

Prepared in cooperation with the California State Water Resources Control Board
A product of the California Groundwater Ambient Monitoring and Assessment (GAMA) Program

Evaluation of Volatile Organic Compound (VOC) Blank Data and Application of Study Reporting Levels to Groundwater Data Collected for the California GAMA Priority Basin Project, May 2004 through September 2010



Scientific Investigations Report 2012–5139

Cover:

Left: Field crew member collecting VOC samples inside a mobile laboratory using long sampling lines. (Photograph by Cathy M. Munday, U.S. Geological Survey.)

Right: Field crew members collecting VOC samples at a well site using short sampling lines. (Photograph by Michael T. Land, U.S. Geological Survey.)

Evaluation of Volatile Organic Compound (VOC) Blank Data and Application of Study Reporting Levels to Groundwater Data Collected for the California GAMA Priority Basin Project, May 2004 through September 2010

By Miranda S. Fram, Lisa D. Olsen, and Kenneth Belitz

A product of the California Groundwater Ambient Monitoring and Assessment
(GAMA) Program

Prepared in cooperation with the California State Water Resources Control Board

Scientific Investigations Report 2012–5139

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

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2012

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit <http://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <http://www.usgs.gov/pubprod>

To order this and other USGS information products, visit <http://store.usgs.gov>

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this report is in the public domain, permission must be secured from the individual copyright owners to reproduce any copyrighted materials contained within this report.

Suggested citation:

Fram, M.S., Olsen, L.D., and Belitz, Kenneth, 2012, Evaluation of volatile organic compound (VOC) blank data and application of study reporting levels to groundwater data collected for the California GAMA Priority Basin Project, May 2004 through September 2010: U.S. Geological Survey Scientific Investigations Report 2012–5139, 94 p.

Contents

Abstract.....	1
Introduction	2
Use of Study Reporting Levels.....	4
Philosophy of Quality-Control Evaluation of Blanks.....	5
Purpose and Scope	6
Methods Used to Collect and Evaluate VOC Data.....	7
Field Methods.....	7
Groundwater Samples	7
Blanks	10
Laboratory Methods.....	11
Data Analysis Methods.....	14
Identification of Representative Field Blanks	15
Definition of Study Reporting Levels (SRLs).....	16
Binomial Probability Approach.....	16
Maximum Concentration Approach	18
Maximum LT-MDL Approach	18
Evaluation of Potential Sources of Contamination to Blanks and Groundwater Samples and Selection of Appropriate SRLs.....	18
Statistical Tests Used in Identification of Representative Field Blanks and Evaluation to Infer Potential Sources of Contamination	19
Quality-Control Assessment Results	20
Identification of VOCs for Which the SRL Approach Can be Applied and of Representative Quality-Control Field Blanks (QCFBs) for Use in Calculation of SRLs	20
Minimal Contamination from the Certified Blank Water	20
Acetone, 2-Butanone, and Tetrahydrofuran Contamination Associated with Methanol.....	20
Inadvertent Field Test of Contamination by Methanol.....	20
Acetone, 2-Butanone, and Tetrahydrofuran Contamination in Field Blanks.....	26
Acetone, 2-Butanone, and Tetrahydrofuran Contamination in Groundwater Samples	26
SRLs for Acetone, 2-Butanone, and Tetrahydrofuran.....	31
Differences Between Sample-Collection Equipment Configurations.....	31
Quality-Control Field Blanks (QCFBs)	32

Contents—Continued

Quality-Control Assessment Results—Continued	
Evaluation of Potential Sources of Contamination, Selection of SRLs, and Application of SRLs to Groundwater Data for VOCs Detected in Blanks	32
Hydrocarbons	32
Ethylbenzene, <i>m</i> - and <i>p</i> -Xylenes, <i>o</i> -Xylene, Benzene, and Styrene	32
Inferred Mechanisms of Contamination	38
SRLs for Ethylbenzene, <i>m</i> - and <i>p</i> -Xylenes, <i>o</i> -Xylene, Benzene, and Styrene	40
Toluene	45
Inferred Mechanisms of Contamination	45
SRL for Toluene	48
1,2,4-Trimethylbenzene	48
Inferred Mechanisms of Contamination	50
SRL for 1,2,4-Trimethylbenzene	53
Chlorinated Organic Solvents	54
Dichloromethane, 1,1-Dichloroethene, and Trichloroethene	54
Tetrachloroethene	54
Other VOCs	54
Bromodichloromethane and Trichlorofluoromethane	54
Carbon Disulfide	61
Inferred Source of Contamination	61
SRL for Carbon Disulfide	61
Chloroform	63
Inferred Source of Contamination	63
SRL for Chloroform	63
Application of SRLs and Maximum LT-MDLS	65
Effect of LT-MDL Changes on VOC Detection Frequencies	65
LT-MDLs and Probabilities of False-Positive Detections	67
Assessment of Methods Used for Determining Study Reporting Levels	67
Summary and Conclusions	69
Acknowledgments	71
References Cited	71
Appendix	74

Figures

Figure 1. Map of the 32 study units sampled for the California GAMA Priority Basin Project, May 2004 through September 2010	3
Figure 2. Graphs showing number of groundwater samples and field and source-solution blanks collected per month by the California GAMA Priority Basin Project, and number of laboratory instrument blanks analyzed per month for volatile organic compounds by the USGS National Water Quality Laboratory, May 2004 through September 2010	8
Figure 3. Graphs comparing detection frequencies in field blanks collected at production wells by the National Water-Quality Assessment (NAWQA) Program and detection frequencies in all field blanks collected with long and short sampling lines by the GAMA Priority Basin Project, and quality-control field blanks collected with long and short sampling lines and inferred to be without contamination by the methanol used to clean field equipment	22
Figure 4. Chromatograms for three vials of a field blank affected by methanol, California GAMA Priority Basin Project, June 25, 2007	25
Figure 5. Time-series graph for concentrations of acetone detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	27
Figure 6. Time-series graph for concentrations of 2-butanone detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	28
Figure 7. Time-series graph for concentrations of tetrahydrofuran detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	29
Figure 8. Time-series graph for concentrations of ethylbenzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	33
Figure 9. Time-series graph for concentrations of <i>m</i> - and <i>p</i> -xylenes detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	34
Figure 10. Time-series graph for concentrations of <i>o</i> -xylene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	35
Figure 11. Time-series graph for concentrations of benzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	36
Figure 12. Time-series graph for concentrations of styrene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	37
Figure 13. Relations between <i>m</i> - and <i>p</i> -xylenes and ethylbenzene, <i>o</i> -xylene, styrene, benzene, toluene, and 1,2,4-trimethylbenzene detected in field blanks, source-solution blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	39

