-blank analysis (sample 4, either one or both vials), but not in the subsequent groundwater sample collected at the same site. That these compounds were not detected in the groundwater sample (sample 5) is likely the result of the native-water rinse reducing low-level contamination in the sampling equipment before sample collection. The VOC *m*- and *p*-xylene was quantified at similar concentrations in both analyses for the field blank (sample 4) from site OH1, but not in any of the analyses for the preceding blanks. Contamination detected in the field-blank analyses possibly was introduced during the field-blank sample-collection process. Benzene was quantified in vial 2 of the field blank from site TX2, but not in vial 3. Toluene was quantified in vial 3 of the field blank from this

Table 6. Possible sources of volatile organic compounds detected in sample types at sites sampled for the Field Contamination Study.

Analyses with quantified concentrations (reported to the National Water Information System database) are **bolded, italicized**; all other analyses were determined to have evidence of presence (indicated by **red font**, some but not all identification criteria were met). Site names are listed in table 3. See “Sample Types” section of report for a more detailed explanation of the samples collected for the Field Contamination Study. VPBW, volatile pesticide-grade blank water; NWQL, U.S. Geological Survey National Water Quality Laboratory; WSC, Water Science Center; N/N, number of analyses with detections per number of analyses per site; --, not applicable]

Volatile organic compound	Compound in sample type 2, but not in sample type 1		Compound in sample type 3, but not in sample type 2		Compound in sample types 3 and 4		Compound in sample type 4, but not in sample type 3		Compound in sample types 4 and 5		Compound in sample types 2, 3, 4, and 5	
	Compound in source-solution blank possibly was added to VPBW during shipment from NWQL to WSC		Compound in field-purged source-solution blank possibly was introduced to VPBW during field purge		Compound in field blank possibly came from field-purged VPBW		Compound in field blank possibly was introduced during the field-blank sample-collection process		Compound in groundwater sample possibly came from sampling equipment		Compound possibly was added during shipment from the WSC to the NWQL	
	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections
	Benzene	5	LA1 (4/4) LA2 (4/4) OH2 (2/4) TX2 (1/4) TX2 (1/4)	4	LA1 (2/2) LA2 (2/2) NM1 (1/2) OHI (2/2) TX2 (1/2) TX2 (1/2)	5	FL1 (1/2) LA2 (1/1)	1	--	0		
	Toluene	9	OH1 (4/4)	1	ID2 (2/2) LA2 (1/2) NM1 (2/2) OHI (2/2) OH2 (1/2)	5	AL2 (1/2) FL1 (1/2) ID1 (2/2) TX1 (2/2) TX2 (1/2) TX2 (1/2)	4	ID2	1		
	Ethylbenzene	1	--	0	--	0	OH1 (2/2)	1	--	0		
m- and p-Xylene	4	NM (1/4)	1	MO2 (1/2) NM1 (2/2)	2	OH1 (2/2) OH2 (2/2) TX2 (1/2)	3	TX2 (1/1)	1	--	0	

Table 6. Possible sources of volatile organic compounds detected in sample types at sites sampled for the Field Contamination Study.—Continued

[Analyses with quantified concentrations (reported to the National Water Information System database) are **bolded, italicized**; all other analyses were determined to have evidence of presence (indicated by **red font**, some but not all identification criteria were met). Site names are listed in table 3. See “Sample Types” section of report for a more detailed explanation of the samples collected for the Field Contamination Study. VPBW, volatile pesticide-grade blank water; NWQL, U.S. Geological Survey National Water Quality Laboratory; WSC, Water Science Center; N/N, number of analyses with detections per number of analyses per site; —, not applicable]

Volatile organic compound	Compound in sample type 2, but not in sample type 1		Compound in sample type 3, but not in sample type 2		Compound in sample types 3 and 4		Compound in sample type 4, but not in sample type 3		Compound in sample types 4 and 5		Compound in sample types 2, 3, 4, and 5	
	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections	Site name (N/N)	Number of sites with detections
<i>o</i> -Xylene	AL1 (1/4)	1	—	0	—	0	NM1 (2/2) OH1 (2/2) OH2 (1/2)	3	—	0	—	0
	AL1 (1/4) FL1 (2/4)	2	—	0	—	0	—	0	—	0	—	0
	FL1 (3/4)	5	AL1 (2/4) FL2 (1/4) MO2 (1/4) MO2 (3/4) NM1 (1/4) OH1 (1/4)	5	FL1 (1/2) MO1 (2/2) MO2 (2/2)	3	—	0	¹ FL1 (1/1)	1	FL1	1
	—	0	—	0	—	0	—	0	—	0	—	0
	AL2 (1/4) MO2 (1/4) NM1 (2/4)	3	FL2 (4/4) OH1 (3/4) OH2 (3/4) TX2 (2/4)	4	FL2 (2/2) MO2 (1/2) OH1 (1/2) OH2 (1/2) TX2 (1/2)	5	—	0	—	0	—	0
	FL1 (1/4)	6	FL2 (3/4)	1	FL2 (1/2) ID1 (2/2) ID2 (2/2) LA1 (2/2) LA2 (2/2) UT1 (2/2)	6	—	0	ID1 (1/1) ID2 (1/1) UT1 (1/1)	3	ID1 ID2 UT1	3
Dichloromethane	—	0	—	0	—	0	ID1 (1/2)	1	—	0	—	0
Acetone	AL2 (1/4) MO2 (1/4) NM1 (2/4)	3	FL2 (4/4) OH1 (3/4) OH2 (3/4) TX2 (2/4)	4	FL2 (2/2) MO2 (1/2) OH1 (1/2) OH2 (1/2) TX2 (1/2)	5	—	0	—	0	—	0
	FL1 (1/4)	6	FL2 (3/4)	1	FL2 (1/2) ID1 (2/2) ID2 (2/2) LA1 (2/2) LA2 (2/2) UT1 (2/2)	6	—	0	ID1 (1/1) ID2 (1/1) UT1 (1/1)	3	ID1 ID2 UT1	3
	—	0	—	0	—	0	—	0	—	0	—	0
Tetrahydrofuran	ID1 (1/4)	1	—	0	—	0	—	0	—	0	—	0

¹Sample type 5 had a quantified concentration, but sample type 4 had evidence of presence.

same site, but not in vial 2. The spotty detections of benzene and toluene in these samples are indicative of the difficulty in assessing contaminant sources, especially when concentrations are near the LT-MDL.

Three VOCs were quantified in the FCS groundwater samples, for a total of eight detections at eight different sites (table A1). Toluene was quantified in water from the supply well in Utah (site UT1), carbon disulfide was quantified in water from both supply wells sampled in Florida (sites FL1 and FL2), and chloroform was quantified in water from the supply wells in Idaho (site ID2) and New Mexico (site NM1), both monitoring wells in Alabama (sites AL1 and AL2), and from a monitoring well in Texas (site TX2). Each one of these VOCs was the only compound quantified in the groundwater sample and none of the analyses of associated blanks from the same site contained quantified concentrations of the VOC detected in the groundwater sample.

Chloroform was the most frequently detected VOC in aquifers studied by NAWQA (Zogorski and others, 2006), a finding that is consistent with the results of the FCS groundwater samples. Chloroform is a disinfection by-product that commonly is present in tap water and in the deionized water derived from tap water used to clean the sampling equipment. Chloroform was not detected in the FCS field blanks, most likely because a sufficient amount of “chloroform-free VPBW” was used to rinse the sampling equipment before the collection of the field blank. It is probable that the relatively high **detection frequency** of chloroform in historical NAWQA field blanks (19.7 percent; table 7) is the result of inadequate rinsing of the sampling equipment with VPBW during cleaning.

The occurrence of carbon disulfide in all of the analyses of blanks collected at site MO1, but not in the associated source-solution analysis done at the NWQL or in the

Table 7. Detection frequency of selected volatile organic compounds stored in the National Water Information System (NWIS) database for historical source-solution and field blanks collected during 1996–2008 for groundwater sampling and for blank analyses for the Field Contamination Study.

[NAWQA, National Water-Quality Assessment; NWQL, U.S. Geological Survey National Water Quality Laboratory; VPBW, volatile pesticide-grade blank water; N, number of analyses (except where footnoted)]

Volatile organic compound (ordered by use group, see table 1)	Detection frequency, in percent					
	1996–2008 NAWQA groundwater sampling		Field Contamination Study			
	NWQL-purged VPBW	NWQL-purged VPBW	NWQL-purged VPBW	NWQL-purged VPBW	Field-purged VPBW	Field-purged VPBW
	N = 418	N = 575	N = 16 Sample 1	N = 64 Sample 2	N = 64 Sample 3	N = 32 Sample 4
	Source- solution blank	Field blank	Source-solution analysis at NWQL	Source-solution blank	Source-solution blank	Field blank
Benzene	5.0	8.9	0	0	1.6	3.1
Toluene	¹ 29.7	² 37.9	0	3.1	0	3.1
Ethylbenzene	3.1	³ 12.4	0	3.1	0	0
<i>m</i> - and <i>p</i> -Xylene	¹ 5.3	³ 17.2	0	0	0	6.2
<i>o</i> -Xylene	2.2	⁴ 7.7	0	0	0	0
Styrene	5.7	9.9	0	0	0	0
1,2,4-Trimethylbenzene	7.7	15.7	0	0	0	0
Carbon disulfide	1.7	9.2	0	7.8	7.8	6.2
Chloroform	2.6	³ 19.7	0	0	0	0
Dichloromethane	3.3	9.2	0	0	0	0
Acetone	6.0	11.5	0	0	0	0
2-Butanone	.5	³ 5.6	0	0	0	0
Tetrahydrofuran	.7	6.6	0	0	0	0

¹The number of analyses was 417.

²The number of analyses was 568.

³The number of analyses was 574.

⁴The number of analyses was 573.

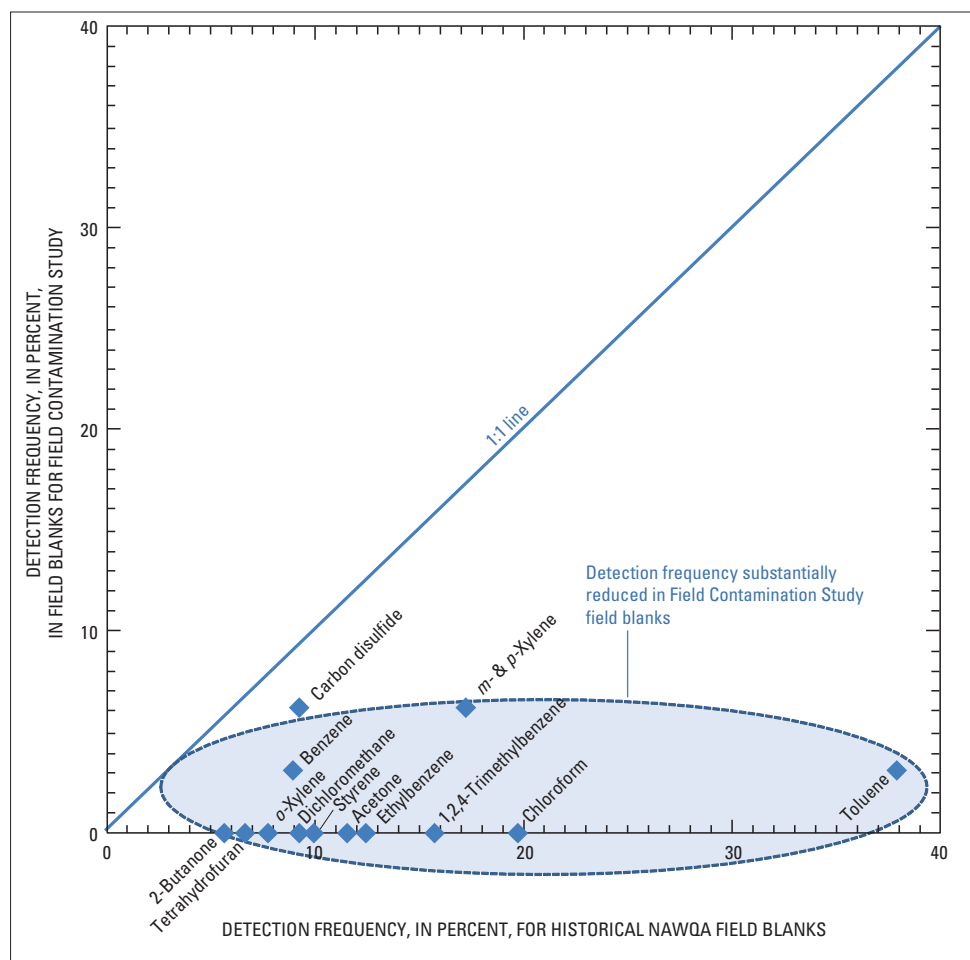
groundwater sample may be because of contamination of the equipment or supplies or attributed to sampling procedures used at this site. Carbon disulfide has been determined to be present on the types of disposable gloves worn by sampling personnel (Lisa Olsen, U.S. Geological Survey, written commun., September 22, 2010) and may be a potential source of contamination. If the quantified detections of carbon disulfide in blanks from sites MO1 and MO2 are not included with other FCS quantified data, then the compound was quantified in only one source-solution blank analysis and in two groundwater samples.

Comparison of Field Contamination Study Results to Historical Source-Solution Blanks and Field Blanks

Based on NWIS quantified data, the 32 FCS field-blank analyses had a substantially lower detection frequency for 12 of the 13 VOCs analyzed than did the more than 560 field blanks collected and analyzed by the NAWQA Program during 1996–2008 (table 7; fig. 9). Of special note, the detection frequency of toluene in field blanks was reduced from 37.9 percent in the historical NAWQA dataset to 3.1 percent in the FCS dataset. VOCs detected in 5 percent or more of the field blanks in the NAWQA dataset, but not detected in the FCS field-blank analyses, were ethylbenzene, *o*-xylene, styrene, 1,2,4-trimethylbenzene, chloroform, dichloromethane, acetone, 2-butanone, and tetrahydrofuran (table 7; fig. 9).

Most of the VOCs had low detection frequencies in source-solution blanks from the historical NAWQA dataset and the FCS dataset. In contrast, toluene was detected in only 3.1 percent of the FCS source-solution blank analyses compared to 29.7 percent in the historical NAWQA dataset. Styrene was not detected in any of the FCS source-solution blank analyses compared to 5.7 percent in the historical NAWQA dataset. Similarly, 1,2,4-trimethylbenzene was not detected in the FCS blanks, but had a detection frequency of 7.7 percent in the source-solution blanks in the historical NAWQA dataset.

Figure 9. Detection frequencies of selected volatile organic compounds in field-blank analyses from the Field Contamination Study and in historical National Water-Quality Assessment (NAWQA) field blanks (1996–2008).



The main exception to the improved FCS field-blank results was the detection of carbon disulfide in two analyses. If the quantified concentrations of carbon disulfide in analyses for blanks from sites MO1 and MO2 are not included in the FCS dataset, then the detection frequency of this VOC is 1.6 percent in source-solution blanks and 0 percent in field blanks, comparable to and lower than, respectively, those of the historical NAWQA dataset. The use of fresh supplies and careful attention to sampling procedures are most likely the cause for the reduction in quantified detections in the FCS field blanks and source-solution blanks compared to historical NAWQA field blanks and source-solution blanks.

Evaluation of Field Contamination Study Results Using Evidence-of-Presence Data for Volatile Organic Compounds

The VOCs with evidence of presence in FCS analyses, but not meeting all of the identification criteria necessary to quantify the results in NWIS, are described in this section. All of the VOCs analyzed, except styrene, chloroform, and dichloromethane, had evidence of presence in more than one sample type, including the source-solution analysis done at the NWQL (table 5; figs. A5–1 to A5–13 in the “Supplemental Information” section at the back of this report). The VOCs benzene, toluene, *m*- and *p*-xylene, carbon

disulfide, acetone, and 2-butanone had much larger detection frequencies of evidence of presence than of quantified detections in the FCS source-solution and field-blank analyses. Evidence of these VOCs at low levels near or less than the LT-MDL may indicate a contamination problem that could affect future datasets if method detection levels were to be lowered.

Possible sources of VOCs with evidence of presence in FCS analyses are listed in table 6. Two important observations are evident from the evidence-of-presence data. First, it appears that many of the selected VOCs in the FCS study are added to the VPBW during shipment from the NWQL to WSCs (column 2 in table 6). After nitrogen purge at the NWQL, bottles of VPBW are enclosed with a tightened screw cap. While this technique appears adequate for analyses reported to NWIS, it may be prudent to develop a better sealing procedure for VPBW bottles. Second, and with the exception of 2-butanone, there is little or no evidence of extrinsic contamination during shipment of VOC samples from WSCs to the NWQL (last column in table 6). This latter observation is consistent with the better sealing of VOC vials with Teflon[®]-faced silicone septa in comparison to sealing with a tightened screw cap on the bottles of VPBW. Possible sources for selected individual VOCs are described further in this section of the report.

Gasoline Hydrocarbons

The VOCs benzene, toluene, ethylbenzene, *m*- and *p*-xylene, *o*-xylene, styrene, and 1,2,4-trimethylbenzene are all hydrocarbons (petroleum products) and most are used in solvents, cleaners, or paints. Benzene (B), toluene (T), ethylbenzene (E), *m*- and *p*-xylene (X), and *o*-xylene (X) are commonly referred to together as BTEX because of their toxicity and large percent volumes in gasoline. Although all five BTEX compounds or compound pairs had evidence of presence individually or together, low-level contamination especially during shipment from the NWQL to the field (table 6) or possibly from the field processing is thought to be a potential source of these compounds in FCS samples.

Benzene

For the FCS, benzene had evidence of presence in 12 percent of the source-solution analyses done at the NWQL, 16 percent of the source-solution blank analyses, 27 percent of the field-purged source-solution blank analyses, 28 percent of the field-blank analyses, and 12 percent of the groundwater samples (table 5; fig. A5–1). Results from the Colorado field-purge experiment described in the “Field Purge of the Volatile Pesticide-Grade Blank Water” section indicated that benzene was not evident in the spiked sample after the field purge, and therefore, that benzene was completely removed by this pilot purging test. In the FCS, benzene had evidence of presence in several of the vials analyzed for the field-purged source-solution blanks (sample 3) and field blanks (sample 4)

collected at five sites. All six of the vials analyzed for the field-purged source-solution blanks and the field blank collected at site LA2 had evidence of benzene (table A1) at concentrations that were about 0.7 times the LT-MDL of 0.008 µg/L and about 3 times the evidence-of-presence concentration in the groundwater sample. The native-water rinse may have removed some of the possible benzene contamination from the sampling equipment before collection of the groundwater sample and the evidence of benzene probably is the result of equipment contamination and not of actual presence in the groundwater. The only other groundwater sample with evidence of benzene was from the supply well in Utah (site UT1). None of the blank analyses from this site had any evidence of presence of benzene. Furthermore, the groundwater sample also had a quantified detection of toluene, leading to the conclusion that benzene likely is present in the groundwater from this site at low concentrations. In addition to site LA2, sites LA1, NM1, OH1, and TX2 had evidence of presence of benzene in one or more field-purged source-solution blanks and field-blank analyses. The native-water rinse could have removed the low-level contamination from the sampling equipment before collection of the groundwater samples at these sites. The possibility also exists that some of the vials collected at these four sites with evidence of presence of benzene could have been contaminated during shipment from the NWQL to the field or back, although it is not clear why all of the VOC vials in the shipment were not affected.

Toluene

The compound toluene had a relatively high frequency of evidence of presence in the FCS analyses (table 5; fig. A5–2), despite the use of field-purged VPBW and other efforts to reduce contamination. Sixty-one of 160 analyses of field source-solution blanks, field-purge source-solution blanks, and field blanks (38 percent) had some evidence of presence, which indicates that toluene likely has a low-level contamination source. By comparison, only 3 of 160 analyses of FCS field source-solution blanks, field-purge source-solution blanks, and field blanks (1.9 percent) had quantified detections of toluene reported to the NWIS database. Although most of the evidence-of-presence concentrations are a fraction of the LT-MDL of 0.009 µg/L, a few are near or greater than the LT-MDL (fig. A5–2, top panel). Toluene even had evidence of presence at concentrations near or less than the LT-MDL in 3 of the 16 source-solution analyses done at the NWQL (19 percent) and in 4 groundwater samples (25 percent) at concentrations less than the LT-MDL.

Results from the Colorado field-purge experiment indicated that there was no evidence of toluene in the spiked sample after the pilot purging test, and therefore, the compound was completely removed by the purging process. All of the sample vials collected at site ID2 and all sample vials except for the groundwater sample at site NM1 had evidence of toluene at concentrations less than the LT-MDL. Based on the Colorado field-purge experiment, it is inferred

that any toluene present in the VPBW would likely have been purged away. Samples from these two sites may have been contaminated during shipment from the field to the NWQL.

Five sites had evidence of toluene in one or both field-blank analyses, but not in a field-purged source-solution blank analysis (sites AL2, FL1, ID1, TX1, and TX2; table 6). Evidence of toluene in these field-blank analyses possibly was introduced during the field-blank sample-collection process. All four of the sites that had evidence of presence in the groundwater sample also had evidence of toluene or a quantified detection in a field-blank analysis (sites AL2, ID1, ID2, and TX2; table 6). For each of these four sites, the evidence-of-presence concentration in the groundwater sample was less than the concentration in one or both field-blank analyses. Both field-blank analyses for site TX2 had similar concentrations of toluene, one quantified and one with evidence of presence, which were about four times higher than the evidence-of-presence concentration in the groundwater sample. The native-water rinse likely removed some of the toluene contamination from the sampling equipment before collection of the groundwater samples that had a corresponding field blank with evidence of toluene.

Toluene was quantified in one groundwater sample (site UT1) at an estimated concentration of 0.02 µg/L, almost an order of magnitude larger than the evidence-of-presence concentration in the four vials analyzed for the source-solution blank and in one vial analyzed for the field-purged source-solution blank collected from the site. The compound had no evidence of presence in the field blank preceding the groundwater sample, indicating that its quantified detection in the groundwater sample likely was not because of contamination during sampling.

Ethylbenzene and Xylenes

The other gasoline hydrocarbons in the BTEX group, ethylbenzene, *m*- and *p*-xylene, and *o*-xylene, also had some evidence of presence in FCS samples (table 5; figs. A5–3, A5–4, and A5–5, respectively). One to two of the source-solution blank analyses for site AL1 had evidence of *m*- and *p*-xylene and *o*-xylene and two analyses had quantified detections of ethylbenzene, but subsequently collected sample types did not have any evidence of presence of these compounds. This may be the result of the field purge with VPBW. Results from the Colorado field-purge experiment indicated that there was no evidence of ethylbenzene, *m*- and *p*-xylene, or *o*-xylene in the spiked sample after the field purge, and therefore, these compounds were completely removed by the pilot purging test.

Ethylbenzene, *m*- and *p*-xylene, and *o*-xylene had evidence of presence (and were quantified in the case of *m*- and *p*-xylene) in both field-blank analyses, but not in the other analyses for site OH1 (table A1). The compounds *m*- and *p*-xylene and *o*-xylene also had evidence of presence in field-blank analyses for sites NM1 and OH2. Several analyses associated with site MO2 had evidence of *m*- and

p-xylene, including the source-solution analysis done at the NWQL, a source-solution blank (vial 3 of sample 2B), a field-purged source-solution blank (vial 3 of sample 3B), and the field blank (vial 3). The cause of these scattered evidence-of-presence results is not known. The only evidence of *m*- and *p*-xylene in an FCS groundwater sample was from site TX2 at a concentration less than 0.1 times the LT-MDL of 0.04 µg/L. The compound also was evident in vial 2 of the field blank collected at site TX2, at about twice the concentration in the groundwater sample indicating that there may be contamination of the sampling equipment and that the evidence of *m*- and *p*-xylene in the groundwater sample may not be representative of its actual presence in the groundwater (table 6).

1,2,4-Trimethylbenzene

The VOC 1,2,4-trimethylbenzene was detected in 15.7 percent of the historical NAWQA field blanks, but not in any of the FCS analyses at quantified concentrations (table 7). It had evidence of presence in 12 percent of the source-solution analyses conducted at the NWQL and in 4.7 percent of the field source-solution blank analyses for the FCS (table 5; fig. A5–7). This relatively infrequent evidence of presence in five analyses associated with four sites at concentrations about 0.2 to 0.6 times the LT-MDL of 0.02 µg/L indicates that 1,2,4-trimethylbenzene could have been introduced at the laboratory or during transport from the laboratory to the field and that it was likely removed during the VPBW field purge.

Carbon Disulfide and Chloroform

Carbon disulfide and chloroform are VOCs that are naturally and anthropogenically produced. Both compounds are used in organic synthesis and as solvents, whereas chloroform also can be formed as a chlorination by-product.

Carbon Disulfide

Carbon disulfide had evidence of presence in 9.4 percent of the source-solution blank analyses, 22 percent of the field-purged source-solution blank analyses, 9.4 percent of the field-blank analyses, and 19 percent of the groundwater samples collected for this study (table 5; fig. A5–8). Evidence-of-presence concentrations of carbon disulfide ranged from about 0.1 to 0.9 times the LT-MDL of 0.02 µg/L. Historically, carbon disulfide was quantified in only 1.7 percent of NAWQA source-solution blanks and 9.2 percent of NAWQA field blanks. Both quantified concentrations of carbon disulfide in FCS groundwater samples are from sites FL1 and FL2. Carbon disulfide had evidence of presence in 3 of 4 source-solution blank analyses, 4 of 4 field-purged source-solution blank analyses, and 1 of 2 field-blank analyses collected at site FL1. Evidence-of-presence concentrations in these analyses were about 20 times smaller than the concentration in the subsequent groundwater sample. Carbon disulfide had evidence of presence in one

field-purged source-solution blank collected at site FL2 at a concentration about 10 times smaller than in the groundwater sample. Based on the evidence-of-presence information, the quantified concentrations of carbon disulfide in the groundwater samples from sites FL1 and FL2 most likely are not affected by low-level contamination.

Carbon disulfide was quantified in one field-purged source-solution blank analysis from site MO2 and had evidence of presence in the other three field-purged source-solution blank analyses and in both field-blank analyses at levels from 0.5 to 0.9 times the LT-MDL. Possible contamination from carbon disulfide at this site may be related to the quantified concentrations measured in all of the source-solution and field-blank analyses from site MO1 (see “Quantified Analytical Results Stored in the National Water Information System Database” section of the report).

Chloroform

Chloroform was not quantified and did not have evidence of presence in any of the 176 FCS blank analyses. The field-blank detection frequency of chloroform was markedly reduced in the FCS in comparison to the historical NAWQA field blanks of 19.7 percent of 574 samples (see table 7). Chloroform was quantified in five groundwater samples and had evidence of presence in one groundwater sample at a concentration less than the LT-MDL of 0.02 µg/L (fig. A5–9). Use of the prescribed volumes of “chloroform-free VPBW” in the cleaning procedure and in the collection of blanks probably explains the lack of evidence of presence of chloroform in the FCS field-blank analyses.

Acetone and 2-Butanone

Acetone, 2-butanone, and sometimes tetrahydrofuran, commonly are found together as co-contaminants in water samples, possibly from their similar use or presence in solvents, including methanol (Guella and others, 2007), glues, and PVC cement, or from their similarities in chemical properties, including the ease with which they tend to partition into water or methanol (U.S. Department of Health and Human Services, 1992, 1994). Acetone and 2-butanone were detected in 11.5 and 5.6 percent, respectively, of field blanks in the historical NAWQA dataset (table 7), possibly because of insufficient rinsing with VPBW to remove residual methanol during the cleaning process.

Acetone

Acetone was not quantified in any of the FCS analyses, but had evidence of presence in 6.2 percent of the source-solution blank analyses, 23 percent of the field-purged source-solution blank analyses, and in 19 percent of the field-blank analyses (table 5; fig. A5–11). Acetone had no evidence of presence in the source-solution analyses done at the NWQL or in the groundwater samples. Results from the Colorado field-purge experiment indicated that acetone was detected after the

field purge at about 0.6 times the spiked concentration and, therefore, the compound was only partially removed from the sample by purging with nitrogen gas. Four sites had evidence of acetone in field-purged source-solution blank analyses (sample type 3), but not in analyses of source-solution blanks (sample type 2) collected before the field purge (table 6). Evidence of presence in the source-solution blank analyses of VPBW that had been field purged may indicate that the acetone was introduced during this process from the nitrogen-gas cylinders, valves, fittings, or the nitrogen gas itself.

Acetone was evident at concentrations about 0.3 times the LT-MDL of 2.0 µg/L in all 4 of the field-purged source-solution blank analyses for site FL2 and in 3 out of 4 field-purged source-solution blank analyses for sites OH1 and OH2. Both of the field-blank analyses for site FL2 and one field-blank analysis from each of sites OH1 and OH2 had evidence of acetone at slightly lower concentrations than in the field-purged source-solution blank analyses. The field-purged VPBW was used to collect the field blanks and may be a source of contamination to these samples. Again, the lack of evidence of presence of acetone in the groundwater samples may be the result of the native water rinsing reducing the contamination evident in the field blanks.

2-Butanone

The VOC 2-butanone was not quantified and indicated no evidence of presence in any of the source-solution analyses done at the NWQL, but had frequent evidence of presence results in FCS source-solution blank analyses (25 percent), field-purged source-solution blank analyses (30 percent), field-blank analyses (34 percent), and groundwater samples (25 percent) (table 5; fig. A5–12). Evidence-of-presence concentrations mostly ranged from about 0.1 to 0.5 times the LT-MDL of 0.8 µg/L. The VOC 2-butanone is used in PVC cement, glues, paints, coatings, and as a cleaning agent (U.S. Department of Health and Human Services, 2009); it also is released to the air from car and truck exhaust (U.S. Department of Health and Human Services, 1992). The VOC 2-butanone also is an impurity in methanol (Guella and others, 2007).

Results from the Colorado field-purge experiment indicated that 2-butanone was still present after the field purge at about 0.4 times the spiked concentration, and therefore, the compound was not completely removed by the pilot purging test. All six sites with evidence of presence in a source-solution blank analysis (FL1, ID1, ID2, LA1, LA2, and UT1) also had evidence of 2-butanone in more than one field-purged source-solution blank analysis (table 6), indicating that the field purge did not remove the compound from the VPBW. Only site FL2 had evidence of 2-butanone in at least one field-purged source-solution blank analysis (sample type 3), but not in a source-solution blank analysis (sample type 2).

Six of seven sites with evidence of presence for 2-butanone in at least one field-purged source-solution blank analysis (sample type 3) also had similar occurrence (table 6)

and concentrations (fig. A5–12) in at least one subsequent field-blank analysis (sample type 4). These six sites accounted for all of the evidence of presence in the field blanks. The four sites where 2-butanone had evidence of presence in the groundwater sample (FL1, ID1, ID2, and UT1) also had evidence of presence in an analysis from a source-solution blank, field-purged source-solution blank, and field blank (except for the field blank at site FL1) collected at the site (table A1). Evidence of presence for 2-butanone in the FCS field samples from a generally consistent group of sites indicates a possible low-level background concentration associated with the shipment of VPBW from the NWQL to the field (resulting in contamination of the sampling equipment), field processing, shipment of the samples from the field to the NWQL, or combinations of these potential contamination sources.

The VOC 2-butanone is a potential contaminant in methanol used to clean the sampling equipment. The methanol used in the FCS is not a likely source of contamination because the source-solution blanks, which do not come in contact with the sampling equipment, also had evidence of 2-butanone. The similarity in the frequency of evidence of presence for 2-butanone in each type of field sample indicates that it may have entered the samples from either the sample vials or acid used for sample preservation. However, the NWQL uses the same vials and acid that were used in the field for their laboratory blanks. Because 2-butanone was not detected in the source-solution blank analyses done at the NWQL, these supplies likely were not contaminated before they were shipped to the field.

Wastewater-Indicator Compounds

A total of 112 WIC samples were analyzed by the NWQL for the FCS (table 8), including 17 source-solution analyses collected at the NWQL (sample 1), 31 source-solution blanks (samples 2A and 2B), 32 field-purged source-solution blanks (samples 3A and 3B), 16 field blanks (sample 4), and 16 groundwater samples (sample 5). A source-solution blank analysis done at the NWQL was available for a site in New Mexico that ultimately was not sampled, and one source-solution sample bottle collected at site OH1 was broken during shipment. Quantified and evidence-of-presence concentrations for the FCS samples and the percent of analyses with a WIC not detected, identified with evidence of presence, and quantified are shown in figures A6–1 to A6–11 in the “Supplemental Information” section at the back of this report.

Quantified Analytical Results Stored in the National Water Information System Database

Concentrations of WICs that met the rigorous identification criteria to be quantified and stored in the NWIS database are described in this section. Twelve of 15 WICs were not detected at quantified concentrations in any of

the samples collected for the FCS (AHTN, benzophenone, caffeine, HHCb, menthol, methyl salicylate, 4-nonylphenol (total, branched), tributyl phosphate, triphenyl phosphate, isophorone, naphthalene, and phenanthrene; table 8). Only camphor, DEET, and phenol were detected at quantified concentrations in the FCS samples. None of the 15 WICs included in this study were present at quantified concentrations in the source-solution analyses done at the NWQL (sample 1). Possible sources of WICs quantified in FCS analyses are listed in table 9 and are described in this section of the report.

Camphor is used in some cough suppressants and topical analgesics (Hazardous Substances Data Bank, 2005; U.S. Department of Health and Human Services, 2009) and its detection in some samples may be attributed to use of such products by sampling personnel. Camphor was quantified in a source-solution blank (sample 2A) collected at site OH2 at a concentration less than the LT-MDL of 0.03 µg/L (fig. A6–3), but not in other samples collected at the site.

Phenol is used in disinfectants and medicinal applications (including ointments, lozenges, cold sore lotions, antiseptic lotions, and lip balms), naturally occurs in petroleum, and can be present in decomposing animal and plant waste (Hazardous Substances Data Bank, 2005; U.S. Department of Health and Human Services, 2009). Phenol was quantified in a source-solution blank (sample 2A) and a field-purged source-solution blank (sample 3A) collected at site MO1 at concentrations about 0.3 times less than the LT-MDL of 0.7 µg/L (fig. A6–7), but it was not detected in other samples from the site. Phenol also was detected in the field blank collected from site MO2; DEET, a compound used in insect repellents, was detected in the groundwater sample from this site at a concentration almost 2 times greater than its LT-MDL of 0.07 µg/L (fig. A6–4). That 4 of the 5 quantified concentrations of WICs in the FCS were from sites MO1 and MO2 may indicate a unique source of contamination associated with sampling equipment, personnel, or conditions at these sites.

With respect to sources of DEET contamination, an experiment at the NWQL in 2004 demonstrated the potential for sample contamination when DEET was worn by field personnel collecting and filtering samples (Mark Sandstrom, U.S. Geological Survey, written commun., May 25, 2004). In this experiment, all water samples collected and filtered by field crews that used insect repellent containing DEET were contaminated with DEET with concentrations between 0.2 and 0.3 µg/L, whereas samples processed by crews that did not use DEET were not contaminated.

Comparison of Field Contamination Study Results to Historical Field Blanks

The 15 WICs analyzed as part of the FCS were selected primarily because of detections in field blanks collected during 2002–08 as part of groundwater sampling for the NAWQA Program. Based on historical NAWQA data, eight of the WICs (benzophenone, caffeine, DEET, 4-nonylphenol

Table 8. Detection frequency of wastewater-indicator compounds (WICs) in Field Contamination Study analyses having quantified results stored in the National Water Information System (NWIS) database and for results of analyses having only evidence of presence reported exclusively to study investigators.

[NWQL, U.S. Geological Survey National Water Quality Laboratory; VPBW, volatile pesticide-grade blank water; N, number of analyses]

Wastewater-indicator compound (ordered by use group, see table 2)	Detection frequency, in percent, of WICs stored in NWIS and <i>as having evidence of presence only</i>									
	NWQL-purged VPBW		NWQL-purged VPBW		Field-purged VPBW		Field-purged VPBW		Groundwater	
	N = 17 Sample 1		N = 31 Samples 2A & 2B		N = 32 Samples 3A & 3B		N = 16 Sample 4		N = 16 Sample 5	
	Source-solution analysis at NWQL		Source-solution blank		Source-solution blank		Field blank		Groundwater sample	
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	0	0	0	0	0	0	0	0	0	0
Benzophenone	0	5.9	0	0	0	0	0	25	0	6.2
Caffeine	0	5.9	0	6.4	0	3.1	0	6.2	0	0
Camphor	0	0	3.2	0	0	3.1	0	6.2	0	0
<i>N,N</i> -Diethyl- <i>meta</i> -toluamide (DEET)	0	0	0	0	0	0	0	25	6.2	19
Hexahydrohexamethyl- cyclopentabenzopyran (HHCB)	0	0	0	0	0	0	0	0	0	0
Menthol	0	0	0	0	0	0	0	0	0	0
Methyl salicylate	0	0	0	6.4	0	3.1	0	6.2	0	0
4-Nonylphenol (total, branched)	0	12	0	0	0	9.4	0	12	0	6.2
Phenol	0	0	3.2	0	0	9.4	3.1	12	0	6.2
Tributyl phosphate	0	0	0	6.4	0	3.1	0	6.2	0	6.2
Triphenyl phosphate	0	0	0	0	0	3.1	0	31	0	0
Isophorone	0	0	0	0	0	0	0	6.2	0	0
Naphthalene	0	0	0	0	0	0	0	0	0	0
Phenanthrene	0	0	0	3.2	0	16	0	19	0	6.2

(total, branched), phenol, triphenyl phosphate, isophorone, and phenanthrene) were detected in more than 5 percent of the historical field blanks (table 10; fig. 10). Only three WICs (benzophenone, 4-nonylphenol (total, branched), and phenol) were detected in more than 5 percent of the historical source-solution blanks. None of the WICs analyzed in the FCS field blanks were detected, except for phenol in one sample. The detection frequencies of phenol in historical source-solution and field blanks (70 and 64 percent, respectively) were much higher than the detection frequency of about 3 percent in the FCS source-solution and field blanks. The detection frequencies of benzophenone and DEET in field blanks also were substantially lower in the FCS dataset (no detections) compared to the historical NAWQA dataset (about 29 and 36 percent, respectively). Camphor was not detected in historical source-solution blanks, but was detected in one FCS source-solution blank.

The use of new supplies and careful attention to sampling procedures are most likely the cause for the reduction in quantified detections of WICs in the FCS field blanks compared to historical NAWQA field blanks. The lower detection frequencies of selected WICs in the FCS field blanks compared to historical NAWQA field blanks indicate that carefully following sampling protocols will result in less contamination in blanks and groundwater samples.

Evaluation of Field Contamination Study Results Using Evidence-of-Presence Data for Wastewater-Indicator Compounds

The WICs not meeting all of the identification criteria, but with evidence of presence in the FCS samples are described in this section. Benzophenone, caffeine, camphor,

Table 9. Possible sources of wastewater-indicator compounds detected in sample types at sites sampled for the Field Contamination Study.

[Analyses with quantified detections (reported to the National Water Information System) are **bolded, italicized**; all other analyses were determined to have evidence of presence (indicated by red font, some but not all identification criteria were met). Site names are listed in table 3. See “Sample Types” section of report for a more detailed explanation of the samples collected for the Field Contamination Study. VPBW, volatile pesticide-grade blank water; NWQL, U.S. Geological Survey National Water Quality Laboratory; WSC, Water Science Center; --, not applicable]

Wastewater-indicator compound	Compound in sample type 2, but not in sample type 1		Compound in sample type 3, but not in sample type 2		Compound in sample types 3 and 4		Compound in sample type 4, but not in sample type 3		Compound in sample types 4 and 5		Compound in sample types 2, 3, 4, and 5	
	Site name and sample(s)	Number of sites	Site name and sample(s)	Number of sites	Site name	Number of sites	Site name	Number of sites	Site name	Number of sites	Site name	Number of sites
Benzophenone	--	0	--	0	--	0	AL1 NM1 OH2 UT1	4	--	0	--	0
Caffeine	LA2 (2A, 2B)	1	LA1 (3A)	1	--	0	MO2	1	--	0	--	0
Camphor	OH2 (2A)	1	--	0	--	0	TX1	1	--	0	--	0
N,N-diethyl- <i>meta</i> -toluamide (DEET)	--	0	--	0	--	0	LA1 MO2 TX1 TX2	4	MO2 TX2	2	--	0
Methyl salicylate	ID2 (2A, 2B)	1	--	0	--	0	OH2	1	--	0	--	0
4-Nonyphenol	--	0	ID2 (3A, 3B) OH2 (3B)	2	ID2	1	UT1	1	ID2	1	--	0
Phenol	MO1 (2A)	1	NM1 (3A) OH2 (3A) UT1 (3A)	3	NM1 OH2	2	MO2	1	MO2	1	--	0
Tributyl phosphate	MO1 (2B) MO2 (2A)	2	--	0	MO1	1	--	0	--	0	--	0
Triphenyl phosphate	--	0	TX1 (3B)	1	--	0	LA1 MO2 OH1 OH2 TX2	5	--	0	--	0
Isophorone	--	0	--	0	--	0	TX2	1	--	0	--	0
Phenanthrene	UT1 (2A)	1	AL1 (3A) FL2 (3B) LA1 (3A) LA2 (3A)	4	AL1 LA1 UT1	3	--	0	--	0	--	0

¹Sample type 5 had a quantified concentration, but sample type 4 had evidence of presence.

Table 10. Detection frequency of selected wastewater-indicator compounds stored in the National Water Information System (NWIS) database for historical source-solution and field blanks collected during 2002–08 for groundwater sampling and for blank analyses for the Field Contamination Study.

[NAWQA, National Water-Quality Assessment; PGBW, pesticide-grade blank water; NWQL, U.S. Geological Survey National Water Quality Laboratory; VPBW, volatile pesticide-grade blank water; N, number of analyses (except where footnoted)]

Wastewater-indicator compound (ordered by use group, see table 2)	Detection frequency, in percent					
	2002–08 NAWQA groundwater sampling		Field Contamination Study			
	PGBW or NWQL-purged VPBW		NWQL-purged VPBW	NWQL-purged VPBW	Field-purged VPBW	Field-purged VPBW
	N = 24	N = 28	N = 17	N = 31	N = 32	N = 16
	Source-solution blank	Field blank	Source-solution analysis at NWQL	Source-solution blank	Source-solution blank	Field blank
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	0	0	0	0	0	0
Benzophenone	8.3	28.6	0	0	0	0
Caffeine	0	7.1	0	0	0	0
Camphor	0	3.6	0	3.2	0	0
<i>N,N</i> -Diethyl- <i>meta</i> -toluamide (DEET)	0	35.7	0	0	0	0
Hexahydrohexamethylcyclopenta-benzopyran (HHCB)	0	0	0	0	0	0
Menthol	0	3.6	0	0	0	0
Methyl salicylate	0	3.6	0	0	0	0
4-Nonylphenol (total, branched)	12.5	10.7	0	0	0	0
Phenol	¹ 70	² 64	0	3.2	3.2	3.1
Tributyl phosphate	0	3.6	0	0	0	0
Triphenyl phosphate	0	7.1	0	0	0	0
Isophorone	4.2	7.1	0	0	0	0
Naphthalene	0	0	0	0	0	0
Phenanthrene	0	7.1	0	0	0	0

¹The number of analyses was 20.

²The number of analyses was 25.

DEET, methyl salicylate, 4-nonylphenol (total, branched), phenol, tributyl phosphate, triphenyl phosphate, and phenanthrene had evidence of presence in more than one FCS sample (table 8), including the source-solution analyses done at the NWQL, with the number of samples having evidence of presence or quantified concentrations ranging from 3 (camphor) to 10 (phenanthrene). The compounds AHTN, HHCB, menthol, and naphthalene had no evidence of presence in any of the FCS samples, whereas isophorone had evidence of presence in only one field blank.

Possible sources for 11 of the WICs included in the FCS, based primarily on evidence of presence data, are listed in table 9 and indicate two salient patterns among some of

the compounds. First, benzophenone, DEET, and triphenyl phosphate all had evidence of presence in field blanks (sample 4) but not in the field-purged source solution blanks (samples 3A and 3B) indicating that these compounds possibly were introduced during the field-blank sample-collection process. This process includes, in part, potential contamination during the cleaning of the equipment, as well as the collection of the field blank.

Second, evidence of presence data for 4-nonylphenol, phenol, and phenanthrene indicate that these three compounds may have been added to the VPBW during the 2-hour field purge, which may be the likely source of these compounds in subsequently collected field blanks. Because the field purge

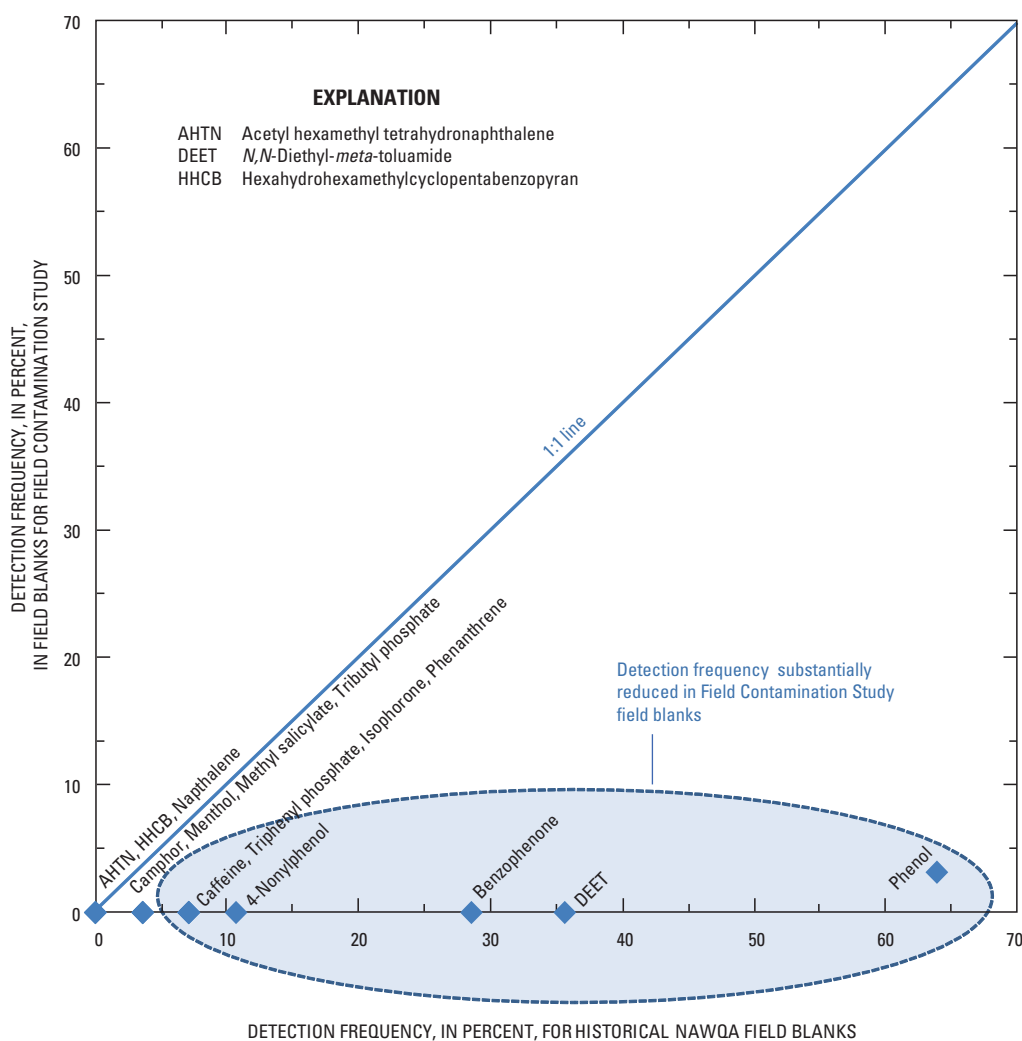


Figure 10. Detection frequencies of selected wastewater-indicator compounds in field blanks collected for the Field Contamination Study and in historical NAWQA field blanks (2002–08).

was a unique aspect of the FCS and not a part of routine field protocols, this source of contamination would not be applicable for NAWQA’s historical source-solution blank and field blank dataset. Possible sources for selected individual WICs are described further in the following sections of the report.