Figures—Continued

Figure 14. Graph showing concentrations of study reporting levels (SRLs) established from field blanks collected for the California GAMA Priority Basin Project, May 2004 through September 2010, and SRLs established from field blanks collected at production wells for the National Water-Quality Assessment (NAWQA) Program	46
Figure 15. Time-series graph for concentrations of toluene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	47
Figure 16. Time-series graph for concentrations of 1,2,4-trimethylbenzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	49
Figure 17. Bar charts showing relations between detection frequencies of 1,2,4-trimethylbenzene in groundwater samples and blanks and whether or not samples for analysis of radon-222 were collected at the same site or previous site, and which GAMA field vehicle visited the site, California GAMA Priority Basin Project, May 2004 through September 2010	51
Figure 18. Time-series graph for concentrations of dichloromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	55
Figure 19. Time-series graph for concentrations of 1,1-dichloroethene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	56
Figure 20. Time-series graph for concentrations of tetrachloroethene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	57
Figure 21. Time-series graph for concentrations of trichloroethene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	58
Figure 22. Time-series graph for concentrations of bromodichloromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	59
Figure 23. Time-series graph for concentrations of trichlorofluoromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	60
Figure 24. Time-series graph for concentrations of carbon disulfide detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	62
Figure 25. Time-series graph for concentrations of chloroform detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010	64
Figure 26. Bar charts showing percentages of groundwater samples in concentration range categories for different long-term method detection levels (LT-MDLs) for chloroform and tetrachloroethene	66

Tables

Table 1. Study unit names, sampling dates, Data Series Reports, and sampling schedules, California GAMA Priority Basin Project, May 2004 through September 2010	4
Table 2. Long-term method detection levels (LT-MDLs) used by the U.S. Geological Survey National Water Quality Laboratory for volatile organic compounds (VOCs), and VOCs detected in groundwater samples and source-solution or field blanks, California GAMA Priority Basin Project, May 2004 through September 2010	12
Table 3. Identification of steps in collection, handling, and analysis of blanks and groundwater samples during which contamination may occur, California GAMA Priority Basin Project	16
Table 4. Detection frequencies in field, source-solution, and laboratory blanks and in groundwater samples for the 18 volatile organic compounds (VOCs) and tentatively identified compounds (TICs) detected in field or source-solution blanks, California GAMA Program, Priority Basin Project, May 2004 through September 2010	21
Table 5. Volatile organic compounds (VOCs) detected in a field blank analyzed in triplicate and determined to be affected by residual methanol from equipment cleaning, California GAMA Priority Basin Project, May 2004 through September 2010	24
Table 6. Detection frequencies for the 17 VOCs and the TICs detected in field blanks and results of statistical tests for differences between subsets of the field blanks, California GAMA Priority Basin Project, May 2005 through September 2010	30
Table 7. Values of study reporting levels (SRLs) for the 18 VOCs detected in field blanks or source-solution blanks determined from the set of 167 quality-control field blanks using four methods, and changes in detection frequencies in the set of 2,026 groundwater samples with application of the different SRLs, California GAMA Priority Basin Project, May 2004 through September 2010	41
Table 8. Study reporting levels (SRLs) and number of data censored by application of the SRLs, California GAMA Priority Basin Project, May 2004 through September 2010	42
Table 9. Raw detection frequencies by study unit of volatile organic compounds (VOCs) before and after application of study reporting units (SRLs), California GAMA Priority Basin Project, May 2004 through September 2010	43
Table 10. Probability of false-positive detections at fractions of the long-term method detection level (LT-MDL), and numbers of detections with concentrations below the threshold, California GAMA Priority Basin Project, May 2004 through September 2010	67

Conversion Factors and Abbreviations and Acronyms

Conversion Factors

Inch/foot to International System of Units (SI)

Multiply	By	To obtain
	Length	
inch (in.)	2.54	centimeter (cm)
foot (ft)	0.3048	meter (m)

International System of Units (SI) to ounce/quart units

Multiply	By	To obtain
	Length	
meter (m)	3.281	feet (ft)
	Volume	
liter (L)	1.05669	quart (qt)
milliliter (mL)	0.033814	ounce (oz)
	Mass	
gram (g)	0.035274	ounce (oz)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F}=(1.8\times^{\circ}\text{C})+32$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g/L}$). One milligram per liter is equivalent to 1 part per million (ppm); 1 microgram per liter is equivalent to 1 part per billion (ppb).

Abbreviations and Acronyms

CDF	cumulative distribution function
CDPH	California Department of Public Health
BD	binomial distribution
GAMA	Groundwater Ambient Monitoring and Assessment Program
LRL	laboratory reporting level
LT-MDL	long-term method detection level
MDL	method detection level
na	no data available
NAWQA	National Water-Quality Assessment (a USGS program)
NWQL	National Water Quality Laboratory (a USGS laboratory)
PBP	Priority Basin Project
PVC	polyvinyl chloride
QC	quality control
QCFB	quality-control field blanks
SRL	study reporting level
TIC	tentatively identified compound
TU	tritium unit
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VOC	volatile organic compound

Evaluation of Volatile Organic Compound (VOC) Blank Data and Application of Study Reporting Levels to Groundwater Data Collected for the California GAMA Priority Basin Project, May 2004 through September 2010

By Miranda S. Fram, Lisa D. Olsen, and Kenneth Belitz

Abstract

Volatile organic compounds (VOCs) were analyzed in quality-control samples collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project. From May 2004 through September 2010, a total of 2,026 groundwater samples, 211 field blanks, and 109 source-solution blanks were collected and analyzed for concentrations of 85 VOCs. Results from analyses of these field and source-solution blanks and of 2,411 laboratory instrument blanks during the same time period were used to assess the quality of data for the 2,026 groundwater samples. Eighteen VOCs were detected in field blanks or source-solution blanks: acetone, benzene, bromodichloromethane, 2-butanone, carbon disulfide, chloroform, 1,1-dichloroethene, dichloromethane, ethylbenzene, tetrachloroethene, styrene, tetrahydrofuran, toluene, trichloroethene, trichlorofluoromethane, 1,2,4-trimethylbenzene, *m*- and *p*-xylenes, and *o*-xylene.

The objective of the evaluation of the VOC-blank data was to determine if study reporting levels (SRLs) were needed for any of the VOCs detected in blanks to ensure the quality of the data from groundwater samples. An SRL is equivalent to a raised reporting level that is used in place of the reporting level used by the analyzing laboratory [long-term method detection level (LT-MDL) or laboratory reporting level (LRL)] to reduce the probability of reporting false-positive detections. Evaluation of VOC-blank data was done in three stages: (1) identification of a set of representative quality-control field blanks (QCFBs) to be used for calculation of SRLs and identification of VOCs amenable to the SRL approach, (2) evaluation of potential sources of contamination to blanks and groundwater samples by VOCs detected in field blanks, and (3) selection of appropriate SRLs from among four potential SRLs for VOCs detected in field blanks and application of those SRLs to the groundwater data. An important conclusion from this study is that to ensure the quality of the data from groundwater samples, it was necessary to apply different methods of determining SRLs from field blank data to different VOCs, rather than use the same method for all VOCs.

Four potential SRL values were defined by using three approaches: two values were defined by using a binomial probability method based on one-sided, nonparametric upper confidence limits, one was defined as equal to the maximum concentration detected in the field blanks, and one was defined as equal to the maximum laboratory method detection level used during the period when samples were collected for the project. The differences in detection frequencies and concentrations among different types of blanks (laboratory instrument blanks, source-solution blanks, and field blanks collected with three different sampling equipment configurations) and groundwater samples were used to infer the sources and mechanisms of contamination for each VOC detection in field blanks. Other chemical data for the groundwater samples (oxidation-reduction state, co-occurrence of VOCs, groundwater age) and ancillary information about the well sites (land use, presence of known sources of contamination) were used to evaluate whether the patterns of detections of VOCs in groundwater samples before and after application of potential SRLs were plausible. On this basis, the appropriate SRL was selected for each VOC that was determined to require an SRL.

The SRLs for ethylbenzene [0.06 microgram per liter ($\mu\text{g/L}$)], *m*- and *p*-xylenes (0.33 $\mu\text{g/L}$), *o*-xylene (0.12 $\mu\text{g/L}$), toluene (0.69 $\mu\text{g/L}$), and 1,2,4-trimethylbenzene (0.56 $\mu\text{g/L}$) corresponded to the highest concentrations detected in the QCFBs and were selected because they resulted in the most censoring of groundwater data. Comparisons of hydrocarbon ratios in groundwater samples and blanks and comparisons between detection frequencies of the five hydrocarbons in groundwater samples and different types of blanks suggested three dominant sources of contamination that affected groundwater samples and blanks: (1) ethylbenzene, *m*- and *p*-xylenes, *o*-xylene, and toluene from fuel or exhaust components sorbed onto sampling lines, (2) toluene from vials and the source blank water, and (3) 1,2,4-trimethylbenzene from materials used for collection of samples for radon-222 analysis.

2 VOC Blank Data and Study Reporting Levels, California GAMA PBP, 2004–2010

The SRL for carbon disulfide (0.03 µg/L) corresponded to the maximum LT-MDL. The most probable source of carbon disulfide contamination is the gloves worn by field and laboratory personnel. Most carbon disulfide detections in groundwater samples occurred in anoxic samples, which is consistent with predicted occurrence of carbon disulfide formed naturally under sulfate-reducing conditions.

No SRL was needed for chloroform for groundwater samples collected at production wells; the detection frequency of chloroform in the QCFBs was less than 3 percent. The maximum LT-MDL (0.02 µg/L) was established as the SRL for chloroform for groundwater samples collected at monitoring wells. No SRLs were established for benzene, bromodichloromethane, 1,1-dichloroethene, dichloromethane, styrene, tetrachloroethene, trichloroethene, or trichlorofluoromethane; the detection frequencies of these VOCs in the QCFBs were less than 3 percent.

The SRL approach could not be applied to acetone, 2-butanone, or tetrahydrofuran because it was not possible to define threshold concentrations above which one could be reasonably certain that detections in groundwater samples were not the result of contamination. The highest concentrations of these three VOCs occurred in groundwater samples and field blanks collected at sites where contamination with the methanol used to clean field equipment or the cement used to join polyvinyl chloride (PVC) piping was documented.

The 2,026 groundwater samples had a total of 2,580 detections of 60 different VOCs. Of those 2,580 detections, 489 were censored by application of the SRLs determined in this report. Of the remaining detections, 231 had concentrations below the highest LT-MDL used during the study period. LT-MDLs changed by less than a factor of 2 between May 2004 and September 2010 for most VOCs, and the changes did not significantly alter reporting of detections with low concentrations. Therefore, censoring at the highest LT-MDL for VOCs that do not have SRLs does not appear to be necessary to ensure comparability between study units sampled at different times during that period.