Benzophenone

Benzophenone, a compound used in soaps, perfumes, lotions, hair mousse, sunscreens, and inks (Hazardous Substances Data Bank, 2005; U.S. Department of Health and Human Services, 2009), had evidence of presence in 4 of 16 field blanks at concentrations that ranged from about 0.2 to 1.1 times the LT-MDL of 0.06 µg/L (fig. A6–1). Evidence of benzophenone in field blanks from these sites, but not in the source-solution blanks, indicates that the compound possibly was introduced during the field-blank sample-collection process. Benzophenone also had evidence of presence in one source-solution analysis done at the NWQL and in one groundwater

sample. The final criteria set for this study to determine if a compound has evidence of presence in a sample is that the concentration has to be twice the concentration in the associated laboratory set blank. Many of the FCS samples had concentrations of benzophenone that were not two times the concentration in the associated laboratory set blank (about 0.1 times the LT-MDL), which may indicate a low-level source of benzophenone contamination of unknown origins, such as in solutions or equipment used at the laboratory. Trace levels of benzophenone have been identified in the dechlorination reagent used when collecting samples of chlorinated water (Sandstrom and Delzer, 2007), but the reagent was not used in the FCS.

Caffeine

Caffeine, a compound present in some foods and drinks (Hazardous Substances Data Bank, 2005), had evidence of presence in four blanks associated with sites LA1 and LA2 (table A1) at concentrations about 0.2 times the LT-MDL of

0.05 µg/L (fig. A6–2). Both source-solution blanks (samples 2A and 2B) collected at site LA2 had similar concentrations of evidence of presence. A field blank collected at site MO2 had evidence of caffeine at a level about 0.8 times the LT-MDL. A possible source of caffeine in the blanks could be the sampling personnel, if they consumed food or drinks containing caffeine before sampling.

Camphor

Camphor, a compound used as an odorant, flavorant, and preservative (Hazardous Substances Data Bank, 2005), had evidence of presence in two FCS samples (fig. A6–3) at concentrations about 0.3 times the LT-MDL of 0.03 µg/L. Camphor had evidence of presence in a field-purged source-solution blank (sample 3A) collected at site OH2 at a concentration similar to the quantified concentration in a source-solution blank. Camphor also had evidence of presence in the field blank collected at site TX1, but not in the source-solution blanks indicating that camphor possibly was introduced during the field-blank sample-collection process.

N,N-Diethyl-*Meta*-Toluamide

Seven FCS samples (4 field blanks and 3 groundwater samples) had evidence of presence of *N,N*-diethyl-*meta*-toluamide (DEET) (fig. A6–4), an insect repellent (Hazardous Substances Data Bank, 2005), at concentrations about 0.1 to 0.8 times the LT-MDL of 0.07 µg/L. Evidence of DEET in field blanks, but not in the source-solution blanks, indicates that the compound possibly was introduced during the field-blank sample-collection process. The field blank collected at site MO2 had evidence of presence at a concentration that was about 0.4 times the quantified concentration in the associated groundwater sample. Because groundwater was pumped through the sampling equipment before collection of the field blank to condition the equipment, it is possible that the DEET was present in the groundwater and that the cleaning procedure did not remove it all from the equipment before collection of the field blank. The groundwater sample from site FL1 had evidence of DEET at a concentration that was about 0.8 times the LT-MDL, but there was no other evidence of presence in any of the blanks from the site. Concentrations for the other five samples with evidence of presence of DEET are less than 0.2 times the LT-MDL, within the range of evidence-of-presence concentrations for other FCS laboratory set blanks, and therefore, may be related to low-level background contamination from an unknown source in solutions, equipment, or personnel at the laboratory.

Methyl Salicylate

Methyl salicylate is used in pain relieving creams and antiseptic mouthwash, and as mint flavoring in chewing gum and candy (U.S. Department of Health and Human Services, 2009). Methyl salicylate had evidence of presence in four FCS samples (fig. A6–5), three of which were source-solution

blanks (samples 2A, 2B, and 3A) collected at site ID2 (table A1). The field blank collected at site OH2 had presence of methyl salicylate at a concentration about 1.1 times the LT-MDL of 0.05 µg/L; the concentrations in two samples from site ID2 were about 0.3 times the LT-MDL. Use of products containing methyl salicylate by sampling personnel may explain its evidence of presence.

4-Nonylphenol

The WIC 4-nonylphenol (total, branched), a surfactant and nonionic detergent metabolite (U.S. Environmental Protection Agency, 1990), had evidence of presence in eight FCS samples (fig. A6–6). The compound had evidence-of-presence concentrations about 0.3 times the LT-MDL of 1 µg/L in the source-solution analyses done at the NWQL (associated with sites ID2 and FL1), and in the field blank from site UT1. The other five FCS samples with evidence of 4-nonylphenol (total, branched), four of which were collected at site ID2, had concentrations about 0.15 times the LT-MDL. Because evidence of presence was observed in the samples collected using field-purged VPBW (samples 3A, 3B, and 4) and in the groundwater sample (sample 5), but not in either of the source-solution blanks (samples 2A and 2B) at site ID2 (table A1), it is likely that the 4-nonylphenol (total, branched) did not carryover from the NWQL-purged VPBW and it may have entered the blank water as part of the field purging process. Also, these lower concentrations are in the range of those estimated for laboratory set blanks for other sample sets in the study (about 0.1 to 0.2 times the LT-MDL) and may indicate an unknown source of low-level contamination in solutions or equipment used at the laboratory.

Phenol

Phenol had evidence of presence in six FCS samples collected after the VPBW field purge (samples 3A, 4, and 5; table A1) at concentrations as low as an order of magnitude smaller than its LT-MDL of 0.7 µg/L (fig. A6–7). The groundwater sample from site MO2 had an evidence-of-presence concentration of phenol that was about the same as the quantified concentration in the preceding field blank, possibly indicating that the groundwater sample was contaminated by the sampling equipment (table 9). The field-purged source-solution blanks (sample 3A) and the field blanks collected at sites NM1 and OH2 had similar concentrations of phenol, although there was no evidence of presence in the other field-purged source-solution blank (sample 3B) from either site. Phenol was possibly introduced to the VPBW during the field purge, and the VPBW may be the source of contamination evident in the field blanks from sites NM1 and OH2 (table 9).

Tributyl Phosphate

Tributyl phosphate is an antifoaming agent and plasticizer, and is used in hydraulic fluids and fire retardants

(Hazardous Substances Data Bank, 2005). Tributyl phosphate had evidence of presence in five FCS samples, four of which were blanks collected at sites MO1 and MO2 (table A1), at concentrations about 0.2 times the LT-MDL of 0.1 µg/L (fig. A6–8). This evidence of presence was not reproduced in the source-solution blanks at other sites and may be related to a unique source of contamination associated with these sites. A groundwater sample from site FL2 had evidence of tributyl phosphate at concentrations about 0.7 times the LT-MDL. Because tributyl phosphate was not evident in any of the blank samples that preceded the collection of the groundwater sample, its presence in the groundwater sample likely was not because of contamination during sampling.

Triphenyl Phosphate

Triphenyl phosphate is used as a plasticizer, in hydraulic fluids, and is added to some plastics as a fire retardant (Hazardous Substances Data Bank, 2005). Triphenyl phosphate had evidence of presence in five field blanks (sites LA1, MO2, OH1, OH2, and TX2) and in one field-purged source-solution blank (site TX1) (table A1) at concentrations ranging from about 0.2 to 0.5 times its LT-MDL of 0.06 µg/L (fig. A6–9). Evidence of triphenyl phosphate in field blanks from these sites, but not in the source-solution blanks, indicates that the compound was possibly introduced during the field-blank sample-collection process (table 9).

Phenanthrene

Phenanthrene, present in pavement- and combustion-derived compounds (Hazardous Substances Data Bank, 2005), had evidence of presence in 10 FCS samples (fig. A6–11), mostly at similar concentrations that were about 0.1 times the LT-MDL of 0.02 µg/L. Evidence of phenanthrene in a field-purged source-solution blank (sample 3), but not in a preceding source-solution blank (sample 2) from sites AL1, FL2, LA1, and LA2 indicates that the compound possibly was introduced to the VPBW during the field purge (table 9). Phenanthrene's presence was evident in a field-purged source-solution blank and in the field blank collected from sites AL1, LA1, and UT1 (table A1). The field-purged VPBW possibly is the source of phenanthrene evident in the associated field blank. Laboratory set blanks associated with seven of the FCS sites had evidence of phenanthrene at concentrations that bracketed all but one of the concentrations in the samples collected in the field. This may indicate an unknown source of low-level contamination in solutions or equipment used at the laboratory.

Case Study: "A Tale of Two Field Blanks"

During the FCS, an opportunity arose to compare the results of two field blanks. One of these field blanks was collected using fresh supplies and a sufficient volume of VPBW to remove all methanol during the final rinse before collection (the "Good Field Blank"); the other field blank was

collected after using methanol that was several years old for equipment cleaning and a volume of VPBW for the final rinse that was likely insufficient for removing the methanol (the "Bad Field Blank"). Both field blanks were collected during the same field trip by the same field crew, and both were shipped to the laboratory in the same manner, so their results are directly comparable. The results of these two field blanks illustrate the importance of using fresh supplies and using a sufficient volume of VPBW for a final rinse before sample collection. This comparison also illustrates the consequences of collecting field blanks that are not representative of potential sources of contamination to associated groundwater samples. Results for some compounds were omitted to simplify this comparison, and results that were determined to have been affected by extrinsic contamination were assigned the Data-Quality Indicator code of "Q" ("reviewed and rejected") in the NWIS database to prevent inadvertent misuse of the data.

Collection of the Good Field Blank

The Good Field Blank was collected in the manner that was described for all field blanks in the FCS. Protocols for equipment cleaning and sample collection were followed, as described in the "Field Methods" section of this report. The cleaning process used 2 liters of fresh methanol purchased immediately before the FCS sampling. The volumes of VPBW specified for the FCS study were used for the final rinse at the end of the cleaning process, for conditioning of the equipment, and collection of the field blank. The VPBW used for the final rinse and to collect the field blank was used within its 14-day holding time. After collection, the Good Field Blank was placed on ice and transported to the laboratory by overnight carrier in the usual manner.

Collection of the Bad Field Blank

The Bad Field Blank was not intentionally collected to be part of the FCS; it was collected for a different study that was conducted during the same period. As with the Good Field Blank, the equipment was cleaned before collection of the Bad Field Blank with the specified 2-liter volume of methanol; however, the methanol was not freshly purchased. This methanol previously had been opened and stored inside a flammables cabinet for several years alongside containers of gasoline, acetone, ethanol, 1-butanol, and other solvents, including some bottles with ground-glass stoppers. This bottle of methanol likely acted as a "sink" for contaminants through time during storage. It is possible that the proper volume of VPBW was not used for the final rinse after the methanol step of the cleaning process, or that the specified volume of VPBW was insufficient for removing gross contamination contributed by the old methanol, resulting in incomplete cleaning of the sampling equipment or incomplete rinsing of the residual methanol from the sampling equipment.

After collection, the Bad Field Blank was placed on ice and transported to the laboratory by overnight carrier in the usual manner.

Results from the Good Field Blank

The Good Field Blank had no detections of the VOCs (table 11) or WICs analyzed for the FCS. For the VOC analysis, the total ion chromatogram for the Good Field Blank was free of contaminants of interest, indicating the five labeled peaks that represent the two internal standards and three surrogate compounds added by the laboratory, with very little background noise (fig. 11B). The cleanliness of the Good Field Blank was not a result of luck—any field blank can be clean if potential sources of contaminants are systematically avoided. Rather, the Good Field Blank was clean despite following an equipment blank that indicated a substantial degree of contamination (table 11, fig. 11A) that was likely caused by the use of old methanol for cleaning and possible insufficient rinsing with VPBW. These data indicate that the combination of following the cleaning protocols and using fresh supplies, including fresh methanol, contributed to the quality of the Good Field Blank.

Results from the Bad Field Blank

The Bad Field Blank had detections of several VOCs on NWQL Schedule 2020 and 24 **tentatively identified compounds** (table 11). The total ion chromatogram indicated a substantial degree of contamination (fig. 11C). The Bad Field Blank and the groundwater sample collected afterwards were not analyzed for WICs because these samples were not collected for the FCS, but rather for a different study with different objectives.

The compounds detected in the Bad Field Blank commonly occur either in gasoline or in glues, paints, inks, lubricants, or other synthetic products that can be found in office and warehouse settings. These compounds were likely present in the methanol that had been stored in the flammables cabinet, as a result of cross-contamination from storage alongside containers of gasoline and solvents. Acetone and 2-butanone, two ketones that are miscible in methanol, had the highest concentrations (260 µg/L and 800 µg/L, respectively), followed by toluene (3.6 µg/L). Lower concentrations were observed for bromomethane, chloromethane, ethylbenzene, and the xylenes. It is hypothesized that contaminated methanol was not sufficiently rinsed from the equipment during the

Table 11. Concentrations of selected volatile organic compounds described in the “Tale of Two Field Blanks” case study.

[**Bolded** values denote detections. µg/L, micrograms per liter; <, less than; NA, not analyzed; E, estimated because of a higher degree of uncertainty than higher concentrations reported for the same compound]

Compound	Equipment blank collected before the Good Field Blank (µg/L)	Good Field Blank (µg/L)	Groundwater sample collected after the Good Field Blank (µg/L)	Bad Field Blank (µg/L)	Groundwater sample collected after the Bad Field Blank (µg/L)
Acetone	82	<4	<4	260	<4
2-Butanone	228	<1.6	<1.6	800	<1.6
Bromodichloromethane	<.04	NA	<.04	<.04	E.070
Bromomethane	<.4	NA	<.04	E.87	<.4
Chloromethane	<.14	NA	<.14	E.31	<.14
Chloroform	<.04	<.04	<.04	<.04	.237
Dibromochloromethane	<.12	NA	<.12	<.12	E.07
Dichloromethane	E.04	<.04	<.04	<.04	<.04
Ethylbenzene	<.04	<.04	<.04	E.063	<.04
Tetrahydrofuran	7.9	< 1.4	<1.4	¹ <21	<1.4
Toluene	.94	<.02	<.02	3.6	<.02
1,1,1-Trichloroethane	<.02	<.02	<.02	<.02	.219
<i>m</i> - and <i>p</i> -Xylene	E.02	<.08	<.08	E.10	<.08
<i>o</i> -Xylene	E.048	<.04	<.04	.186	<.04
Number of tentatively identified compounds	23	NA	0	24	0

¹Raised reporting limit because of 1:25 dilution for this analysis.

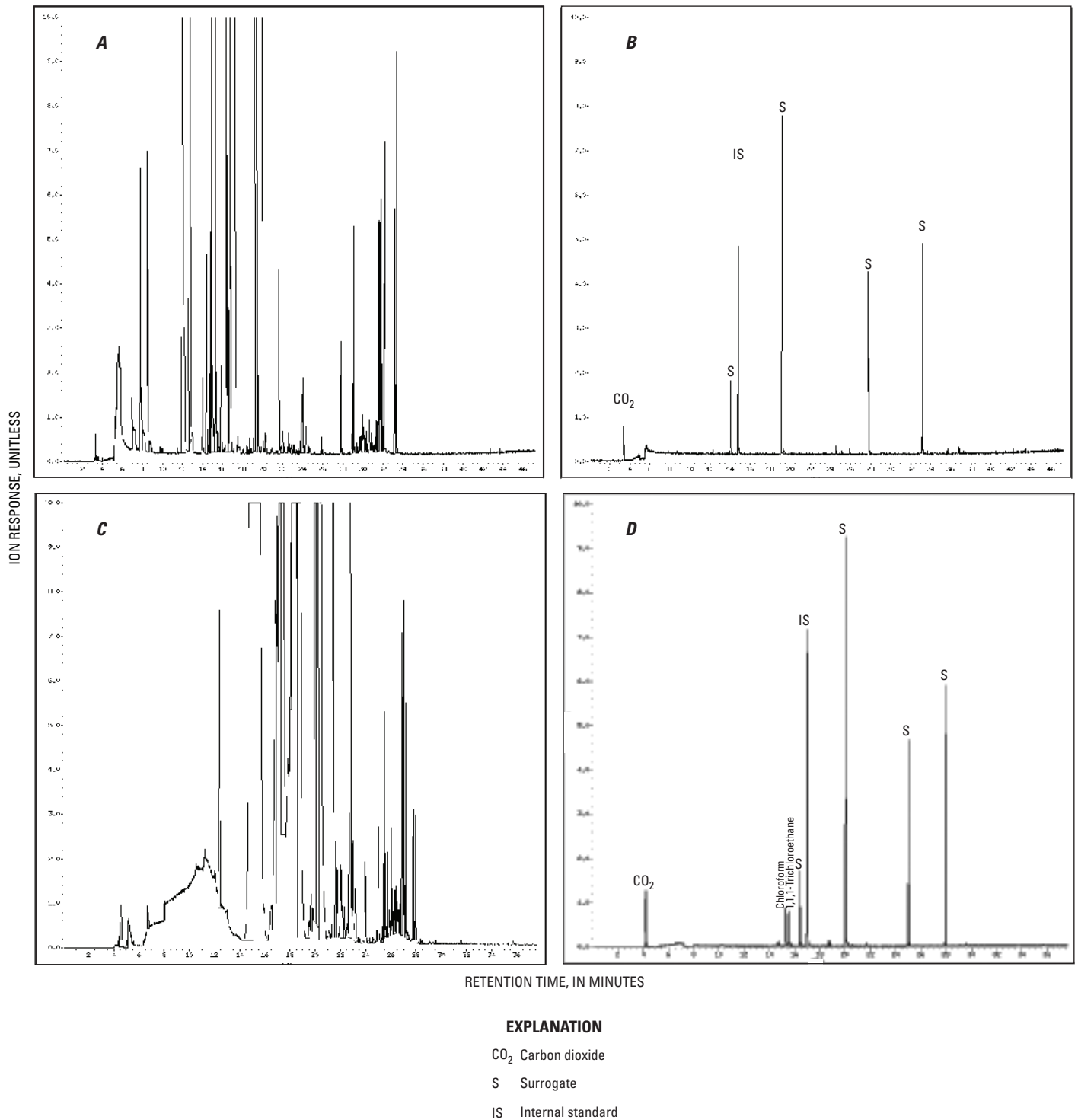


Figure 11. Total ion chromatograms from analyses of volatile organic compounds for *A*, the equipment blank collected before the Good Field Blank, *B*, the Good Field Blank, *C*, the Bad Field Blank, and *D*, the groundwater sample collected after the Bad Field Blank.

cleaning process, either as a result of inadvertently using a smaller volume of VPBW in the final rinse step or, more likely, because the contaminant concentrations were too high to be completely removed by the specified volume of VPBW. These factors also may have affected the equipment blank because it contained many of the same VOCs with lower concentrations than the Bad Field Blank.

The Bad Field Blank initially caught the attention of the Field QC Workgroup for Organics because it had the highest toluene concentration of the field blanks collected during water years 1997–2008 for the NAWQA Program. It was serendipitous that the Bad Field Blank was collected by a field crew that participated in the FCS and during the same field trip as the FCS, which allowed the comparison in this case study. After determining that the Bad Field Blank was collected after cleaning the equipment with methanol that was likely contaminated, the results of the previous and subsequent groundwater samples were considered to determine whether those data were affected by the same processes that had contaminated the Bad Field Blank. The groundwater sample collected after the Good Field Blank and before the Bad Field Blank had no detections of VOCs (table 11); this means the contamination in the Bad Field Blank could not have come from carryover from the previous sample. The groundwater sample collected after the Bad Field Blank (table 11, fig. 11D) had detections of different VOCs than were indicated in the Bad Field Blank, including three disinfection by-products (chloroform, bromodichloromethane, and dibromochloromethane) that could credibly co-occur in groundwater. The volume of native water that rinsed the equipment during well purging likely removed any contamination from residual methanol; however, if the subsequent groundwater sample had contained any of the compounds indicated in the Bad Field Blank, there would have been no way to tell whether those compounds had come from the groundwater being sampled or from residual methanol contamination. Because the Bad Field Blank was contaminated in a manner that did not affect the subsequent groundwater sample, and because the field crew confirmed the likely source of contamination, the Bad Field Blank results were considered “reviewed and rejected.” The groundwater sample was considered to be representative of the water sampled.

Consequences of Collecting Nonrepresentative Field Blanks

Although it is evident from the Good Field Blank (table 11) that it is possible for field crews to collect field blanks that are free from extrinsic contamination, it also is evident that poor-quality field blanks can be collected by using contaminated methanol and not adequately rinsing the methanol from the equipment. The volumes of VPBW specified through the calculations in the NFM (U.S. Geological Survey, variously dated) for the final rinse step in the cleaning process

are appropriate for typical groundwater sampling scenarios of ambient waters and do not assume gross contamination of the equipment. Equipment exposed to high concentrations of contaminants could require procedures that are more rigorous and involve cleaning agents that differ from those commonly used (Lapham and others, 1995).

Poor-quality field blanks generally are not as obvious as the Bad Field Blank in this case study. Whenever a field blank is collected after cleaning with contaminated methanol (or cleaning with an insufficient volume of blank water for the final rinse, or otherwise deviating from protocols), there is a risk that the field blank will represent sources of contamination that do not affect the environmental sample. The interpretation of field-blank data depends on an assumption that the field blanks are representative of the conditions under which the environmental samples were collected. Inclusion of poor-quality, *nonrepresentative* field blanks in assessing the quality of the environmental samples can cause overstatement of the magnitude of contamination affecting the samples and possibly rejection of data that are of good quality. If too many nonrepresentative field blanks are collected, it can be impossible to tell whether the environmental data are of acceptable quality. Even if all nonrepresentative field blanks could be identified and rejected, a consequence could be an insufficient number of representative field blanks for use in interpreting the environmental data, and thus, the environmental data would be of unknown quality.

In the case of the Bad Field Blank, there was a sound basis for rejecting the field blank, and it could be inferred that the native-water rinse of the sampling equipment that occurred during purging of the well removed the residual contamination before the groundwater sample was collected; however, this conclusion could only be reached because, coincidentally, none of the compounds detected in that groundwater sample were present in the Bad Field Blank.

Implications for Sample Collection to Reduce Extrinsic Contamination

The main findings of the Field Contamination Study are that if supplies are ordered just before sampling, if storage areas are clean, and if equipment cleaning and sample collection procedures are closely followed, then contamination from VOCs and WICs historically detected in source-solution blanks and field blanks occurs much less frequently in blanks and thereby reduces the potential of contaminating groundwater samples. The design of the FCS does not allow determining which aspect(s) of the study (that is, fresh supplies, clean storage area, equipment cleaning, conditioning of sampling line, or other aspects) were most important in reducing extrinsic contamination. Furthermore, additional research of the extrinsic contamination to ascertain the relative importance of the many aspects of the field protocols does not appear to be warranted because of the complexity and

large costs of such research. Rather, it appears more prudent to give emphasis to the necessity of carefully following all instructions for equipment cleaning and field sampling protocols and increasing the level of training for all field personnel.

Extrinsic sources of contamination introduced to source-solution blanks and field blanks make it difficult or even impossible to characterize the data quality for groundwater samples and can cause detections of compounds in groundwater samples to be questioned. Adhering to the following instructions will help reduce the introduction of VOCs and WICs to blanks and environmental samples collected in the field. Many of these points also are made in OWQ Technical Memorandum 2009.04 (Mohrman, 2009) and in the NFM (U.S. Geological Survey, variously dated).