Introduction

The California State Water Resources Control Board, in collaboration with the U.S. Geological Survey (USGS) and the Lawrence Livermore National Laboratory, initiated the Groundwater Ambient Monitoring and Assessment (GAMA) Program (<http://www.swrcb.ca.gov/gama>) to assess the quality of groundwater in aquifers used for drinking-water supply and to establish a baseline groundwater-quality

monitoring program. The GAMA Program currently consists of four projects: the GAMA Priority Basin Project (PBP), conducted by the USGS (<http://ca.water.usgs.gov/gama>), the GAMA Domestic Well Project and GeoTracker GAMA, both conducted by the State Water Resources Control Board, and GAMA Special Studies, conducted by Lawrence Livermore National Laboratory. The USGS, in collaboration with the State Water Resources Control Board, developed the project design for the PBP (Belitz and others, 2003; California State Water Resources Control Board, 2003). For the PBP, California's groundwater basins were prioritized primarily on the basis of the number of municipal and community drinking-water supply wells. The 116 priority basins, representing 95 percent of the wells in basins, as well as selected areas outside of defined groundwater basins, were grouped into 35 study units to be sampled between 2004 and 2012. Groundwater samples were collected from 2,026 sites in the first 32 study units from May 2004 through September 2010 ([fig. 1](#); [tables 1, A1](#)).

Volatile organic compounds (VOCs) were analyzed in samples collected from all 2,026 sites. VOC analyses were conducted at the USGS National Water Quality Laboratory (NWQL). The NWQL uses methods that detect concentrations much lower than the detection limits required for analyses made for regulatory purposes (California Department of Public Health, 2011). Detections of VOCs (and other anthropogenic organic compounds) at these low concentrations may be used to trace water from the landscape, where it may have been affected by anthropogenic contaminants, to aquifer systems.

Before interpretations of environmental processes are made using VOC data from groundwater samples, the potential presence of confounding VOC detections that are the result of contamination during sample collection, handling, or analysis must be evaluated. Contamination during sample collection, handling, or analysis (also known as “extrinsic” contamination) may be the result of contact between groundwater samples and surfaces, liquids, or vapors encountered during any of these steps. Detections in groundwater samples that are the result of extrinsic contamination do not reflect the occurrence of VOCs in the aquifer from which the groundwater sample was collected. These must be carefully isolated from VOC detections in a groundwater sample that are representative of VOC contamination of the aquifer (that is, intrinsic contamination). All VOC contamination discussed in this report is extrinsic.

In this study, field blanks were collected at 211 of the sites at which groundwater samples were collected. VOC data from the field blanks, associated source-solution blanks, and laboratory instrument blanks analyzed during the same time period were used to evaluate extrinsic contamination.



Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006,
Albers Equal Area Conic Projection

Figure 1. The 32 study units sampled for the California GAMA Priority Basin Project, May 2004 through September 2010. See [table 1](#) for study unit names.

Table 1. Study unit names, sampling dates, Data Series Reports, and sampling schedules, California GAMA Priority Basin Project, May 2004 through September 2010.

[USGS, U.S. Geological Survey. **Map codes** (figure 1): D, Desert study units; M, Mountain study units; N, North and Central Coast study units; S, South Coast study units; V, Central Valley study units]

Study unit	Map code	Sampling dates	Data Series Report number
San Diego Drainages	S5	May–July 2004	129
North San Francisco Bay	N3	August–November 2004	167
Northern San Joaquin	V4	December 2004–February 2005	196
Southern Sacramento Valley	V3	March–June 2005	285
San Gabriel–San Fernando	S3	May–July 2005	356
Monterey–Salinas	N6	July–September 2005	258
Southeast San Joaquin	V7	October–December 2005	351
Kern Basin	V8	January–March 2006	337
Central Eastside	V5	March–May 2006	325
Central Sierra Nevada	M4	May 2006	335
Southern Sierra Nevada	M3	June 2006	301
Middle Sacramento Valley	V2	June–August 2006	385
Southern California Coastal Plain	S2	August–November 2006	387
Owens–Indian Wells	M2	September–December 2006	427
Santa Ana–San Jacinto	S4	November 2006–February 2007	404
Coachella Valley	D3	February–March 2007	373
Santa Clarita–Ventura	S1	April–May 2007	408
San Francisco Bay	N4	April–June 2007	396
Tahoe–Martis	M5	June–September 2007	432
Colorado River	D4	October–December 2007	474
Northern Sacramento Valley	V1	October 2007–January 2008	452
Antelope Valley	D1	January–April 2008	479
Mojave	D2	February–April 2008	440
Madera–Chowchilla	V6	April–May 2008	455
Santa Maria–Lompoc	N7	May–November 2008	504
Sierra Nevada Regional	M1	June–October 2008	534
Livermore–Gilroy–Cuyama	N5	August–November 2008	463
Central Desert–Borrego	D5	December 2008–March 2010	659
Ukiah–Clear Lake	N2	June–July 2009	609
Eureka–Crescent City	N1	July–October 2009	609
Western San Joaquin Valley	V9	March–June 2010	706
Cascades–Modoc Plateau	M6	July–October 2010	688

Use of Study Reporting Levels

Contamination of a sample during sample collection, handling, or analysis may result in addition of constituents that are being analyzed—in this case, VOCs. Such addition may increase the concentration of a constituent already present at detectable levels in the sample, or result in detection of a constituent that would not otherwise be reported as detected.

Comparison of concentrations in environmental samples to the concentrations in benchmarks established for drinking water provides a context for the concentrations detected in groundwater samples (for example, Belitz and others, 2010; Landon and others, 2010; Toccalino and others, 2010). For the GAMA-PBP, the benchmarks used for comparison were those

from the U.S. Environmental Protection Agency (USEPA) and the California Department of Public Health (CDPH), and included regulatory (USEPA and CDPH maximum contaminant levels) and non-regulatory benchmarks (CDPH notification levels, and USEPA lifetime health advisory levels and risk-specific doses) (California Department of Public Health, 2006, 2008, 2010; U.S. Environmental Protection Agency, 2009a,b). For most VOCs, contamination generally does not affect use of the data to assess whether concentrations in environmental samples are above or below benchmarks; however, data for VOCs often are reported as detection frequencies at any concentration, and the presence of low concentrations of VOCs can be used as a tracer indicating the presence of a component of modern groundwater. Therefore,

extrinsic contamination that results in detection of a VOC that would otherwise not be reported as detected may have a significant effect on interpretation of the environmental data.

A detection is confirmation of a compound's presence in a sample relative to specified reporting criteria. One typical practice is to use the data as reported by the laboratory. The USGS NWQL's reporting conventions for VOCs are discussed in the section "[Laboratory Methods](#)." The GAMA Program uses study reporting levels (SRLs) to limit the effects of potential extrinsic contamination indicated by detections in blanks. SRLs are defined at a higher concentration than the reporting levels used by the laboratory. By raising the reporting level, samples with low concentrations of VOCs that may be the result of extrinsic contamination are re-defined as having non-detections. This avoids over-estimating the prevalence of the VOC in the aquifer system. An SRL may also be defined to provide a uniform reporting level if laboratory reporting levels have changed over the lifetime of the project. Finally, an SRL may be defined to match the project's data-quality objectives for constraints on the probabilities of false positives and false negatives.

Detections in environmental samples with concentrations less than or equal to the SRL are then considered to have an unacceptably high probability of resulting from contamination by the processes that affected the field blanks. A remark code is added to these results, and the detections reported by the laboratory are not counted as detections in the environmental data. Environmental samples having concentrations greater than the SRL may also have been contaminated, but the probability that the amount of contamination would have been sufficient to result in a reported detection, when the true concentration was a non-detection, is acceptably low.

Philosophy of Quality-Control Evaluation of Blanks

There are three philosophical issues to consider when designing methods for quality-control evaluation of blanks to determine SRLs. The first issue is whether contamination is a process that results in contamination of samples with up to a certain amount of a constituent (characteristic concentration), or a process that affects a certain percentage of samples (characteristic frequency), or a process that results in addition of an unpredictable amount of a constituent to an unpredictable percentage of samples. Methods based on the premise that contamination has a characteristic concentration generally work by ranking the concentrations in the field blanks and selecting a threshold rank whose concentration is defined as the SRL. Methods based on the premise that contamination has a characteristic frequency assume that the detection frequency in the field-blank dataset is the frequency with which environmental samples are contaminated by the process that affects field blanks. The SRL is then defined by

the concentration in environmental samples below which the detection frequency in the environmental samples is equal to the detection frequency at any concentration in the field blanks. Such a method implicitly assumes that contamination is responsible for the detections with the lowest concentrations within the distribution observed in the environmental samples. It is also possible that the amount and frequency of contamination of environmental samples are not predictable from the field-blank data. In this case, the field blanks cannot be used to define an SRL, and the quality of the data for environmental samples cannot be assessed.

The second philosophical issue is that field blanks, source-solution blanks, and groundwater samples may be treated either as independent populations (statistical approach) or as paired samples (deterministic approach). In deterministic approaches, information about the sequence of collection of blanks and environmental samples is used in the evaluation; in statistical approaches, the blanks and environmental samples are treated as independent populations. In a deterministic method, paired field blank and environmental samples and paired field blank and source-solution blank samples are examined. A deterministic method is often believed to be appropriate when looking for evidence of carryover between sequential samples (field blank/environmental sample pairs) or for evidence of prior contamination of source blank water (field blank/source-solution blank pairs) (for example, Bender and others, 2011). However, there is a universal drawback of this approach. If field blanks, source-solution blanks, and environmental samples are not assumed to be independent populations, then quality-control assessment requires collecting a field blank and a source-solution blank with every environmental sample.

In statistical approaches, a field blank collected at a particular site is assumed to be statistically representative of conditions under which environmental samples are collected at all sites. Field blanks are not directly compared to the "paired" environmental sample collected at the same site. Similarly, a source-solution blank collected at a particular site is considered representative of source-solution blanks that could be collected at any site. Methods that determine the SRL by identifying a threshold rank and defining the concentration in the field blank with that rank as the SRL, and methods that involve comparison of cumulative frequency distributions (CDF), are based on the assumption that blanks and environmental samples are independent populations. Statistical approaches were used for this study.

The third philosophical issue is that different methods for determining SRLs may be used for different constituents, or the same method may be used for all constituents. In general, analyses of blanks to assess the quality of environmental data have been based on a single method being applied to all constituents (for example, Martin and others, 1999; Olsen and others, 2010; Bender and others, 2011). However, in a large group of constituents like the VOCs, there will be multiple

mechanisms by which contamination may be introduced during sample collection, handling, and analysis. VOCs with different sources and physical and chemical properties will be affected by different contamination mechanisms, thus, it may be necessary to use different methods for determining SRLs for different VOCs. This approach requires the ability to make accurate inferences both from patterns of detections in blanks and environmental samples and about likely mechanisms of contamination for different VOCs.

In addition to the philosophical issues, it is important to consider the robustness of the results when selecting an approach to determine SRLs from field-blank data. In this context, robustness refers to how sensitive a particular screening method is to small changes in the field-blank dataset. For example, use of a threshold, such as the concentration in a field blank with a specified rank, would not be robust if picking one rank up or down produced radically different results in terms of the percentage of the environmental data that were then below the SRL. In this context, ‘rank’ refers to ordinal number of a particular field blank in a set of field blanks organized in sequence by concentration.

Computed detection frequencies of VOCs in groundwater also are sensitive to data reporting conventions. Reporting conventions commonly are defined to ensure that the data meet criteria of acceptable probability for differentiating between true detections and false-positive detections. The primary metric used by the USGS NWQL for defining detections is the long-term method detection level (LT-MDL); however, for the VOCs, the NWQL also reports concentrations below the LT-MDL (Connor and others, 1998). Detections below the LT-MDL have a greater than 1-percent probability of being false-positive detections (Childress and others, 1999). Reporting data below the LT-MDL is not in itself a problem; however, the probabilities of false-positive detections should be evaluated in comparison to project data-quality objectives. In addition, LT-MDLs may change over time, potentially resulting in a variably censored dataset. To compare detection frequencies across the period of study, a dataset may need to be re-censored to a common reporting level (for example, Zogorski and others, 2006).