1. Purchase sampling supplies, such as sample vials and bottles, foam sleeves, preservatives, and VPBW just before sampling. Use fresh supplies to avoid or reduce extrinsic contamination.
2. Store sampling supplies and equipment in a dedicated VOC- and WIC-free area.
3. Load sampling supplies and precleaned sampling equipment into field vehicles just before going to the field site.
4. Transport sampling supplies and equipment to the field site in a manner that minimizes the risk of contamination. Keep away from known sources of contamination.
5. Collect an annual equipment blank before starting the field work to help assure the cleanliness of the sampling equipment and supplies. Do not collect environmental samples until equipment blank data have been reviewed to verify the cleanliness of the equipment.
6. Avoid exposure to compounds to be analyzed in the water samples immediately before sampling. This could include the consumption of food and drinks containing methyl salicylate (mint flavoring) and caffeine; smoking of menthol cigarettes; use of personal-care products, such as mosquito repellent, ointments, sunscreen, mouthwash, or cough drops; and exposure to solvents and gasoline that contain compounds to be analyzed in the water samples.
7. Use sufficient amounts of VPBW from fresh, unopened bottles for the final rinse of the sampling equipment cleaning procedure to remove remaining methanol residue from sampling equipment.
8. Use fresh, unopened bottles of VPBW to collect a source-solution blank and a field blank. The NWQL specifies use of the VPBW within 14 days of the purge date listed on the bottle label.
9. Use sufficient amounts of VPBW from fresh, unopened bottles to condition the sampling equipment before collecting a field blank (in addition to the amount used for the final rinse of the cleaning procedure) and to collect a field blank.
10. Rinse the short section of sample line between the flow manifold and the sample-collection chamber with at least 10 sample-tubing volumes of VPBW before collecting the field blank.
11. Flush sampling equipment with native groundwater before collection of the groundwater sample using, at a minimum, the volume specified for well purging requirements in chapter A4 of the NFM (U.S. Geological Survey, 2006).
12. Rinse the short section of sample line between the flow manifold and the sample-collection chamber with at least 10 sample-tubing volumes of groundwater before collecting the groundwater sample.
13. Use a ballpoint pen to complete sample labels. Do not use permanent markers that contain VOCs. Label the vials 1, 2, and 3 and fill the VOC vials sequentially, matching the vial labels so that the laboratory analyst can preferentially analyze vial 3 first.
14. Ship the samples to the NWQL daily and by way of overnight delivery to reduce contamination from other sources.
15. Purchase pesticide-grade methanol for cleaning sampling equipment just before sampling. Use fresh methanol to avoid or reduce contamination from longer-term storage.
16. Store methanol in a separate flammables cabinet, as required, and avoid long-term storage. Previously opened bottles of methanol will act as a sink for VOCs from products containing VOCs that may be stored in the same cabinet or in a nearby cabinet.
17. Use the amount of methanol specified in chapter A3 of the NFM (Wilde, 2004) to clean sampling equipment (about 2 liters of methanol to clean a submersible pump and sample tubing).

Although the detection frequency of toluene, ethylbenzene, and camphor was less in the source-solution blanks using field-purged VPBW than in the source-solution blanks using NWQL-purged VPBW, the detection frequencies for other VOCs and WICs remained the same. Therefore, nitrogen-purging of blank water in the field is thought to be unnecessary if fresh supplies are used and if the field protocols are rigorously followed.

Summary

The Field Contamination Study (FCS) was designed by members of the U.S. Geological Survey (USGS) Office of Water Quality's Field Quality Control Workgroup for Organics to determine the field processes that tend to result in clean field blanks and to identify potential sources of contamination to blanks collected in the field from selected volatile organic compounds (VOCs) and wastewater-indicator compounds (WICs). The VOCs and WICs analyzed in the FCS were detected in blanks collected during 1996–2008 and 2002–08, respectively, by the USGS National Water-Quality Assessment (NAWQA) Program. To minimize the number of variables, the study required ordering of supplies just before sampling, storage of supplies and equipment in clean areas, use of sufficient amounts of purge and trap volatile-grade methanol and volatile pesticide-grade blank water (VPBW) to clean sampling equipment and to collect field blanks, and the shipment of samples to the USGS National Water Quality Laboratory (NWQL) within 24 hours of collection. The VPBW also was purged in the field with nitrogen gas to assist in determining sources of contamination or methods to reduce contamination to source-solution blanks.

Blanks and groundwater samples were collected for the FCS during 2008–09 at 16 sites, which were a mix of water-supply and monitoring wells located in 9 States. Five different sample types were collected at each site: (1) a source-solution blank collected at the NWQL using laboratory-purged VPBW, (2) source-solution blanks collected in the field using laboratory-purged VPBW, (3) source-solution blanks collected in the field using field-purged VPBW, (4) a field blank collected using field-purged VPBW, and (5) a groundwater sample collected from a well. The source-solution blank and field-blank analyses were used to identify, quantify, and document extrinsic contamination and to help determine the sources and causes of data-quality problems that can affect groundwater samples. Extrinsic contamination originates from a process or source that is external to the medium being sampled and was the focus of the FCS.

Concentrations of compounds detected in FCS analyses were quantified and stored in the USGS National Water Information System (NWIS) database after meeting rigorous identification and quantification criteria. The study also utilized information provided by laboratory analysts about evidence indicating the presence of selected compounds, using less rigorous identification criteria than is required for reporting quantified data. For the FCS, these data are considered adequate to indicate “evidence of presence,” and were used only for diagnostic purposes. All but two of the VOCs analyzed for in this study had some evidence of presence. Evidence of VOCs and WICs at low concentrations near or less than the long-term method detection level can indicate a contamination problem that could affect future datasets if method detection levels were to be lowered.

Seven VOCs included in this study, *o*-xylene, styrene, 1,2,4-trimethylbenzene, dichloromethane, acetone, 2-butanone, and tetrahydrofuran, were not quantified in any of the samples collected. Benzene, toluene, ethylbenzene, *m*- and *p*-xylene, carbon disulfide, and chloroform were quantified in analyses of FCS blanks or in groundwater samples. None of the 13 VOCs and 16 WICs included in this study were quantified in the VPBW collected and analyzed at the NWQL. This finding indicates that the VPBW was “contaminant free” when it was shipped from the laboratory to each of the field offices, although some compounds were present in some of the samples below minimum detection levels based on evidence-of-presence data. Toluene, *m*- and *p*-xylene, benzene, and carbon disulfide were each quantified in an FCS field-blank analysis, but not in the associated groundwater sample. The native-water rinse of the sampling equipment conducted just before collection of the groundwater sample likely reduced low-level contamination with respect to these compounds.

Analyses of VOCs in source-solution blanks and field blanks collected during the FCS had lower detection frequencies than in the historical dataset collected by the NAWQA Program during 1996–2008. The detection frequency of toluene in field blanks was reduced by about an order of magnitude from about 38 percent in the historical NAWQA dataset to 3.1 percent in the FCS dataset. Other VOCs quantified in 5 percent or more of the field blanks in the NAWQA dataset, but not quantified in the FCS field-blank analyses, were ethylbenzene, *o*-xylene, styrene, 1,2,4-trimethylbenzene, chloroform, dichloromethane, acetone, 2-butanone, and tetrahydrofuran. The lower detection frequencies of most VOCs for the FCS, compared to historical NAWQA data, most likely can be attributed to the collective use of fresh supplies and rigorous adherence to the protocols for cleaning equipment and collecting samples.

The compound toluene had a relatively high frequency of evidence of presence in the FCS samples analyses, despite the use of field-purged VPBW and other efforts to reduce sample contamination, an indication that toluene likely has a low-level contamination source. Five sites had evidence of toluene in one or both field-blank analyses, but not in a field-purged source-solution blank analysis. Toluene in these analyses possibly was introduced during the field-blank sample-collection process (that includes the cleaning of equipment and blank collection). Chloroform, a disinfection by-product that is commonly present in tap water used to clean sampling equipment, was not quantified and had no evidence of presence in the FCS field-blank analyses. It is probable that the relatively high detection frequency of chloroform in historical NAWQA field blanks (about 20 percent) is the result of inadequate rinsing with sufficient volumes of VPBW in the final step of the cleaning protocol. Evidence of 2-butanone in FCS field samples from a generally consistent group of sites indicates a possible low-level background concentration associated with the shipment of VPBW from the NWQL to the

field (resulting in contamination of the sampling equipment) or associated with shipment of the samples from the field to the NWQL.

For WICs, only camphor, *N,N*-diethyl-*meta*-toluamide (DEET), and phenol were detected at quantified concentrations in the FCS samples. Phenol had a high detection frequency in source-solution and field blanks (70 and 64 percent, respectively) collected by the NAWQA Program during 2002–08, compared to a detection frequency of about 3 percent in the FCS source-solution and field blanks. The detection frequency of benzophenone and DEET in field blanks also was substantially less in the FCS dataset (no detections) compared to historical NAWQA data (about 29 and 36 percent, respectively). Evidence of presence of benzophenone, caffeine, camphor, DEET, and methyl salicylate in FCS source-solution blanks, field-purged source-solution blanks, and field blanks possibly could be attributed to products containing these compounds being used by sampling personnel. Evidence of triphenyl phosphate in field blanks from five sites, but not in the source-solution blanks, indicates that the compound was possibly introduced during the field-blank sample-collection process.

The main findings of the FCS are that if supplies are ordered just before sampling, if storage areas are clean, and if equipment cleaning and sample collection procedures are closely followed, then contamination from VOCs and WICs historically detected in source-solution blanks and field blanks occurs much less frequently in blanks and reduces the potential contamination to groundwater samples. Although the detection frequency of toluene, ethylbenzene, and camphor was less in the source-solution blanks using field-purged VPBW than in the source-solution blanks using NWQL-purged VPBW, the detection frequencies for other VOCs and WICs remained the same. Therefore, nitrogen-purging of blank water in the field is thought to be unnecessary if fresh supplies are used and if field protocols are rigorously followed.

Extrinsic contamination introduced to source-solution blanks and field blanks can make it difficult to understand the quality of groundwater sample data and can cause detections of compounds in groundwater samples to be questioned. Following field procedures, such as using sufficient amounts of VPBW from fresh, unopened bottles (1) in the final rinse of the cleaning procedure, (2) to condition the sampling equipment before collecting a field blank, and (3) to collect a field blank, will minimize the potential for introduction of VOCs and WICs to blanks and environmental samples.

Acknowledgments

The authors would like to thank the USGS personnel in the field and laboratory for the long hours spent collecting and processing the samples for this study. Donna Rose (VOCs) and Steve Smith (WICs) with the NWQL analyzed

the samples collected as part of the FCS. Both chemists were helpful in providing additional information from the laboratory analyses in a timely and logical manner and were involved in the interpretation of these data. The effort provided by the National Field Supply Service to purge the source-solution water used for the FCS and to ship the water to the field is appreciated. Laura Bexfield, Greg Delzer, Tim Oden, and Doug Stevenson are acknowledged for providing reviews that greatly improved the report. The authors also thank Janet Carter for helping to move this report through the review process to publication.

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Glossary

Blank water Water that is intended to be free of analytes of interest. Also called source-solution water. Volatile pesticide-grade blank water was used in the collection of field blanks and source-solution blanks for the Field Contamination Study.

Detection frequency The frequency of detection of an individual compound is computed as the number of samples with a detection of an individual compound divided by the number of samples in which the compound was analyzed, multiplied by 100.

Evidence of presence For this study, the quantitation ion is present and greater than 2 times the maximum response in a bracketing laboratory set blank and at least one qualification ion is present. These data normally are censored (that is, stored as being less than (<) the laboratory reporting level) in the U.S. Geological Survey National Water Information System (NWIS) database.

Extrinsic contamination Contamination of an environmental sample or quality-control sample that originates from a process or source that is external to the medium being sampled and, therefore, is not representative of the medium being sampled.

Field blank A blank composed of volatile pesticide-grade blank water for the Field Contamination Study that is collected in the field in the same manner as the groundwater samples, except for native-water rinsing, and subjected to all aspects of sample collection including contact with the sample tubing, sample preservation, and shipment to the U.S. Geological Survey National Water Quality Laboratory.

Gasoline hydrocarbon A straight, branched, or cyclic structured organic compound containing only carbon and hydrogen atoms that is a common ingredient in gasoline and other petroleum product formulations. Benzene, toluene,

ethylbenzene, and xylenes, commonly referred to as BTEX, are the primary subset of the gasoline hydrocarbons.

Internal standard (IS) A compound not expected to be found in any environmental sample that is added to every sample extract in a known amount. The internal standard is used to measure the relative gas chromatographic/mass spectrometric (GC/MS) responses of other compounds and surrogates in each sample.

Laboratory blank A blank prepared in the laboratory that undergoes all sample preparation and analysis steps used for environmental samples; this type of blank can be used to determine the laboratory response to a sample that does not contain the compounds of interest or to determine the background response for analytical methods.

Laboratory set blank A blank analyzed throughout the analytical sequence. The set blanks are prepared from volatile-grade blank water. The purpose of the set blanks is to measure and record laboratory background concentrations (Connor and others, 1998).

Laboratory reporting level (LRL) The LRL is usually set equal to twice the most recently determined long-term method-detection level (LT-MDL). The LRL controls false negative error; the probability of falsely reporting a nondetection for a sample that contains a compound at a concentration equal to or greater than the LRL is predicted to be less than or equal to 1 percent. Results for a compound not detected are reported as “less than” (<) the LRL. The NWQL continuously collects quality-control data for analytical methods to determine LT-MDLs and establish LRLs. These values are re-evaluated annually and, therefore, may change.

Long-term method-detection level (LT-MDL) A detection level derived by determining the standard deviation of a minimum of 24 spiked sample

measurements analyzed for an extended period of time by multiple instruments, multiple analysts, and multiple calibrations. The LT-MDL data are collected continuously throughout the year to assess variations in method performance. The chance of falsely reporting a concentration at or greater than the LT-MDL for a sample that did not contain the compound is predicted to be less than or equal to 1 percent (Childress and others, 1999).

Reagent spike A spike prepared using volatile-grade blank water and a standard spike solution independent of the calibration standards; it also serves as a third party check of the calibration standard (Connor and others, 1998).

Quantified All criteria for identification and quantitation steps are met and the result is reported to the National Water Information System (NWIS) database. See “Compound Identification and Quantitation” section of this report for a detailed description.

Source-solution blank A blank consisting of freshly opened blank water (source solution) transferred directly into sample vials or bottles under clean conditions in the field, and sent directly to a laboratory to confirm that it is free of the compounds of interest.

Surrogate compound A compound not expected to be found in any environmental

sample, which is added to every sample in a known amount before sample processing. The surrogate is used to monitor method performance for each sample.

Tentatively identified compound A compound detected in a sample that is tentatively identified by comparing the analytical mass spectrum to reference spectra in the mass-spectra computer-data system library compiled by the National Institute of Standards and Technology (<http://www.nist.gov/srd/nist1a.cfm>).

Volatile organic compound (VOC) An organic chemical that has a high vapor pressure relative to its water solubility. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, refrigerants, some compounds used in organic synthesis, and some by-products of water chlorination.

Wastewater-indicator compound (WIC) An organic chemical typically associated with industrial and household wastewater, as well as some that are known or suspected endocrine-disrupting compounds (Zaugg and others, 2007). WICs include fungicides; gasoline hydrocarbons; manufacturing additives; organic synthesis compounds; pavement- and combustion-derived compounds; personal-care and domestic-use products; plant- or animal-derived biochemicals; and solvents (Carter and others, 2007).

Supplemental Information

Instructions Provided to Sampling Personnel for the Field Purge of Volatile Pesticide-Grade Blank Water

This section describes the instructions provided to sampling personnel for the field purge of volatile pesticide-grade blank water (VPBW) as part of the Field Contamination Study. Assemble the nitrogen-purging chamber frame outside of the sampling vehicle in the manner shown in figure A1. Make sure all connections are tight. Place the purging chamber on a table or level ground so that the VPBW bottles sit level, minimizing the potential for tipping over and spilling/breaking the bottles. Once the purging chamber frame is assembled, place a sample-collection chamber bag across the inside bottom of the frame. Cover the upper part of the frame by splitting a large sample-collection chamber bag down one side and attaching to the inside of the frame with provided clamps, leaving the front open.

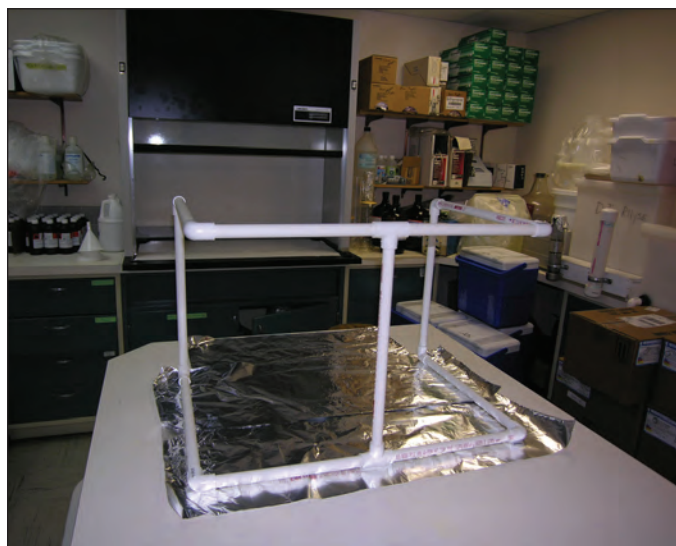


Figure A1. Nitrogen-purging chamber frame (photograph by David Bender).

The purging manifold valves, fittings (fig. A2), and Teflon[®] lines have been precleaned and bagged, and are ready for assembly and use in the field. Make sure the regulator valves are closed. Prepare the prepurified nitrogen tank by opening the valve to blow out any dust or debris in the valve. Attach the regulator to the prepurified nitrogen tank (G size tank, about 36 cubic feet of prepurified nitrogen). Wearing gloves, attach the 1/4-inch Teflon[®] feed line to the outlet port on the regulator using the attached brass Swagelok[™] (compression) fittings. Attach the 1/4-inch feed line from the regulator to the inlet port on the manifold valve assembly (center tee on valve assembly) using the attached brass Swagelok[™] fittings. Swagelok[™] connections should be hand tight plus one-quarter turn. Attach 1/4-inch Teflon[®] tubing to

the outlets for each valve using Swagelok[™] nylon front and back ferrules and run the other end of the tubing into the back of the purging chamber (fig. A3). Make sure all Swagelok[™] connections are tight.



Figure A2. Valves and fittings used with the field-purge apparatus.

Wearing gloves, place resealable plastic bags and pill bottles with stainless steel bubblers and 1/4-inch to 1/8-inch reducers into the purging chamber. Inside the purging chamber, remove one stainless steel bubbler from its bag and remove one pill bottle and one reducer from its resealable plastic bag and attach the 1/4-inch x 1/8-inch reducer (1/8-inch end) to the stainless steel bubbler and tighten (note: do not dispose of pill bottles). Attach the 1/4-inch to 1/8-inch reducers to each 1/4-inch feed line from the valves using the Swagelok[™] nylon front and back ferrules, and place the bubbler assembly back into the resealable plastic bag to cover. Repeat for additional lines. See figure A3 for a photograph of the nitrogen-purging apparatus.



Figure A3. Assembled field-purge apparatus (photograph by David Bender).

Close all regulator valves and manifold valves. Open the nitrogen tank and adjust the main regulator valve to achieve an outlet pressure of about 10 pounds per square inch (psi). Open the regulator outlet valve about one-quarter turn. Open the manifold valve(s) for the number of bottles to purge, about one-half turn. Open the regulator outlet valve to purge the lines for about 10–15 seconds to remove any air, dust, or other debris from the manifold and lines. Close the regulator outlet valve.

Place the VPBW bottles inside the purging chamber. Open the regulator outlet valve about one-quarter turn. Uncap the VPBW bottle, remove the stainless steel bubbler assembly from the resealable plastic bag and place the bubbler and feed line into the VPBW bottle (fig. A4); make sure the bubbler rests on the bottom of the bottle. Repeat for each bottle. Adjust the regulator outlet pressure to 10 psi (with the regulator outlet valve closed) using the main regulator valve. Each VPBW bottle will have a similar bubbling rate; if not, adjust the manifold valve(s) to get similar bubbling rates in each bottle. Readjust the outlet pressure on the regulator to about 10 psi with the regulator outlet valve closed. The purge rate should be about 5–10 milliliters per second. Purge each bottle of VPBW continuously for 2 hours, adjusting the outlet pressure periodically to maintain an outlet pressure of about 10 psi with the regulator outlet valve closed.

After approximately 2 hours, remove the stainless steel bubbler assembly, recap the VPBW bottle, shut off the manifold valve for the feed line, and remove the VPBW bottle from the purging chamber for use in the final rinse of the cleaning

protocol, collection of the source-solution blank, conditioning of sample line, and collection of field-blank samples. Repeat for the other VPBW bottles.

Disassemble the field-purge apparatus and repack all pieces in the provided case for transport to the next site or for return shipment to David Bender, U.S. Geological Survey, 1608 Mt. View Road, Rapid City, SD, 57702. If the purge apparatus is to be used at a subsequent site, field clean all equipment that has been in contact with the VPBW, such as the lines from the manifold to the VPBW bottles and the stainless steel bubblers, before packaging for transport.

Analytical Results Stored in the National Water Information System (NWIS) Database

Quantified analytical results from the Field Contamination Study are stored in the National Water Information System (NWIS) database. The analytical results are presented in table A1.

Concentrations and Detection Frequencies of Selected Volatile Organic Compounds in Field Contamination Study Samples

Concentrations of a selected volatile organic compound (upper panel) and the percentage of analyses where the same compound was not detected, had evidence of presence, or was quantified (lower panel) in a Field Contamination Study sample type are shown in figures A5–1 to A5–13. The position, shape, and shade of the data point(s) plotted on the upper panel correspond to its classification in the “Evidence of Presence” (+) and “Quantified” (Δ) groups labeled in the lower panel. The numbers at the top of the upper panel indicate the number of samples in each classification within each sample type. The numbers on the top of the lower panel indicate the total number of sample analyses in each sample type. Volatile organic compounds shown in the figures are benzene, toluene, ethylbenzene, *m*- and *p*-xylene, *o*-xylene, styrene, 1,2,4-trimethylbenzene, carbon disulfide, chloroform, dichloromethane, acetone, 2-butanone, and tetrahydrofuran.



Figure A4. Field apparatus for purging volatile pesticide-grade blank water (photograph by Deborah Parlman).