Purpose and Scope

The purpose of evaluating VOC-blank data is to characterize potential contamination of environmental samples during sample collection, handling, and analysis (extrinsic contamination). This characterization is necessary to distinguish between VOC detections that may be due to extrinsic contamination and VOC detections that are representative of VOC concentrations in the aquifer from which the sample was collected. SRLs that are higher than the reporting levels used by the laboratory may be defined for VOCs having evidence for extrinsic contamination. Detections

with concentrations below the SRLs are considered to have an unacceptably high probability of resulting from contamination, and therefore should not be considered detections for the purpose of interpreting the environmental data.

The purposes of this report are as follows:

- To present multiple methods for evaluating blanks and establishing SRLs, and to describe the processes used to select the appropriate SRL for each compound.
- To evaluate which field blanks are representative of processes likely to affect environmental samples, and if there are differences between field blanks collected with different sample-collection equipment configurations.
- To present results of a field experiment conducted to demonstrate the effect of contamination of field blanks with the methanol used to clean sample-collection equipment.
- To infer likely sources of VOC contamination during sample collection, handling, and analysis on the basis of comparison of detection frequencies and concentrations in field blanks, source-solution blanks, laboratory instrument blanks, and environmental samples.
- To put SRLs in context by comparing them to LT-MDLs and by comparing the effects of application of different SRLs on the environmental dataset.

The work presented here is based on 2,026 groundwater samples, 211 field blanks, and 109 source-solution blanks collected from May 2004 through September 2010 for the first 32 study units of the California GAMA-PBP, and 2,411 laboratory instrument blanks analyzed during the same period. The groundwater samples were collected from production wells by using two different sampling equipment configurations (long sampling lines and short sampling lines) and from monitoring wells with monitoring-well sampling equipment.

An evaluation of blanks is presented for each of the 18 VOCs that were detected in field or source-solution blanks (acetone, benzene, bromodichloromethane, carbon disulfide, chloroform, 1,1-dichloroethene, dichloromethane, ethylbenzene, 2-butanone, styrene, tetrachloroethene, tetrahydrofuran, toluene, trichloroethene, trichlorofluoromethane, 1,2,4-trimethylbenzene, *m*- and *p*-xylenes, and *o*-xylene).

The methods presented for evaluation of blanks and for selection of SRLs are widely applicable and can be used by USGS and non-USGS scientists who work with large datasets of water-quality measurements from blanks and environmental samples. This report makes inferences about the sources of VOC contamination on the basis of comparisons between

detection frequencies in different types of blanks and our understanding of field and laboratory practices. Targeted studies to evaluate these inferences were not undertaken as part of this project.

The SRLs established in this report can be used for data reporting and interpretive data analysis for all USGS-GAMA projects. The SRLs also can be used by other USGS groundwater studies, such as National Water-Quality Assessment (NAWQA) Program studies, that used sampling methods similar to those used by the GAMA-PBP. The SRLs established in this report may be particularly useful for projects that have smaller quality-control (QC) datasets than those used for GAMA projects. These smaller QC datasets limit researchers' ability to make comprehensive QC assessments and develop their own SRLs.

Methods Used to Collect and Evaluate VOC Data

Methods used to collect and evaluate VOC data for this study include (1) field methods for collecting groundwater samples and blanks; (2) laboratory methods for analysis of all samples; (3) data analysis methods for identifying representative field blanks and calculating SRLs; (4) evaluation methods for inferring potential sources of contamination and selecting appropriate SRLs; and (5) statistical methods for testing the significance of differences between subsets of samples.

Field Methods

Because the purpose of this evaluation of VOC field-blank data is to characterize potential contamination of environmental samples, the data collection process will be described for the groundwater samples as well as for the field and source-solution blanks. Groundwater samples were collected for VOC analysis from May 2004 through September 2010 from 2,026 sites in 32 study units distributed throughout California ([fig. 1](#)). Field blanks were collected at 211 of the sites (10.4 percent). Groundwater sample data, along with assessments of the corresponding QC data on a study unit basis, are given in USGS Data Series Reports for each study unit ([table 1](#)). Of the 2,026 sites, 167 were monitoring wells, 34 were developed springs, and 1,825 were production wells.

Groundwater Samples

Groundwater samples to be used for VOC analysis were collected in accordance with the protocols established by the USGS National Field Manual (U.S. Geological Survey, variously dated). These protocols ensure that a sample that is representative of the groundwater in the aquifer is collected from each site and that samples are handled in a consistent way that minimizes the potential for contamination of the samples. Three protocols were used ([fig. 2A](#)):

- monitoring-well pumps for the 167 monitoring wells;
- short sampling lines for the 34 developed springs and 1,199 of the production wells; and
- long sampling lines for the other 626 production wells.

“Short” and “long” refer to the length of the Teflon® tubing used to route the water from the well to the sample bottles. For sites sampled with short sampling lines, the Teflon® tubing attached to the sampling point was approximately 18 inches (in.) long, and samples were collected outdoors at the sampling point. For sites sampled with long sampling lines, a 25-foot (ft) or 32-ft length of Teflon® tubing was attached to the sampling point and routed inside a mobile laboratory. On rare occasions, the two lengths of tubing were connected to each other (making 57 ft).

The GAMA-PBP used a tiered sampling strategy in many study units. Samples for a core suite of analytes were collected at all wells, and samples for a larger suite of analytes were collected at a subset of the wells. Short sampling lines generally were used at sites where samples for the core suite of analytes were being collected, and long sampling lines generally were used at sites where samples for the larger suite of analytes were being collected. Both the long and short sampling line configurations were used in 24 study units; only the long sampling line configuration was used in 6 study units. For two study units where vehicular access to many of the sites was limited, only the short sampling line configuration was used.

Many of the wells sampled by GAMA were production wells that were in continuous use; therefore, no additional purging of the wells was required. Sampling lines were attached to the well, and water was routed through a flow-through chamber with a multi-parameter probe for measurement of field parameters (water temperature, specific conductance, pH, and dissolved oxygen). Field parameter readings were recorded every 5 minutes, and sample collection commenced after at least four consecutive readings with the same values. For wells that were not in continuous use, wells were pumped to purge at least three casing-volumes of water from the well before measurement of field parameters began.