[All values are in micrograms per liter and are **bolded**, if not associated with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

Table A1. Concentrations stored in the National Water Information System (NWIS) database for volatile organic compounds and wastewater-indicator compounds in samples collected for the Field Contamination Study.—Continued

[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a less than (<) symbol. Values highlighted with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

Table A1. Concentrations stored in the National Water Information System (NWIS) database for volatile organic compounds and wastewater-indicator compounds in samples collected for the Field Contamination Study.—Continued

[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

Table A1. Concentrations stored in the National Water Information System (NWIS) database for volatile organic compounds and wastewater-indicator compounds in samples collected for the Field Contamination Study.—Continued

[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

Volatile organic compound	Source-solution analysis at NWQL (Sample 1)	Source-solution blank			Field-purged source-solution blank			Ground-water sample (Sample 5)
	(Sample 2A, vial 2)	(Sample 2A, vial 3)	(Sample 2B, vial 2)	(Sample 2B, vial 3)	(Sample 3A, vial 2)	(Sample 3A, vial 3)	(Sample 3B, vial 2)	(Sample 4, vial 3)
Site ID2, Idaho well BPW6, station identification number 430339115502201, field samples collected on 11/6/2008								
Benzene	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16	<0.16
Toluene	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18	<0.18
Ethylbenzene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
m- and p-Xylene	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8	<0.8
o-Xylene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Styrene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
1,2,4-Trimethylbenzene	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Carbon disulfide	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Chloroform	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Dichloromethane	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Acetone	<4	<4	<4	<4	<4	<4	<4	<4
2-Butanone	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6
Tetrahydrofuran	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4
Wastewater-indicator compound	Source-solution blank			Field-purged source-solution blank			Ground-water sample (Sample 5)	
	(Sample 2A)	(Sample 2B)	(Sample 3A)	(Sample 3B)	(Sample 4)	(Sample 5)		
Site ID2, Idaho well BPW6, station identification number 430339115502201, field samples collected on 11/6/2008								
Acetyl hexamethyl tetrahydronaphthalene (AHTN)	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5		
Benzophenone	<12	<12	<12	<12	<12	<12		
Caffeine	<1	<1	<1	<1	<1	<1		
Camphor	<06	<06	<06	<06	<06	<06		
N,N-Diethyl-meta-toluidine (DEET)	<14	<14	<14	<14	<14	<14		
Hexahydroxymethylcyclopentabenzopyran (HHCB)	<5	<5	<5	<5	<5	<5		
Menthol	<4	<4	<4	<4	<4	<4		
Methyl salicylate	<1	<1	<1	<1	<1	<1		
4-Nonylphenol (total, branched)	<2	<2	<2	<2	<2	<2		
Phenol	<1.4	<1.4	<1.4	<1.4	<1.4	<1.4		
Tributyl phosphate	<2	<2	<2	<2	<2	<2		
Triphenyl phosphate	<12	<12	<12	<12	<12	<12		
Isophorone	<08	<08	<08	<08	<08	<08		
Naphthalene	<04	<04	<04	<04	<04	<04		
Phenanthrene	<04	<04	<04	<04	<04	<04		

Table A1. Concentrations stored in the National Water Information System (NWIS) database for volatile organic compounds and wastewater-indicator compounds in samples collected for the Field Contamination Study.—Continued

[All values are in micrograms per liter and are *bolded, italicized*, if not associated with a less than (<) symbol. Values highlighted with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

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[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

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[illegible]

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[illegible]

Table A1. Concentrations stored in the National Water Information System (NWIS) database for volatile organic compounds and wastewater-indicator compounds in samples collected for the Field Contamination Study.—Continued

[All values are in micrograms per liter and are **bolded, italicized**, if not associated with a less than (<) symbol. Values highlighted with a gray background were determined to have evidence of presence (some but not all identification criteria were met). E, estimated value; NWQL, U.S. Geological Survey National Water Quality Laboratory. See "Sample Types" section of report for a more detailed explanation of the samples collected for the Field Contamination Study]

[illegible]

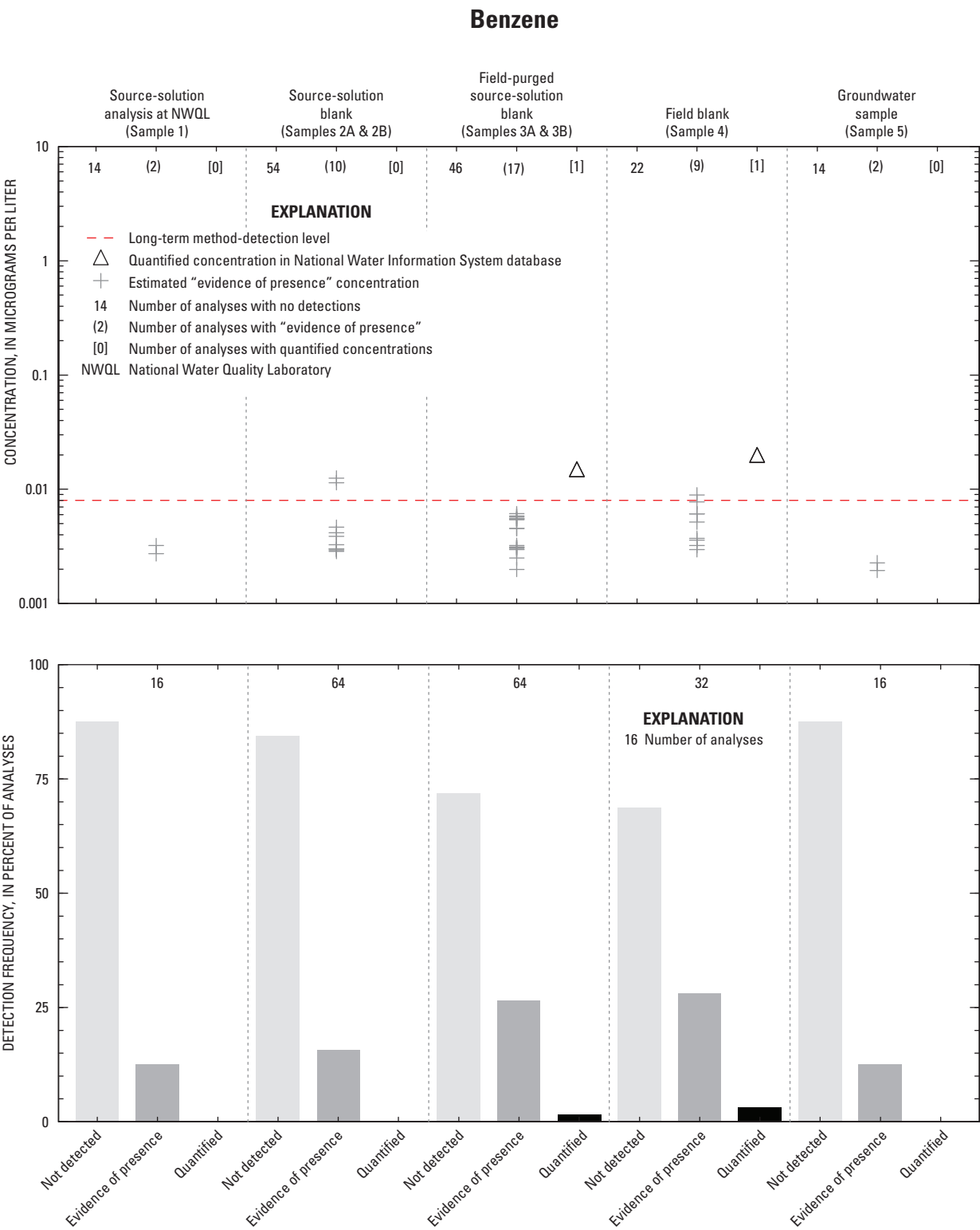


Figure A5-1. Concentrations and detection frequencies of benzene in analyses from the Field Contamination Study.

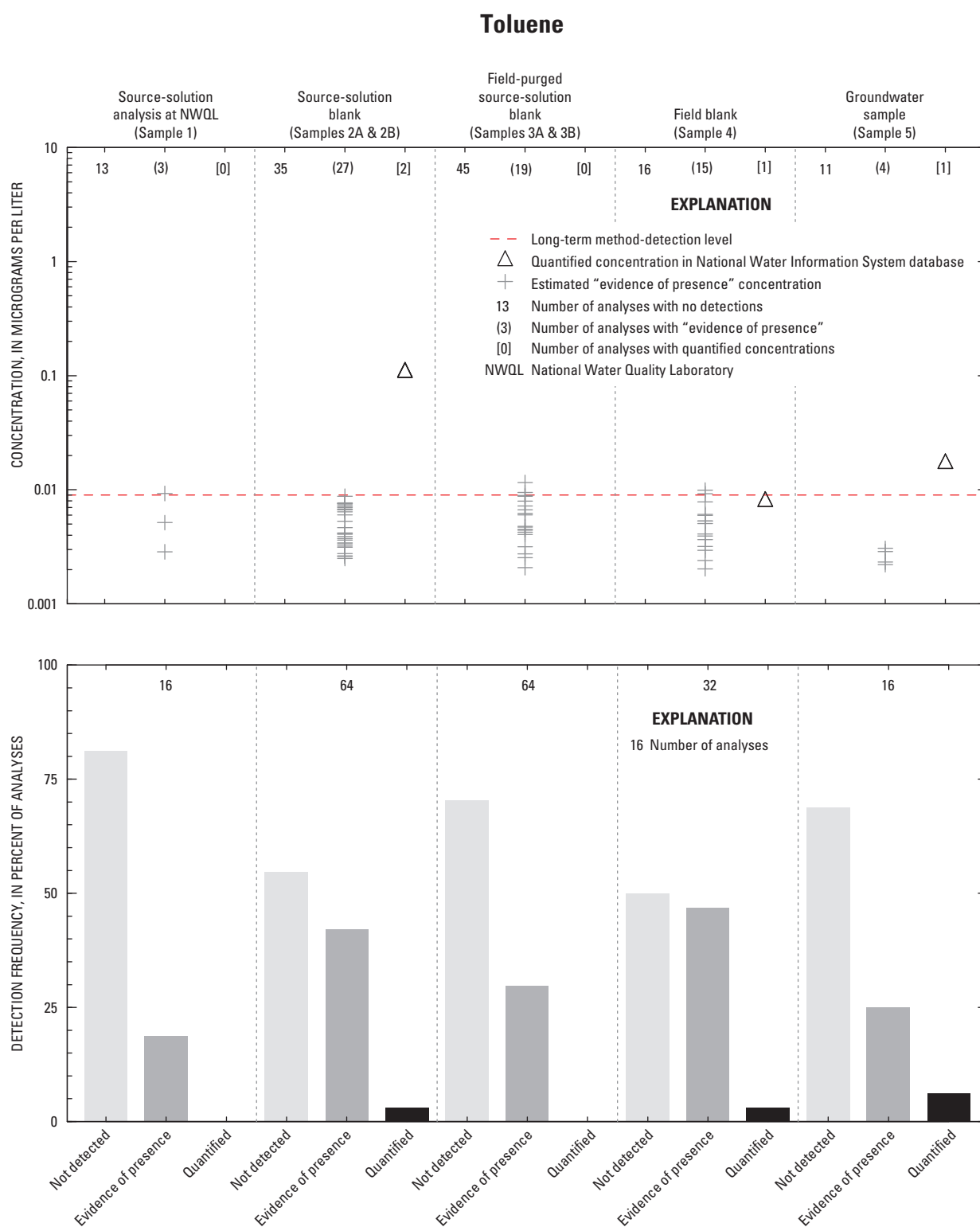


Figure A5-2. Concentrations and detection frequencies of toluene in analyses from the Field Contamination Study.

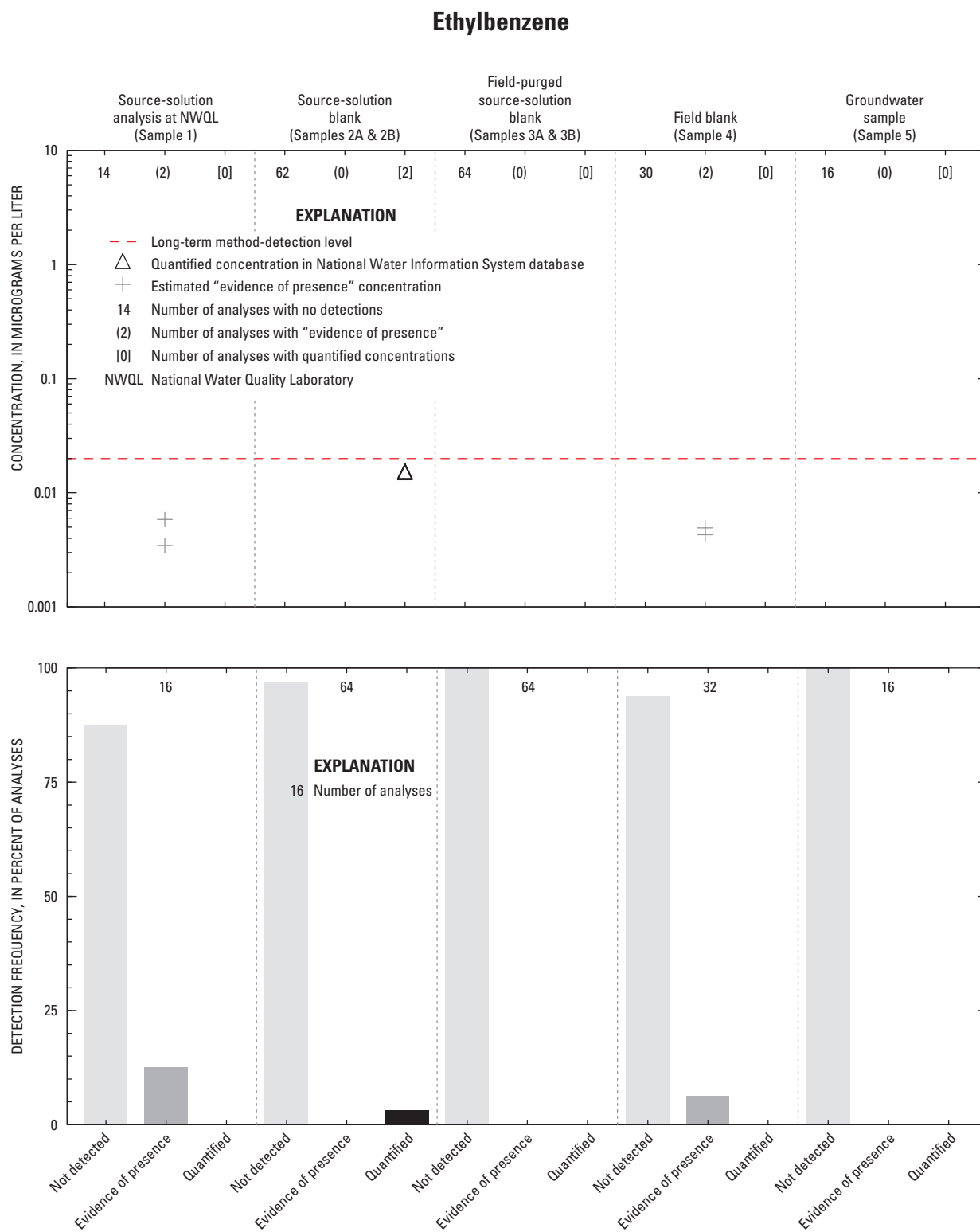


Figure A5-3. Concentrations and detection frequencies of ethylbenzene in analyses from the Field Contamination Study.

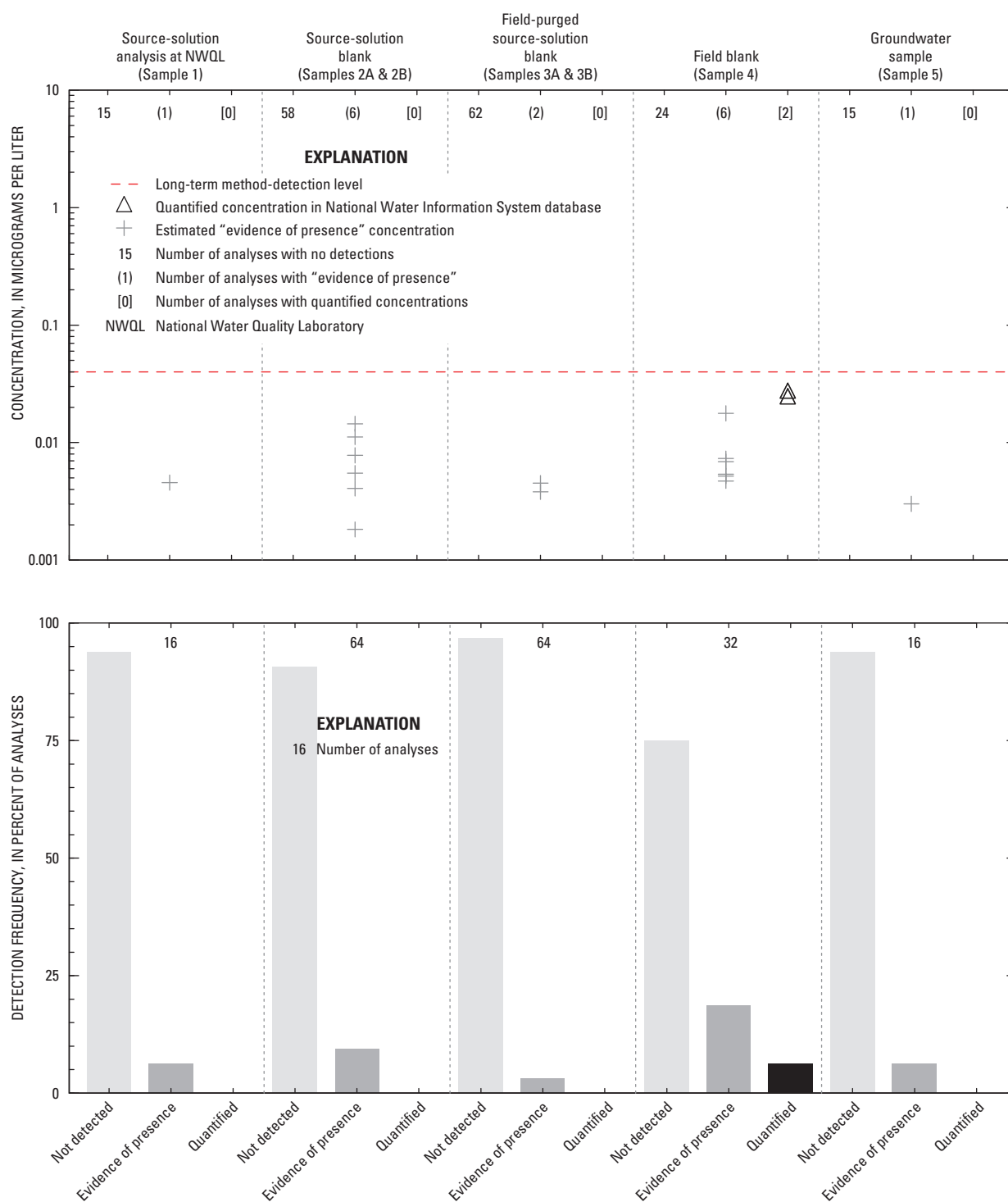
***m*- and *p*-Xylene**

Figure A5-4. Concentrations and detection frequencies of *m*- and *p*-xylene in analyses from the Field Contamination Study.

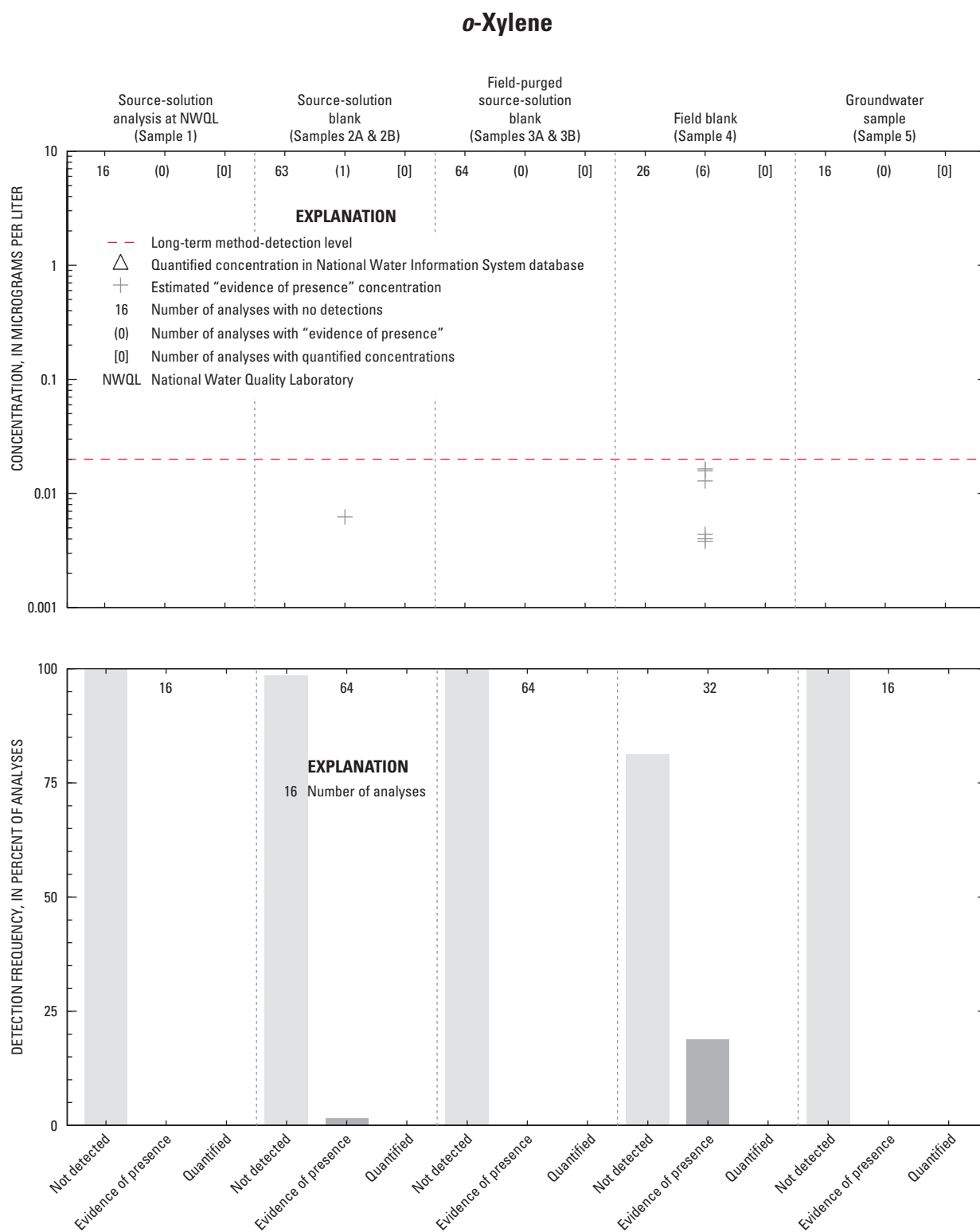


Figure A5-5. Concentrations and detection frequencies of *o*-xylene in analyses from the Field Contamination Study.

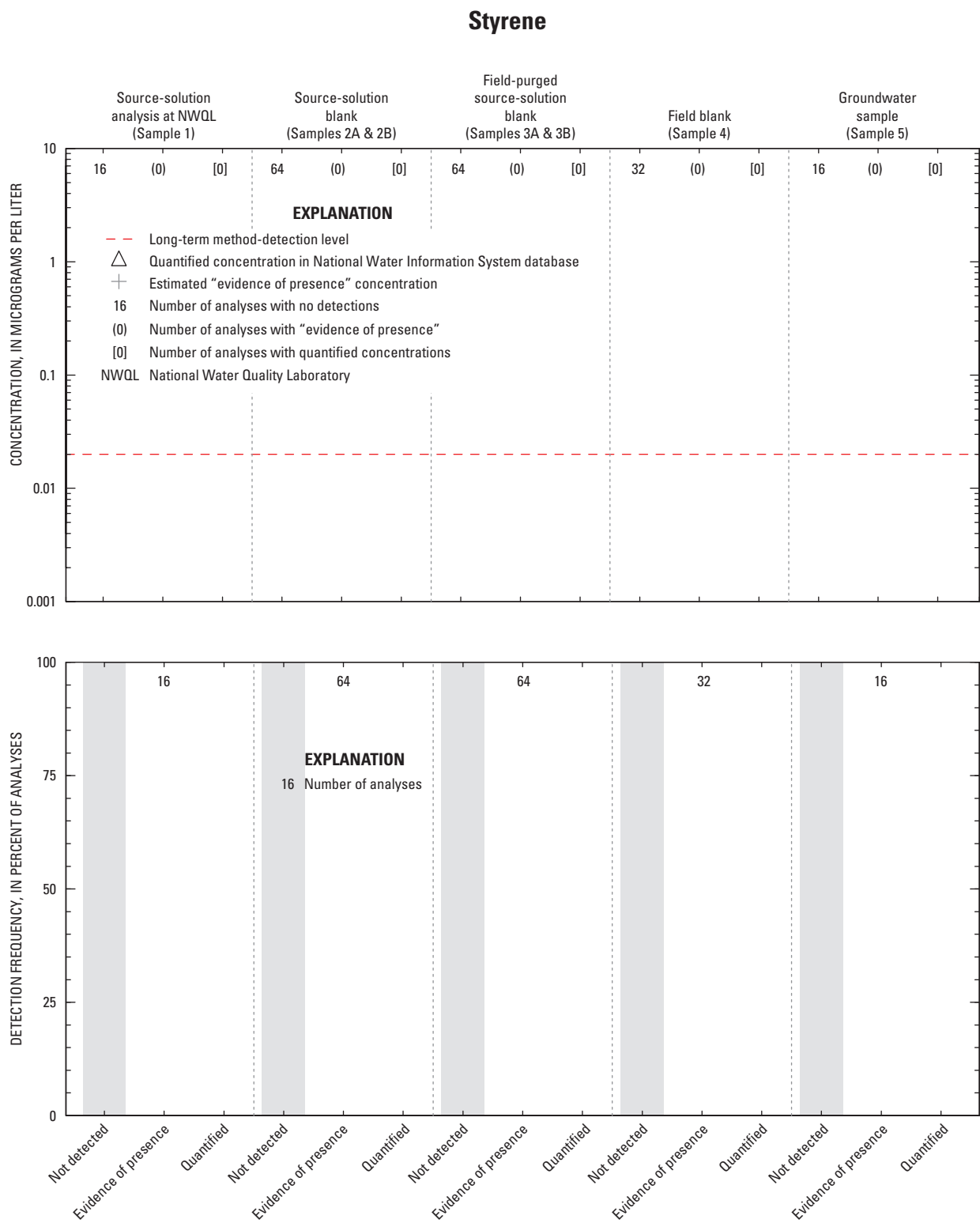


Figure A5–6. Concentrations and detection frequencies of styrene in analyses from the Field Contamination Study.