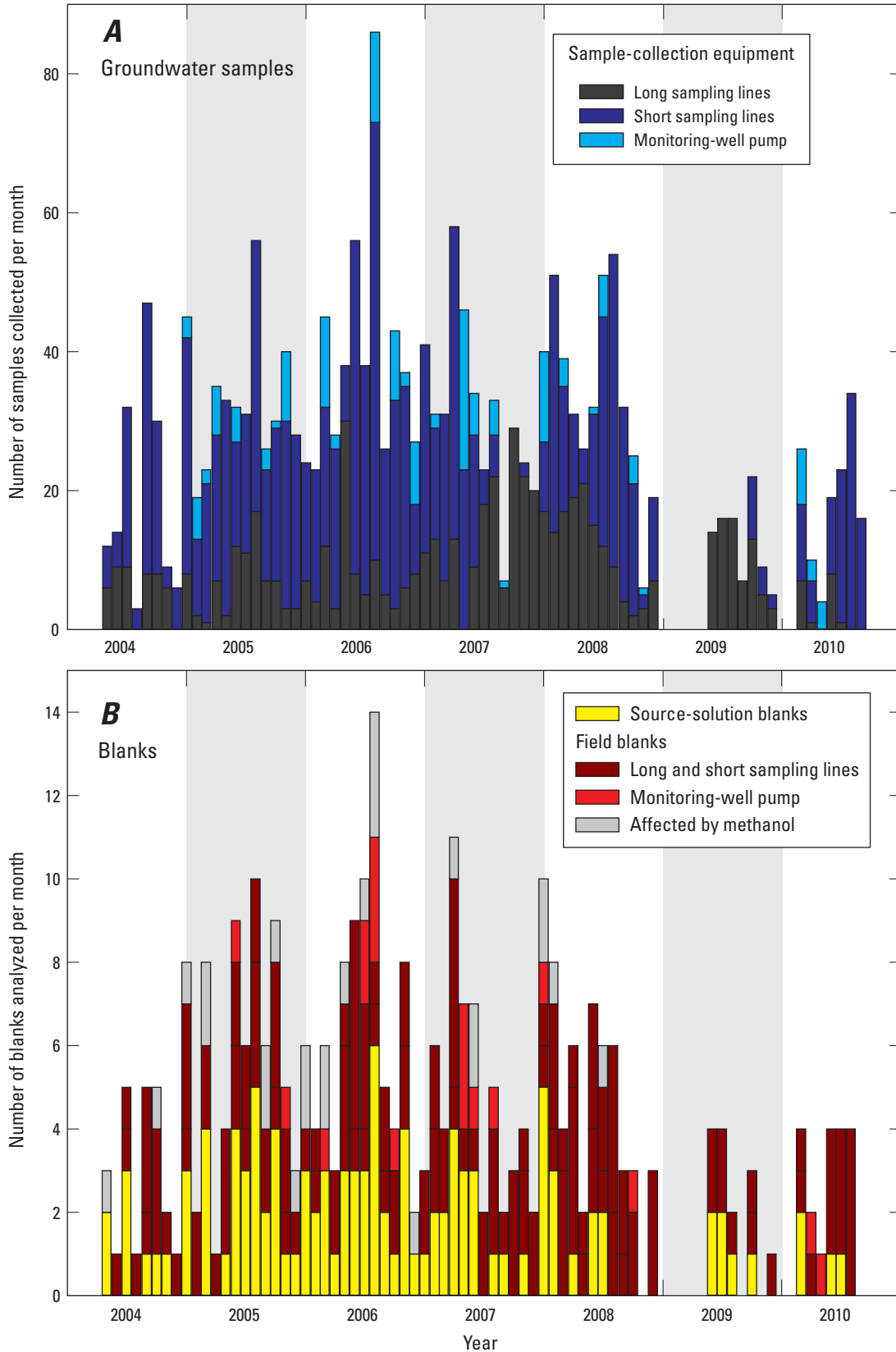
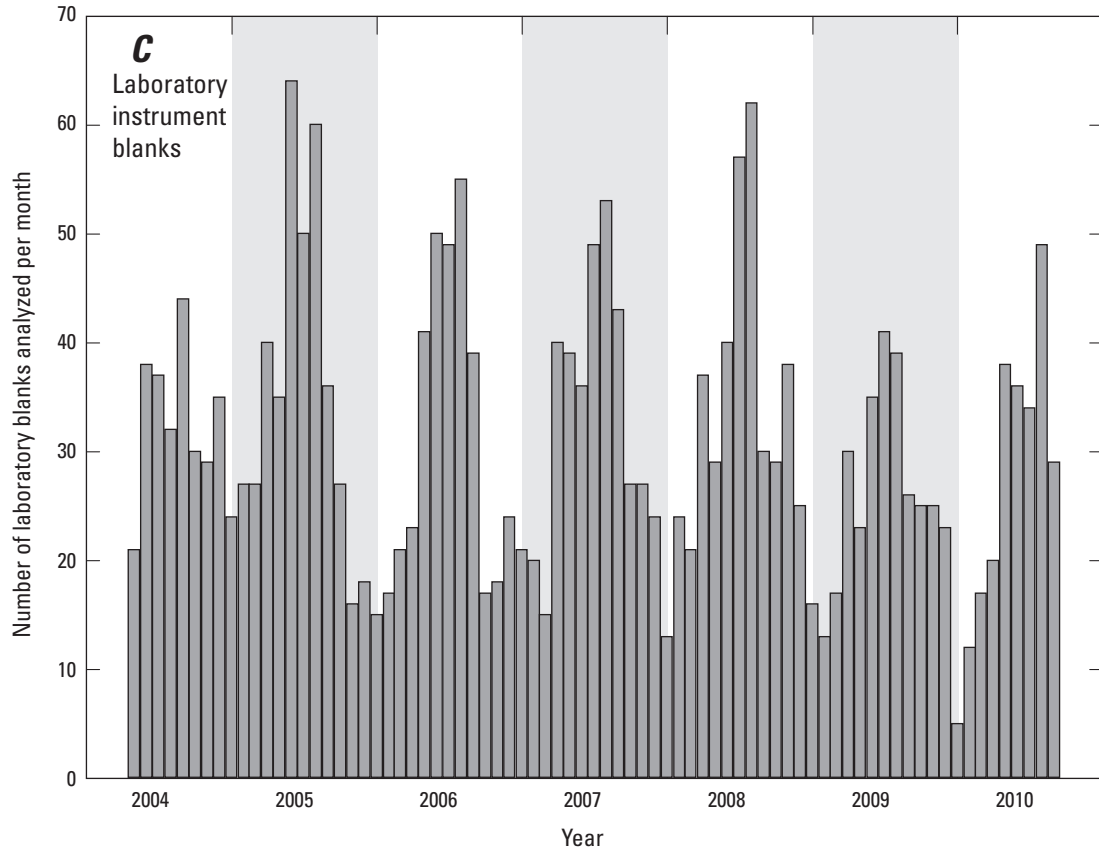