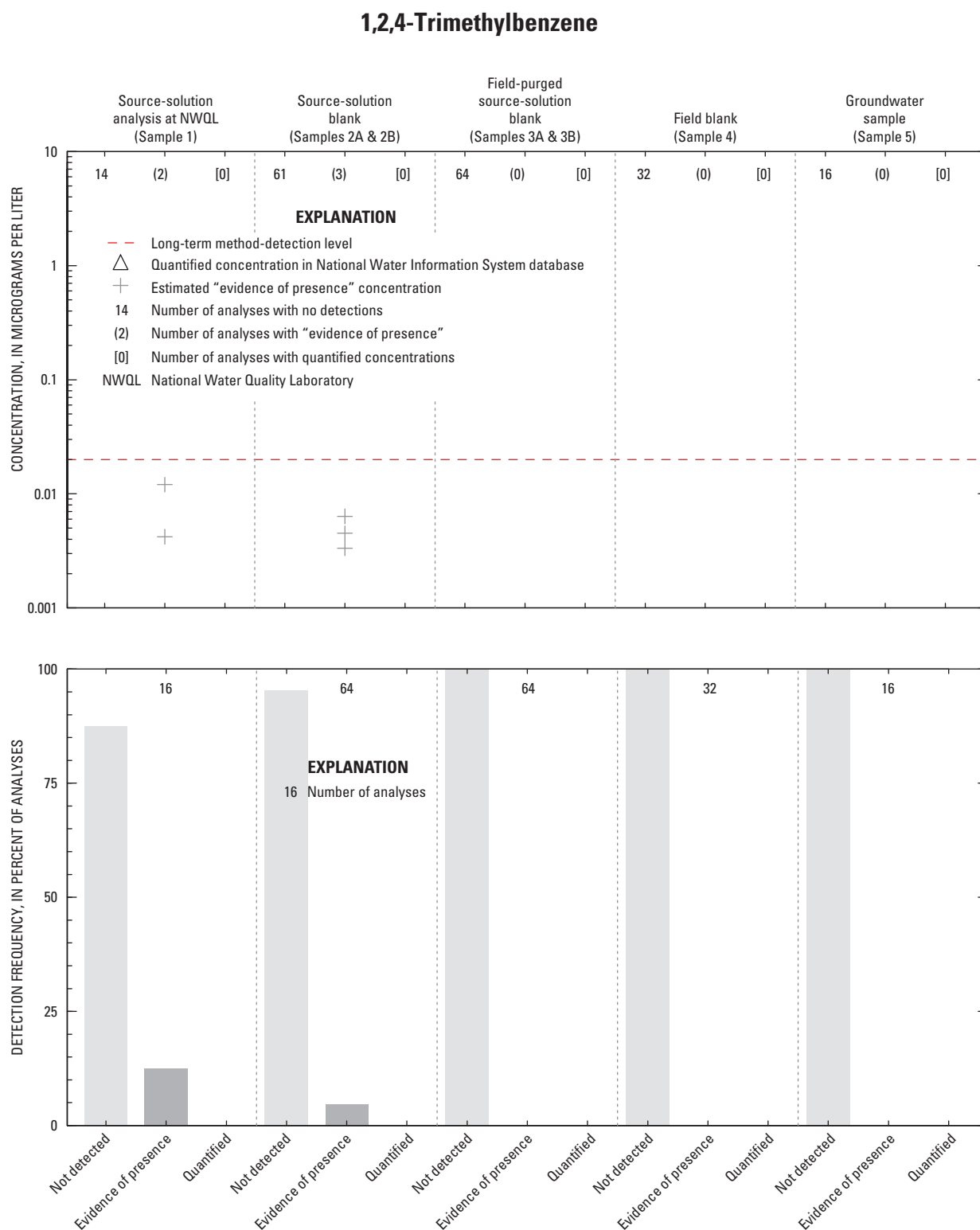


Figure A5-7. Concentrations and detection frequencies of 1,2,4-trimethylbenzene in analyses from the Field Contamination Study.

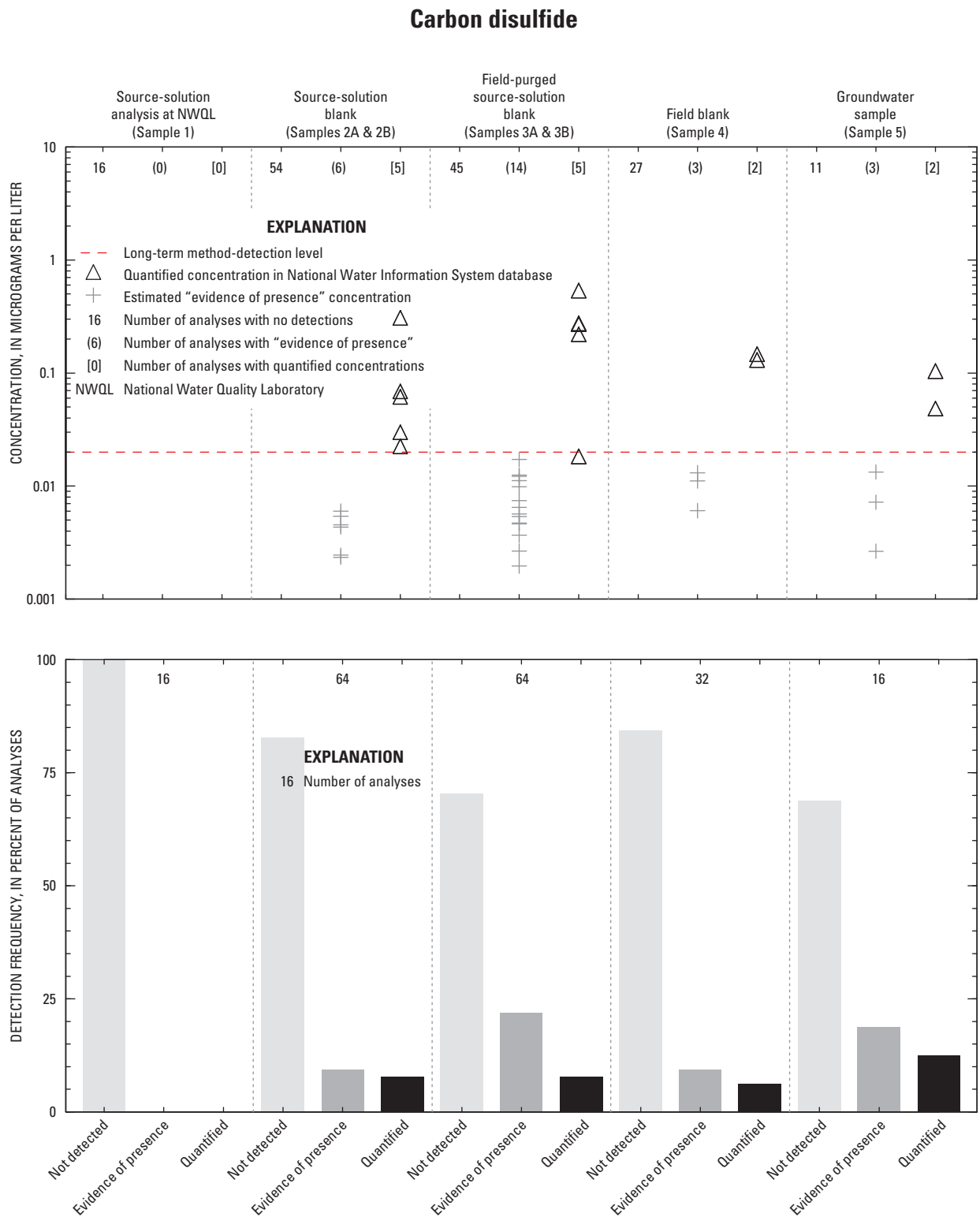


Figure A5-8. Concentrations and detection frequencies of carbon disulfide in analyses from the Field Contamination Study.

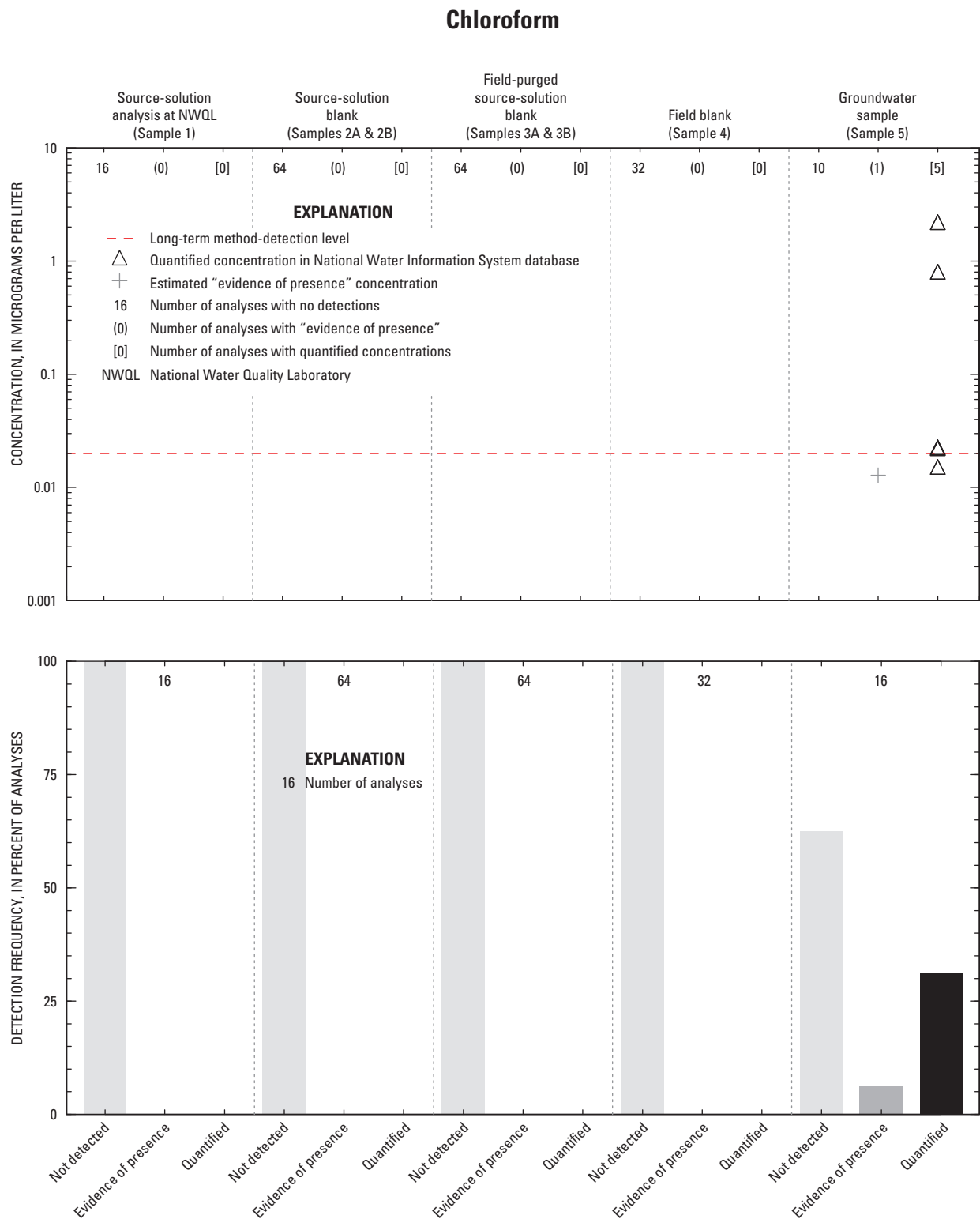


Figure A5–9. Concentrations and detection frequencies of chloroform in analyses from the Field Contamination Study.

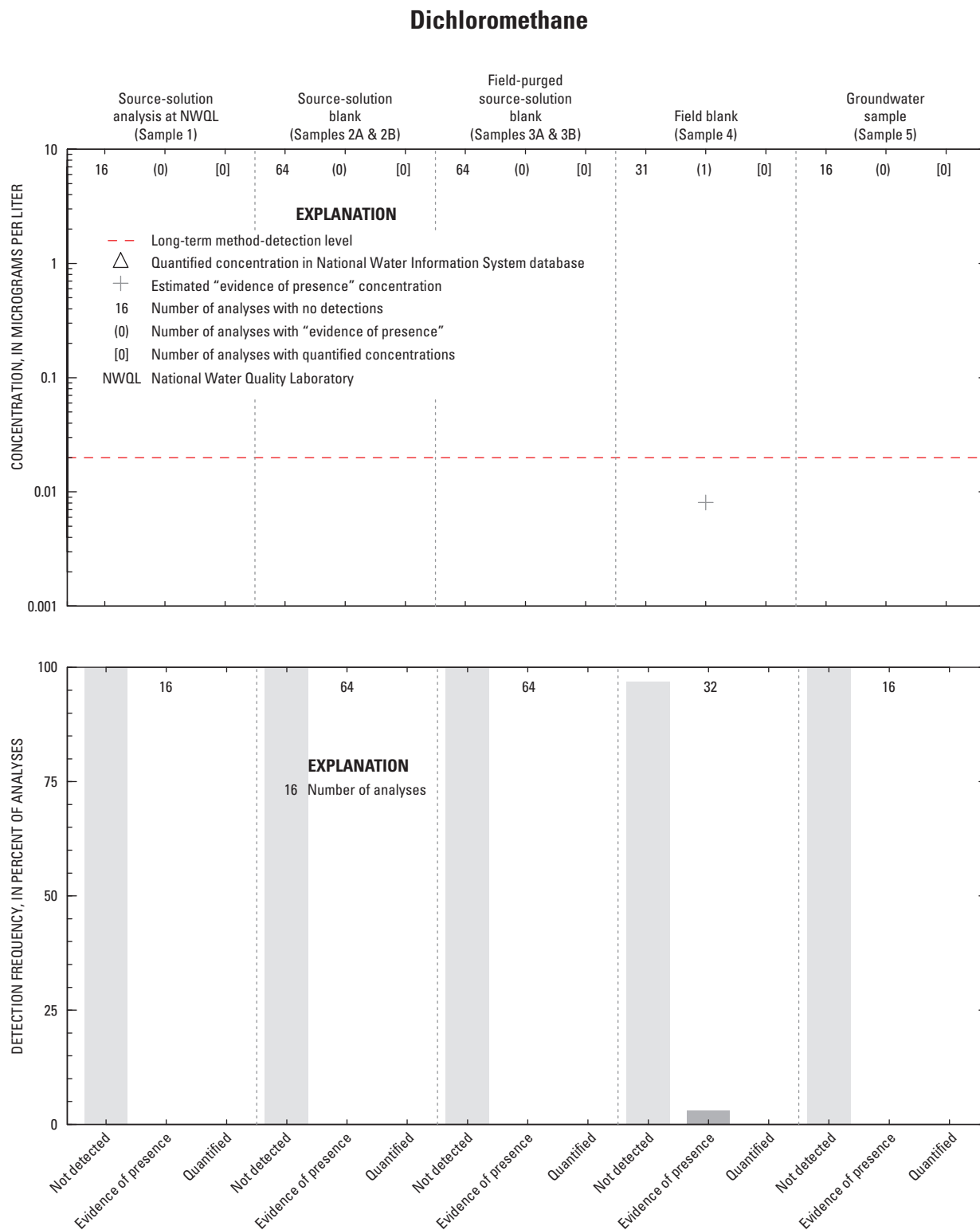


Figure A5–10. Concentrations and detection frequencies of dichloromethane in analyses from the Field Contamination Study.

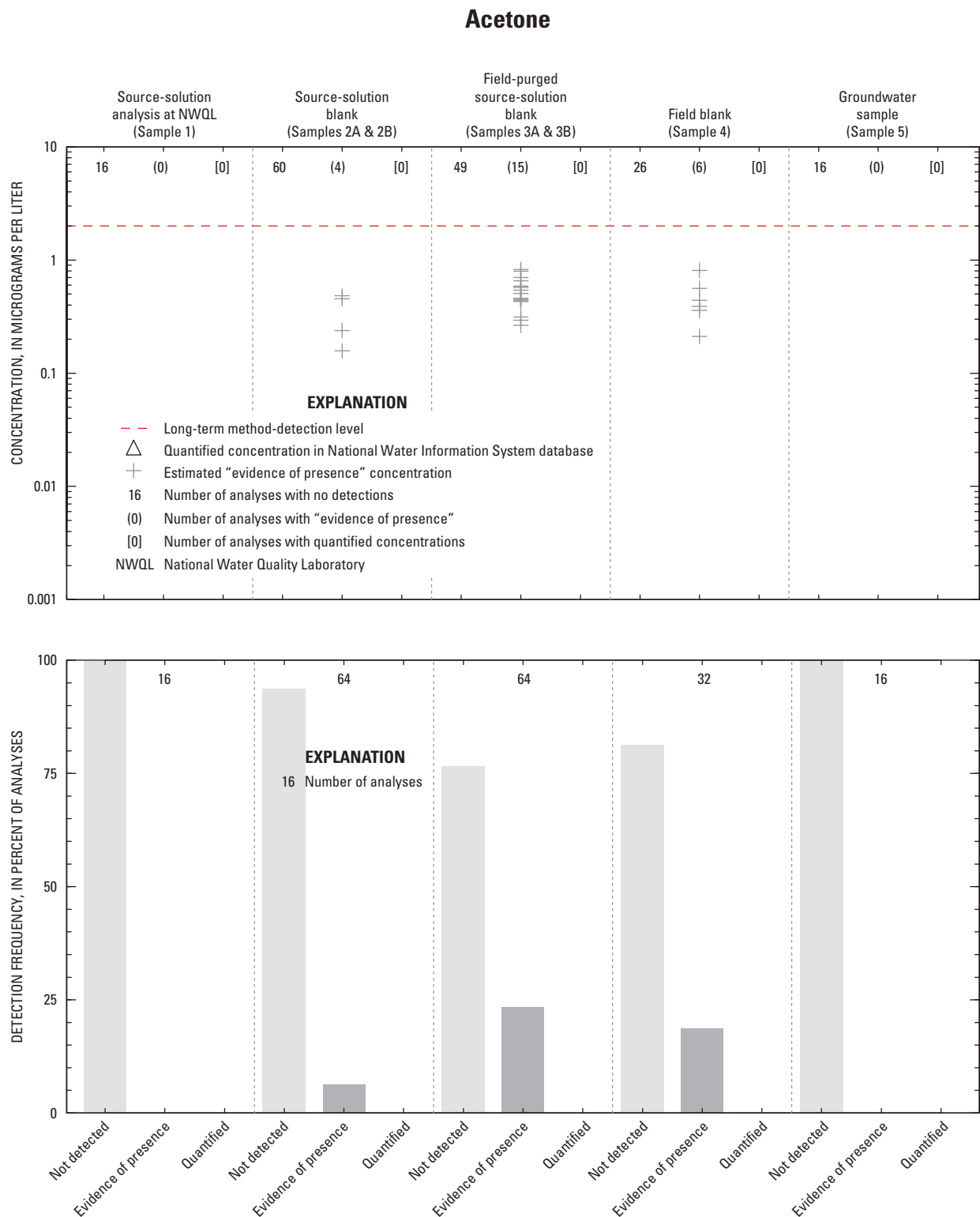


Figure A5-11. Concentrations and detection frequencies of acetone in analyses from the Field Contamination Study.

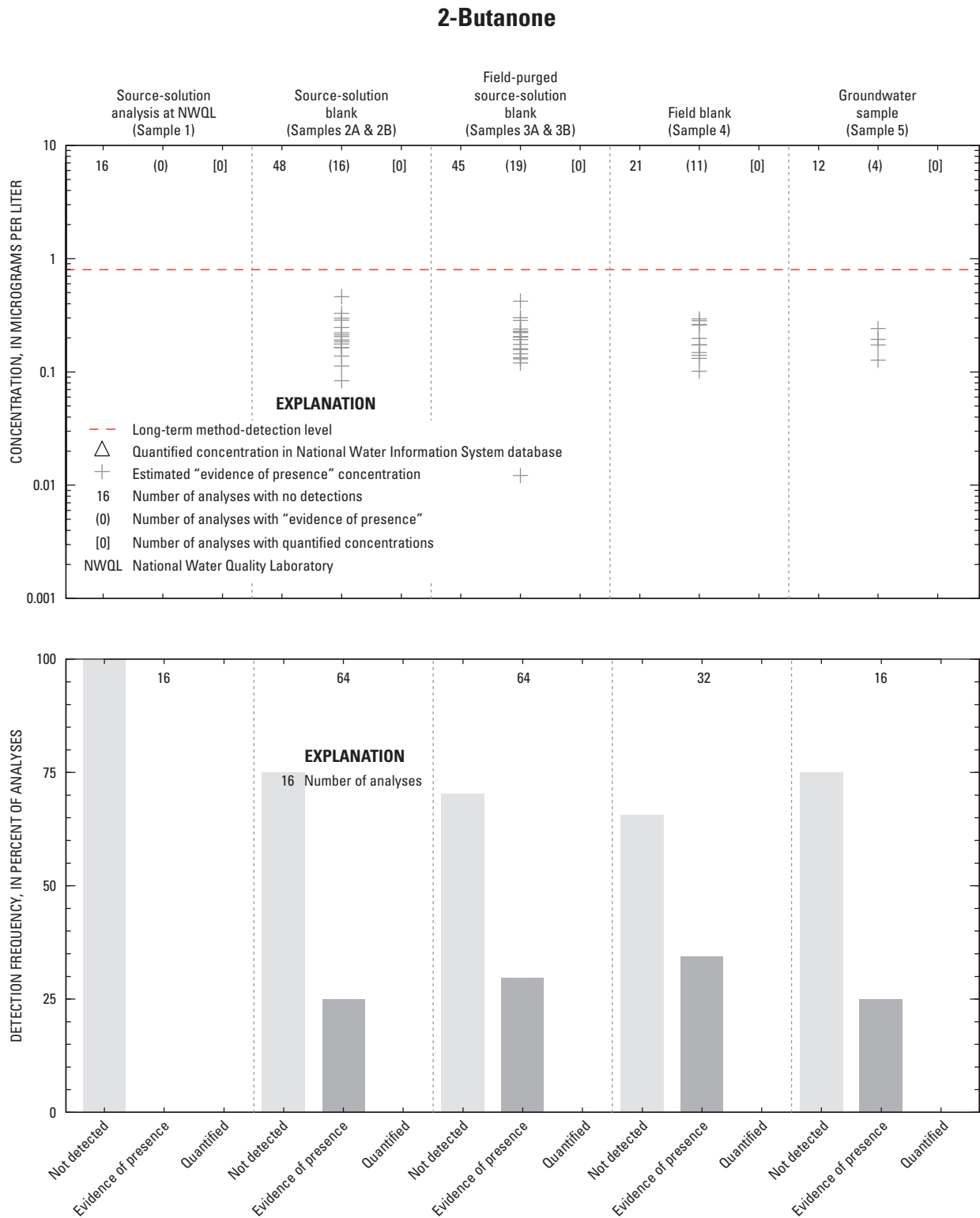


Figure A5-12. Concentrations and detection frequencies of 2-butanone in analyses from the Field Contamination Study.

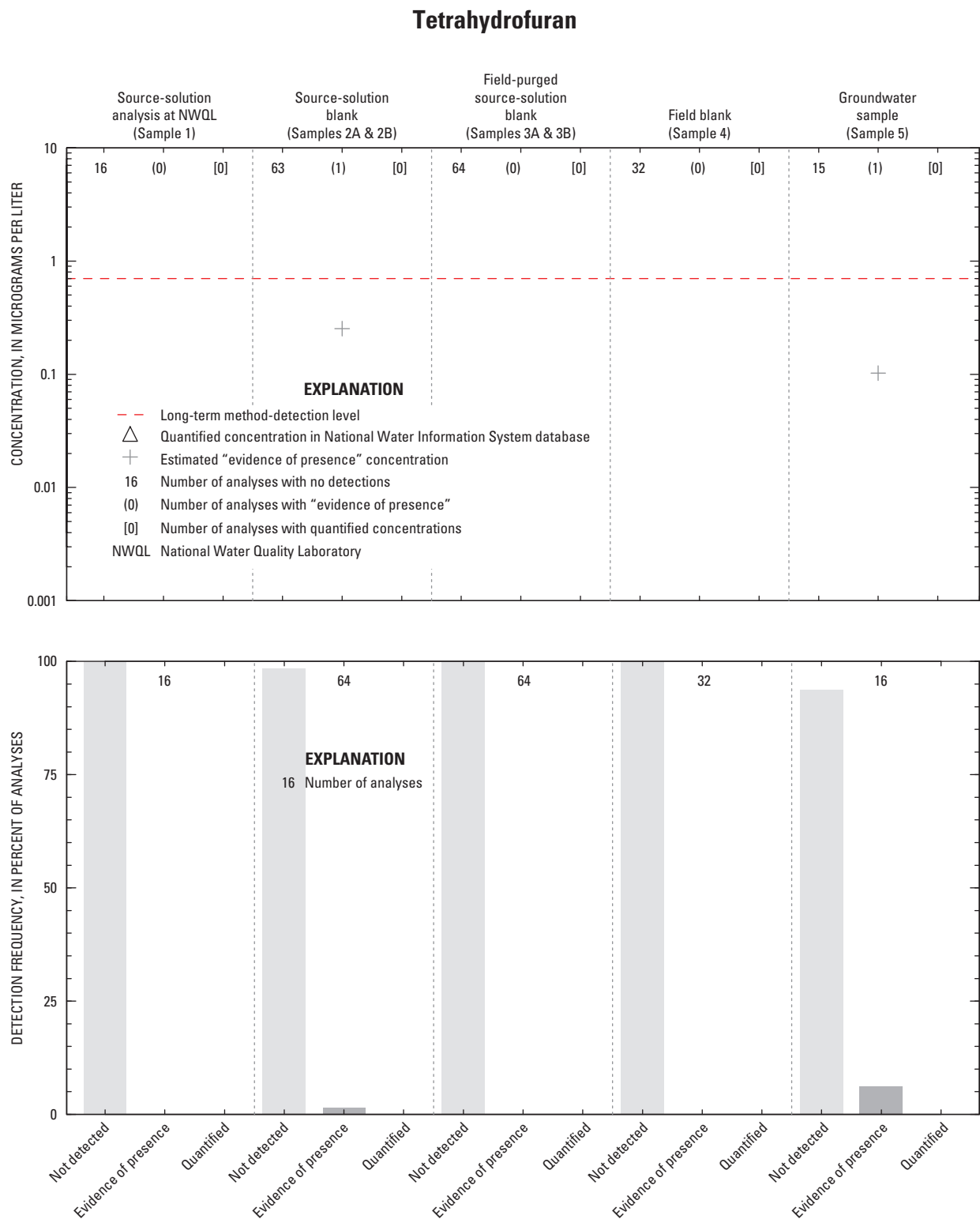


Figure A5–13. Concentrations and detection frequencies of tetrahydrofuran in analyses from the Field Contamination Study.

Concentrations and Detection Frequencies of Selected Wastewater-Indicator Compounds in Field Contamination Study Samples

Concentrations of a selected wastewater-indicator compound (upper panel) and the percent of analyses where the same compound was not detected, had evidence of presence, or was quantified (lower panel) in a Field Contamination Study sample type are shown in figures A6–1 to A6–11. The position, shape, and shade of the data point(s) plotted on the

upper panel correspond to its classification in the “Evidence of Presence” (+) and “Quantified” (Δ) groups labeled in the lower panel. The numbers at the top of the upper panel indicate the number of samples in each classification within each sample type. The numbers on the top of the lower panel indicate the total number of sample analyses in each sample type. Wastewater-indicator compounds on the figures in this section are benzophenone, caffeine, camphor, *N,N*-diethyl-*meta*-toluamide (DEET), methyl salicylate, 4-nonylphenol (total, branched), phenol, tributyl phosphate, triphenyl phosphate, isophorone, and phenanthrene.

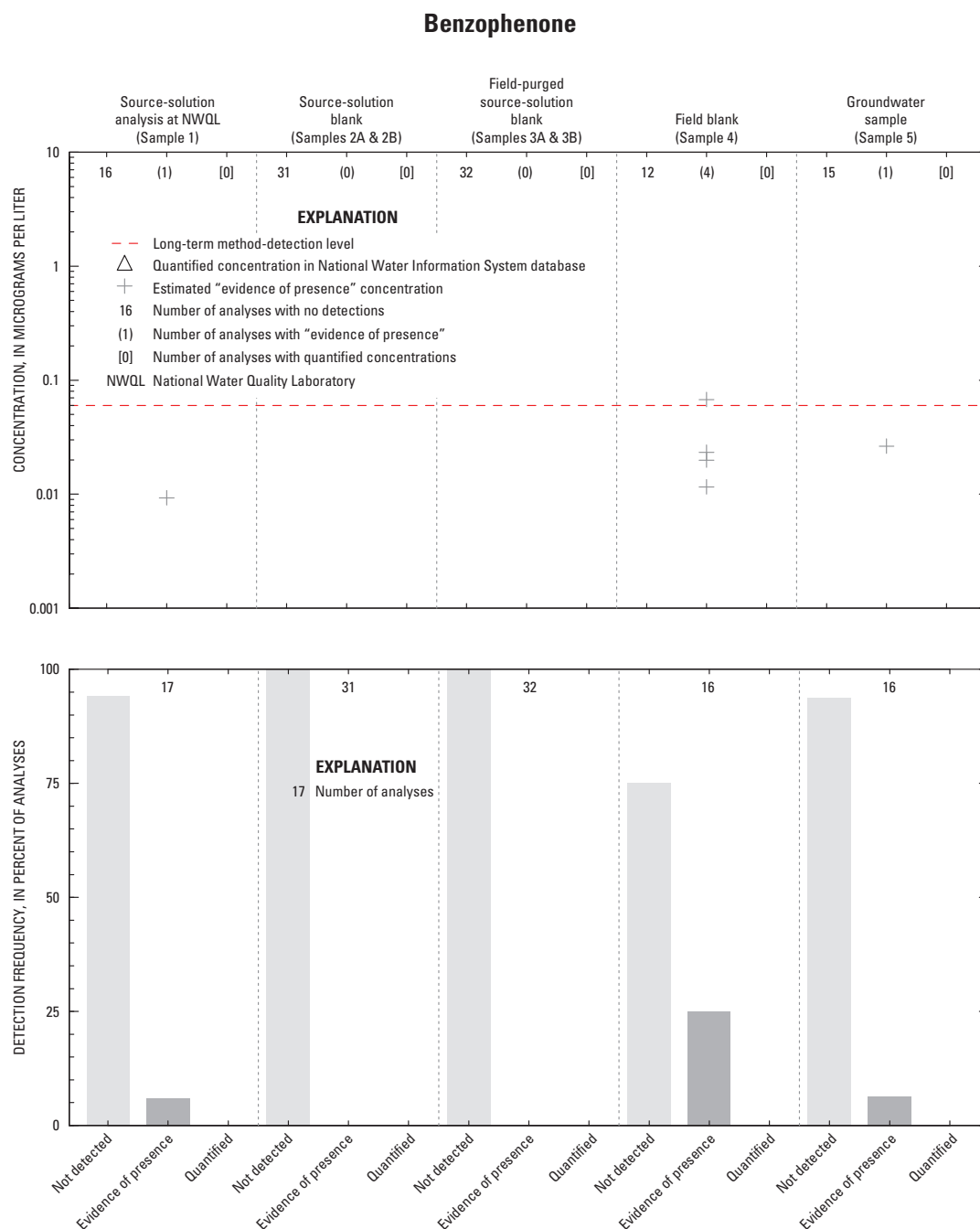


Figure A6–1. Concentrations and detection frequencies of benzophenone in analyses from the Field Contamination Study.

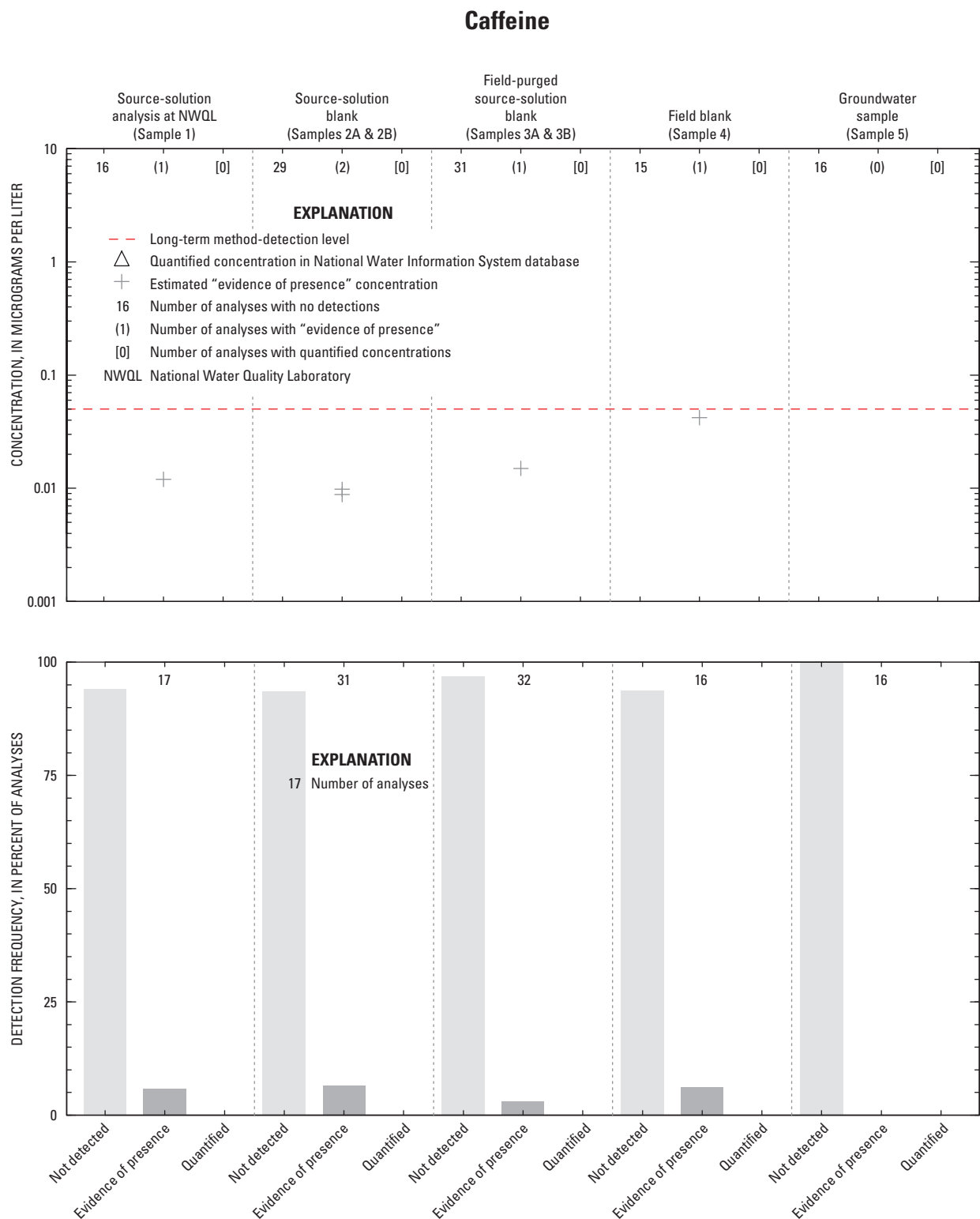


Figure A6–2. Concentrations and detection frequencies of caffeine in analyses from the Field Contamination Study.

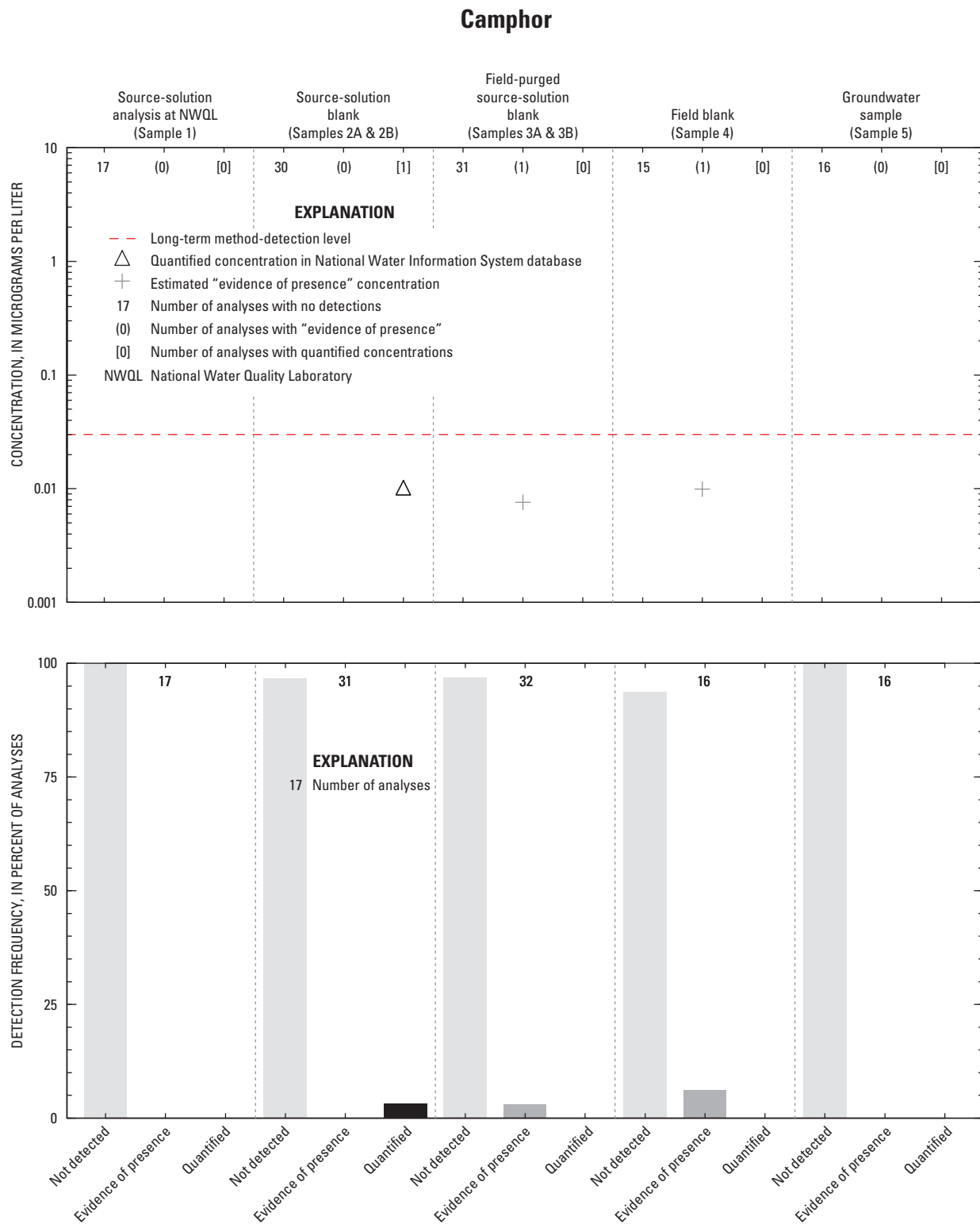


Figure A6-3. Concentrations and detection frequencies of camphor in analyses from the Field Contamination Study.

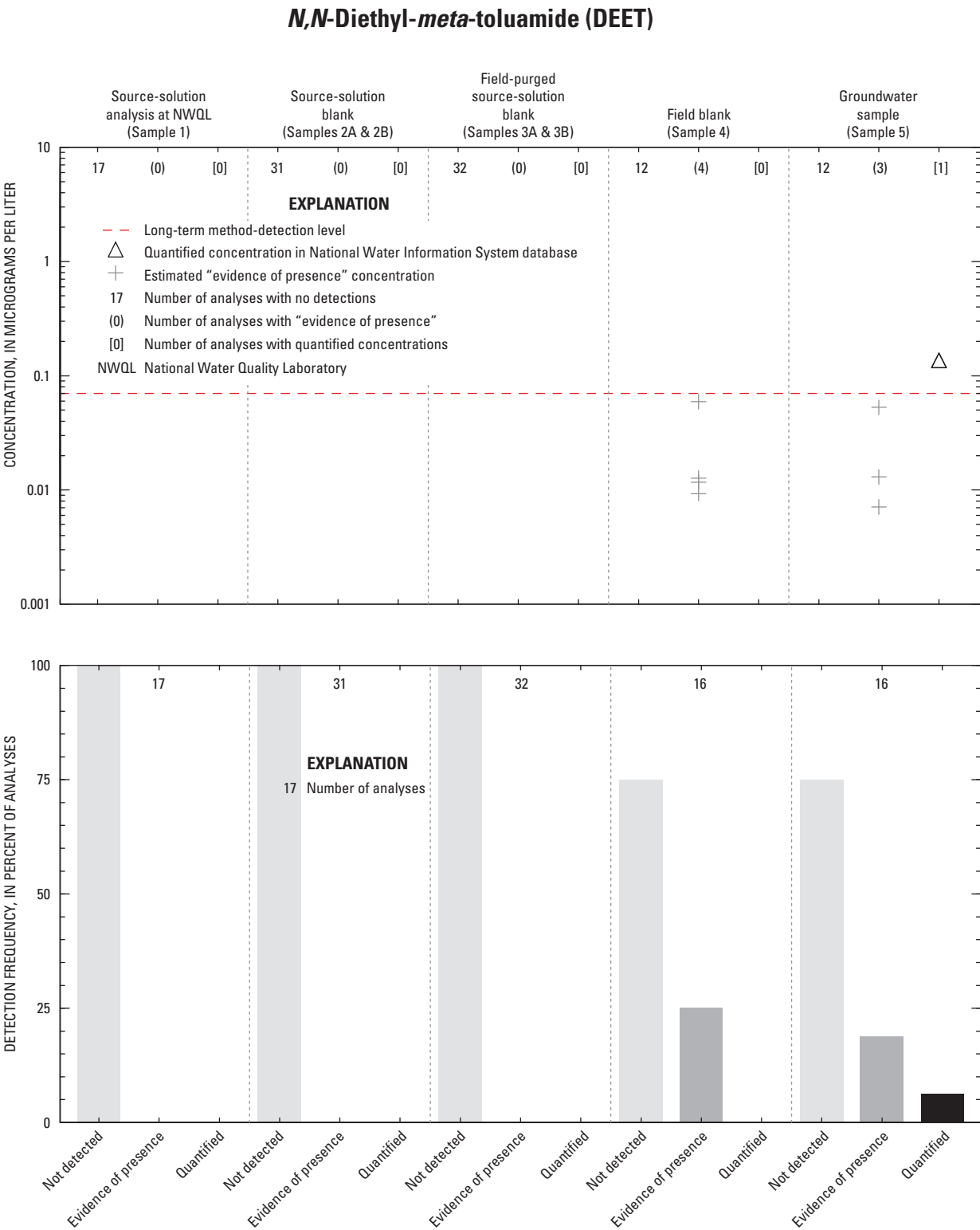


Figure A6-4. Concentrations and detection frequencies of *N,N*-diethyl-*meta*-toluamide (DEET) in analyses from the Field Contamination Study.

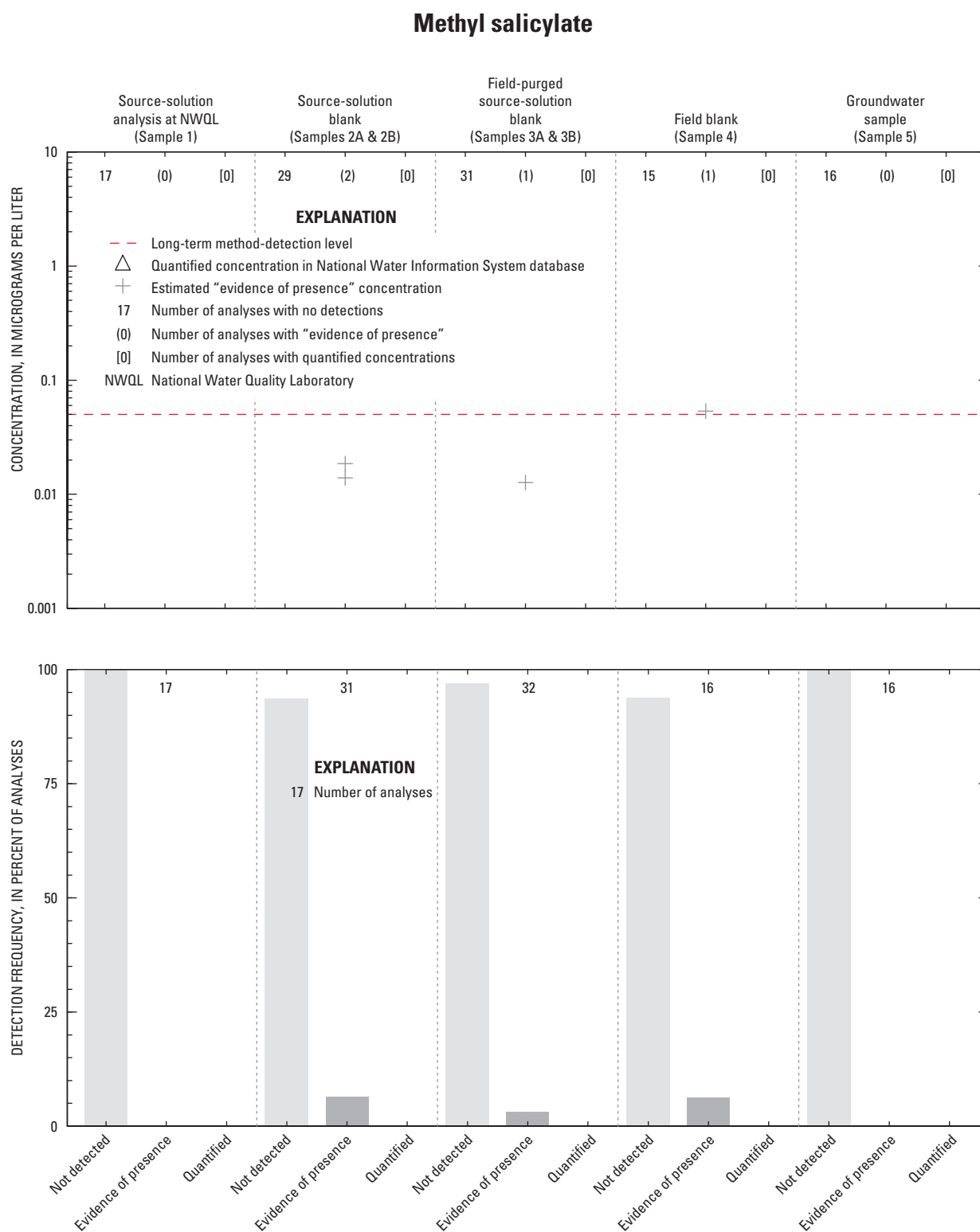


Figure A6-5. Concentrations and detection frequencies of methyl salicylate in analyses from the Field Contamination Study.

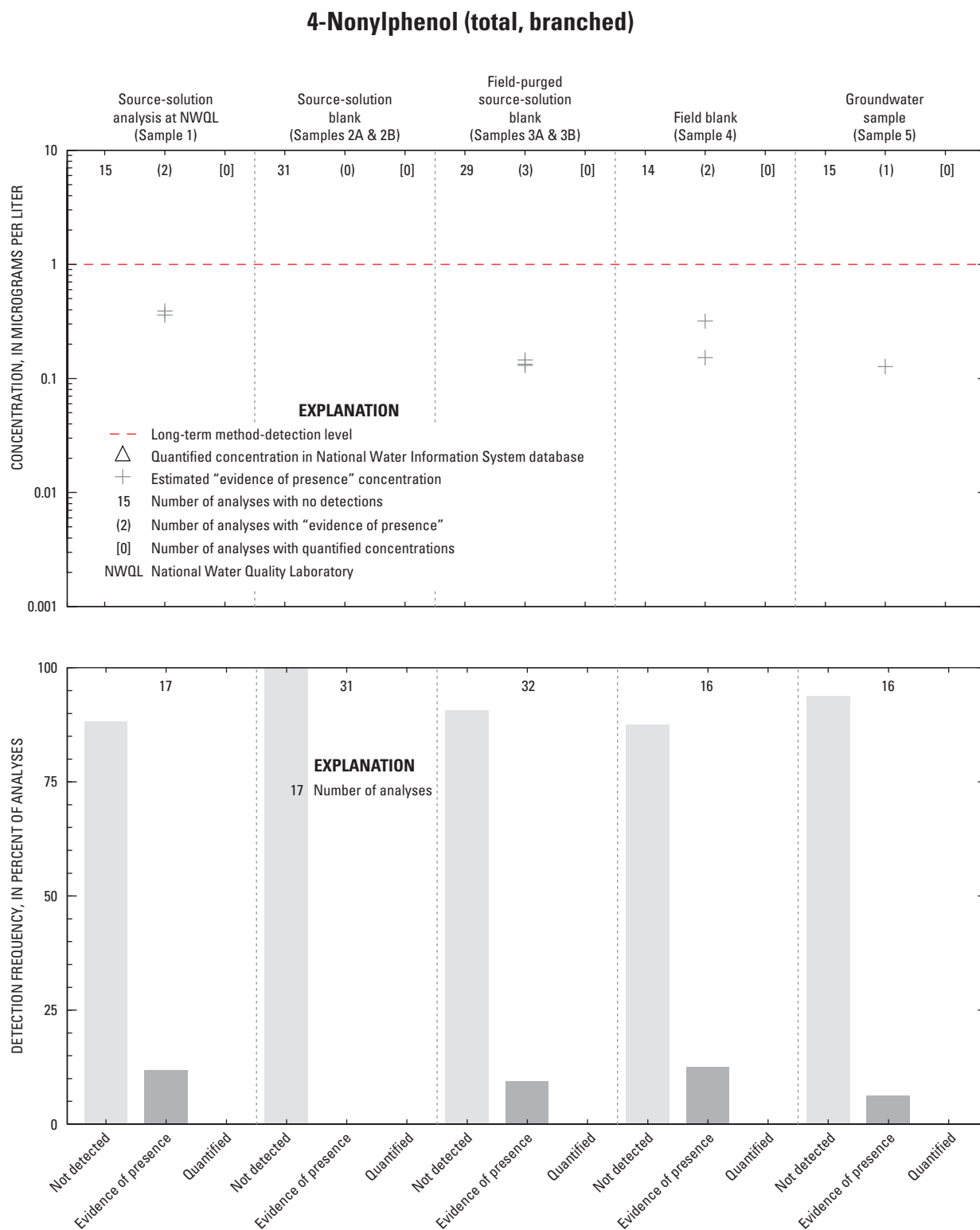


Figure A6-6. Concentrations and detection frequencies of 4-nonylphenol (total, branched) in analyses from the Field Contamination Study.

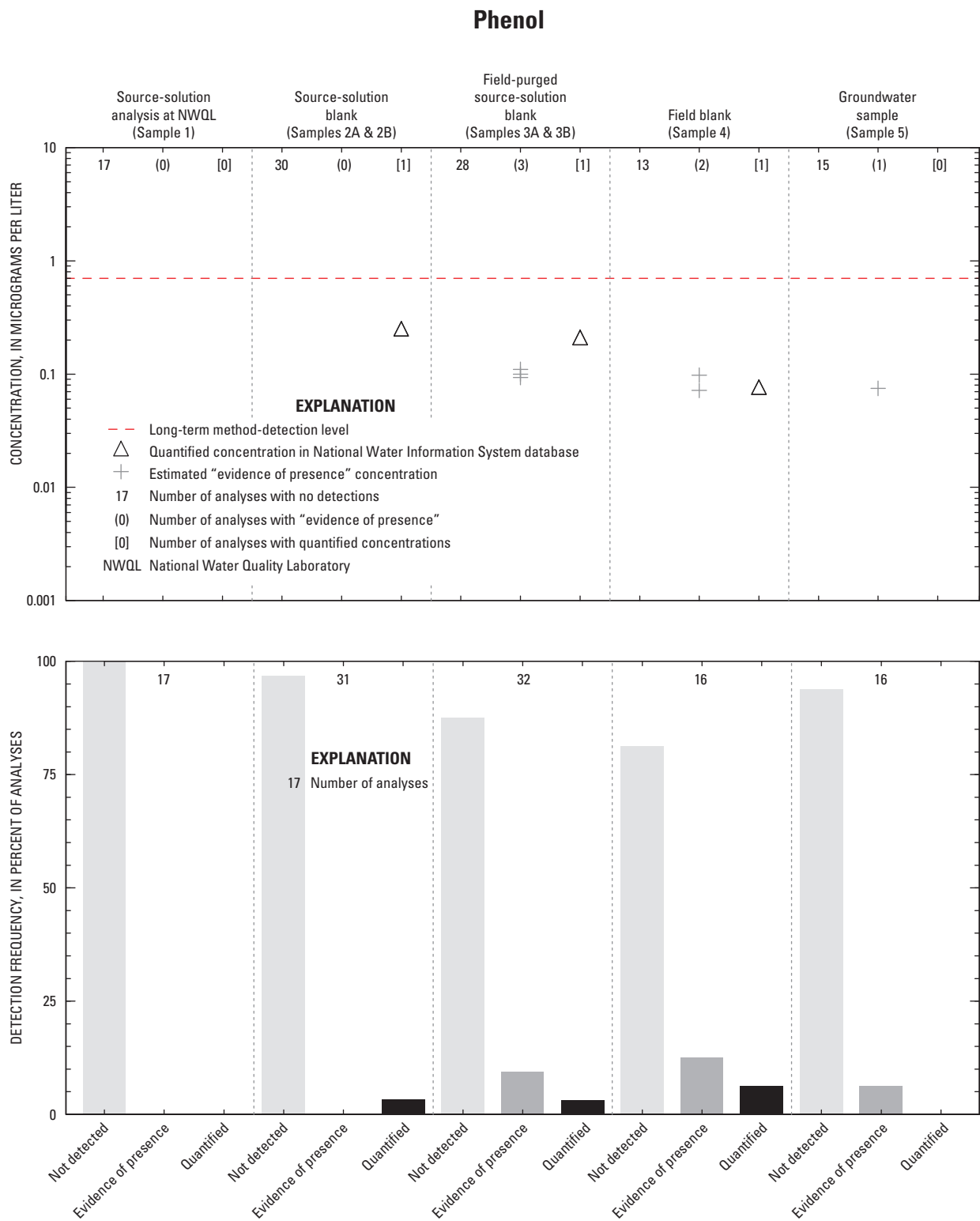


Figure A6–7. Concentrations and detection frequencies of phenol in analyses from the Field Contamination Study.

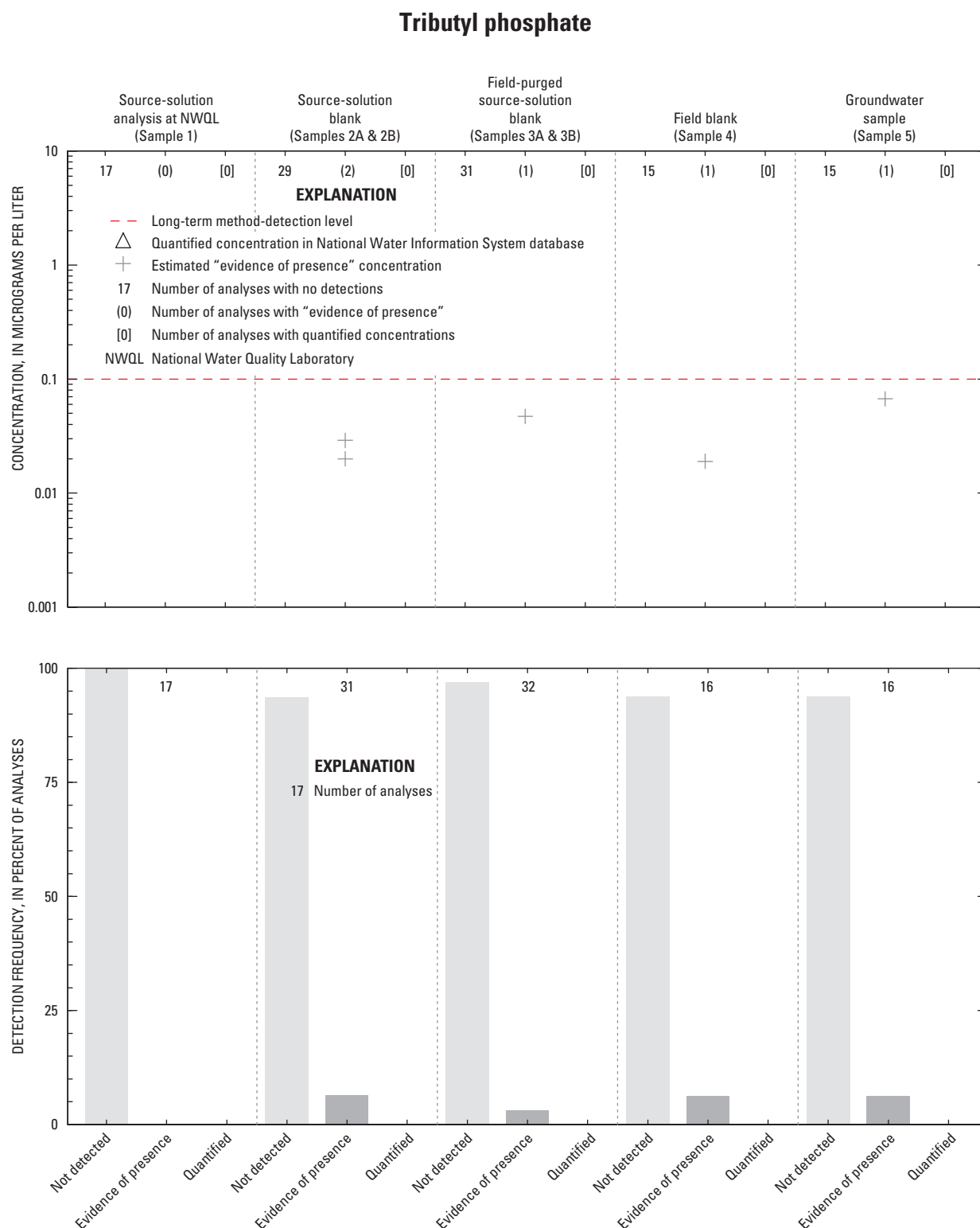


Figure A6–8. Concentrations and detection frequencies of tributyl phosphate in analyses from the Field Contamination Study.

Triphenyl phosphate

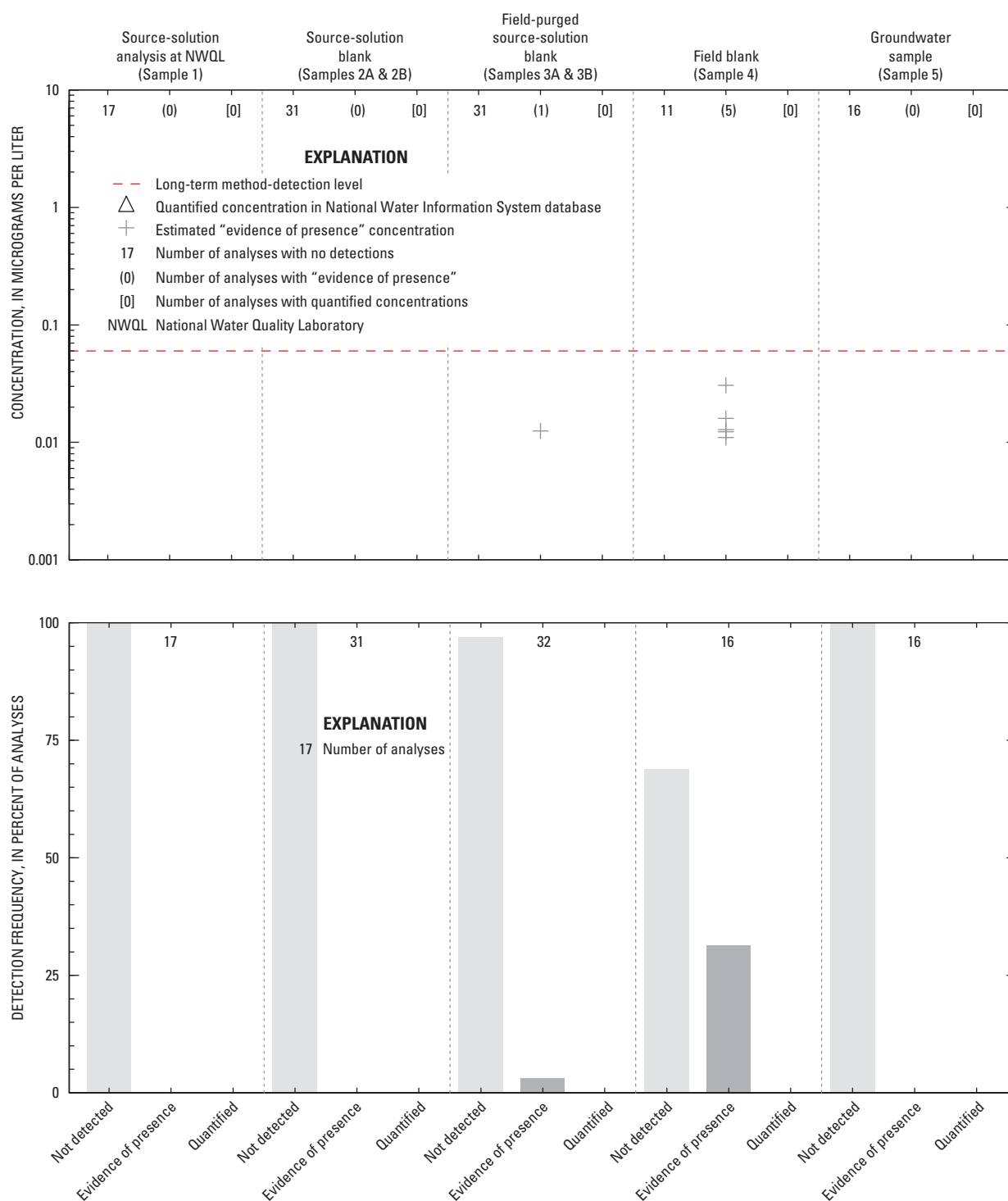


Figure A6-9. Concentrations and detection frequencies of triphenyl phosphate in analyses from the Field Contamination Study.

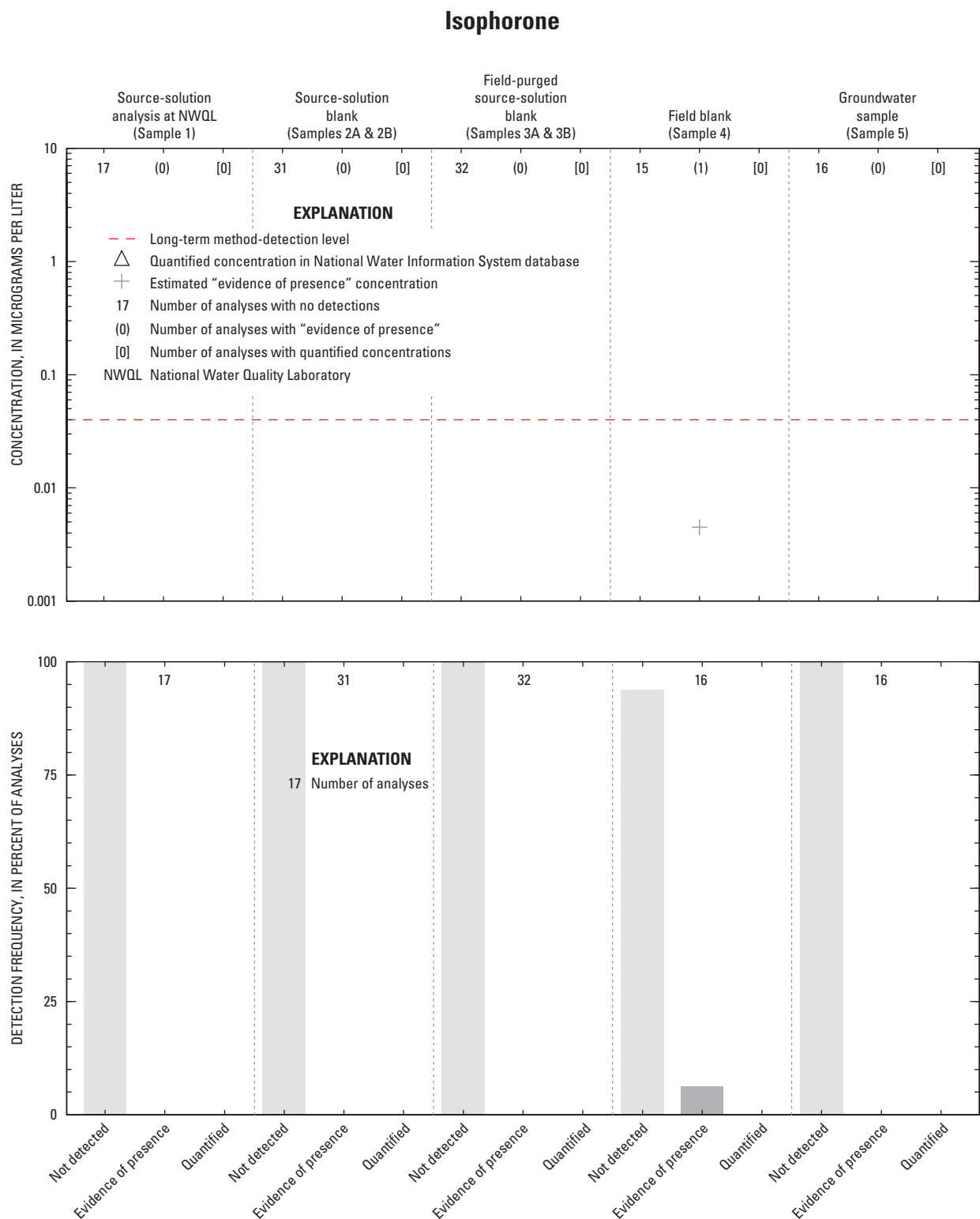


Figure A6–10. Concentrations and detection frequencies of isophorone in analyses from the Field Contamination Study.

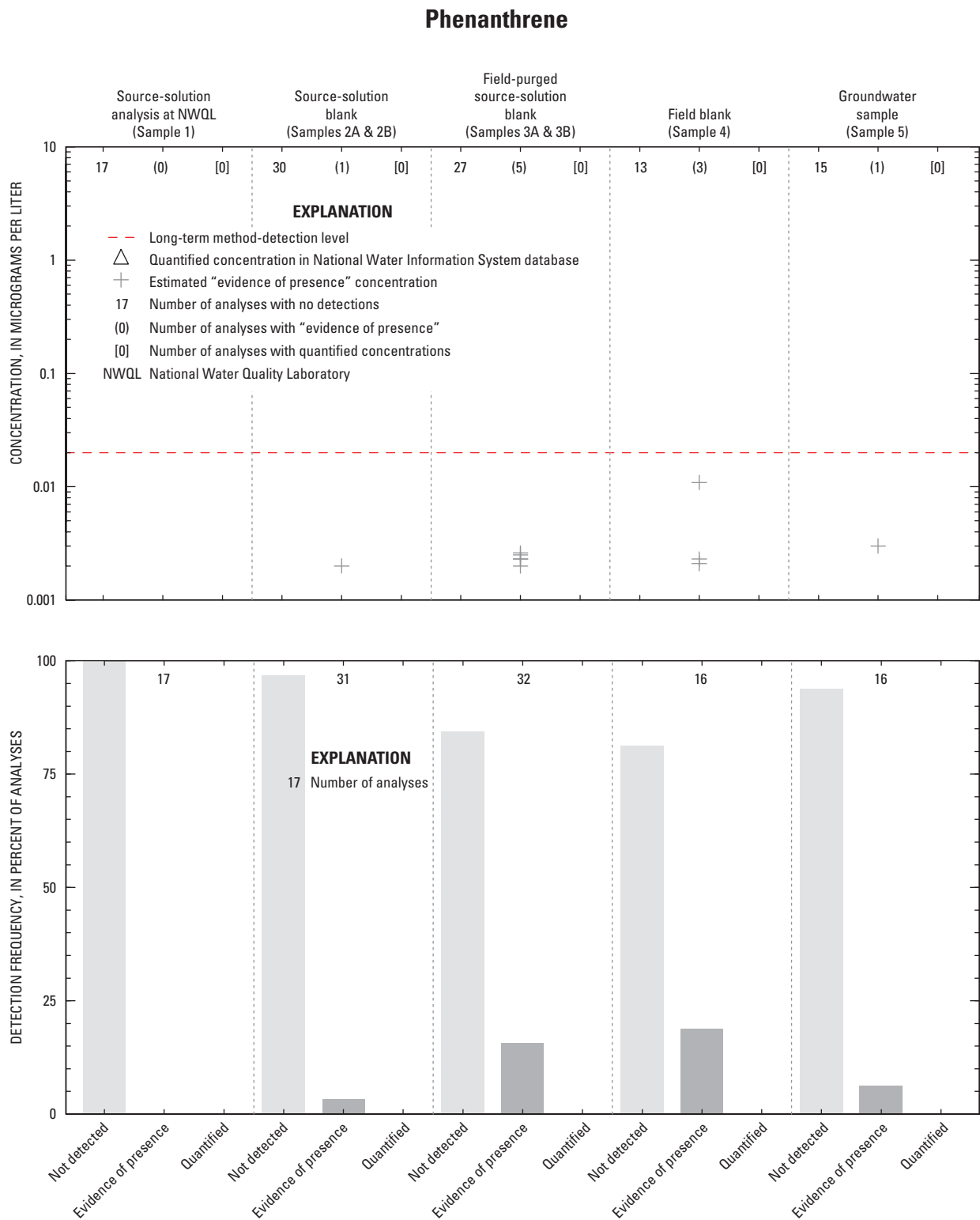


Figure A6–11. Concentrations and detection frequencies of phenanthrene in analyses from the Field Contamination Study.

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Back cover. Upper left: Assembled field-purge apparatus. Photograph by David Bender.
Lower right: Nitrogen-purging chamber frame. Photograph by David Bender.