Figure 2. Number of (A) groundwater samples and (B) field and source-solution blanks collected per month by the California GAMA Priority Basin Project, and (C) number of laboratory instrument blanks analyzed per month for volatile organic compounds by the USGS National Water Quality Laboratory, May 2004 through September 2010.



Groundwater samples and field blanks were collected with three types of sampling equipment. Short or long sampling lines were used at production wells, where short (18 inches) and long (25 feet) refer to the length of Teflon® line used to route the water from the source to the sample bottles. Monitoring wells were sampled with monitoring-well pumps and long sampling lines.

Figure 2.—Continued

Production wells (and developed springs) were sampled by using Teflon® tubing (short or long sampling lines) with stainless-steel fittings attached to the sampling point (hose bib) on the well discharge pipe as close to the wellhead as possible. At some wells, additional fittings made of brass, steel, or stainless steel had to be used to construct a sampling point with a hose bib. The sampling point was located upstream of any wellhead treatment system or water storage tank, except for infrequent cases in which this was not possible. For sites sampled with short sampling lines, samples were collected outdoors at the sampling point. For sites sampled with long sampling lines, the tubing was connected to a Teflon® flow-control manifold with stainless-steel fittings, and samples were collected inside an enclosed chamber inside the mobile laboratory. Monitoring wells usually were sampled by using a stainless-steel Grundfos submersible pump with a 300-ft Teflon® discharge line. The discharge line was connected to the flow-control manifold inside the mobile lab with a long (25 ft) Teflon® sampling line.

All fittings and lengths of tubing were cleaned thoroughly between collection of each sample. For the monitoring-well pump and the long sampling line configurations, a peristaltic pump was used to pump the following sequence of cleaning solutions through the fittings and lines: tap water, dilute solution of non-phosphate laboratory detergent (Liquinox®), deionized water, methanol, deionized water, and finally certified blank water (Wilde, 2004). For the short sampling line configuration, the same cleaning solutions were poured through the fittings and lines in the same order. The short sampling lines generally were cleaned in the laboratory, and clean lines wrapped in plastic wrap and aluminum foil were transported to the field site. The long sampling lines and monitoring-well pump generally were cleaned at the field site immediately following sample collection, although on rare occasions, the lines were cleaned immediately prior to sample collection at the next field site. Fittings used to attach a hose bib to the well discharge pipe (if needed) were cleaned at the field site immediately prior to use during the early years of the GAMA-PBP, and were cleaned in the laboratory during the later years of the project. The full sampling line configuration (short, long, or monitoring well) was attached before well purging and measurement of field parameters began, thus the lines generally were rinsed with a large volume of groundwater before sample collection.

Groundwater samples to be analyzed for VOCs were collected in pre-baked 40-milliliter (mL) amber glass vials with Teflon-septa caps. The VOC vials were the first set of sample containers filled during sample collection. The vials were bottom-filled and purged with at least three vial volumes of sample water before being filled to the top to eliminate entrainment of ambient air. Three to five drops of 6 N certified hydrochloric acid were added as a preservative, and the vials were sealed with no headspace or bubbles. The hydrochloric

acid was certified by the USGS NWQL and was dispensed from a Teflon® dropper bottle. The dropper bottle of acid was kept sealed in a plastic container provided by the USGS NWQL in a cooler with ice between uses and was replaced approximately every 2 months. Three VOC vials were collected for each sample. Vials were packed in protective foam sleeves, sealed in ziplock bags, and placed in a cooler with ice inside the mobile lab until they were shipped to the laboratory. Samples were shipped in coolers packed with ice by overnight carrier to the USGS NWQL within a day or two of collection.

Blanks

Field blanks were collected at 10.4 percent of the sites (211 of 2,026 sites) to determine if equipment, procedures, or conditions in the field, during transit, or in the laboratory introduced contamination to the samples. Field blanks and source-solution blanks to be analyzed for VOCs were collected using certified blank water purchased from the USGS Field Supply Service (One Stop). The certified blank water is contracted in large lots, and each lot is tested by the NWQL. Lots are for sale for approximately 6 to 12 months. Certified blank water is purchased in 4-liter amber glass bottles and is used within 1 week of delivery.

For the long and short line configurations, field blanks were collected by pumping the certified blank water through the sampling equipment using a portable peristaltic pump. In some cases, field blanks for the short line configuration were collected by pouring blank water through the sampling equipment. For the monitoring-well configuration, field blanks were collected by immersing the monitoring-well pump in a dedicated Teflon standpipe containing the certified blank water. During the early years of the GAMA-PBP, the portable peristaltic pump used for collection of field blanks also was used for pumping cleaning solutions through lines between samples. During the later years of the project, a dedicated pump was used for collection of field blanks, and the pump commonly was cleaned in the laboratory prior to transport to the field site. Of the 211 field blanks, 22 were collected with monitoring-well equipment, 112 with short sampling lines, and 77 with long sampling lines ([fig. 2B](#)).

Source-solution blanks were collected at 109 of the 211 sites at which field blanks were collected ([fig. 2B](#)). Source-solution blanks were collected by pouring blank water directly into the sample vials, which were then preserved, stored, shipped, and analyzed in the same manner as the field blanks. Source-solution blanks are subject to the same potential sources of contamination as the field blanks, with the exception of contact with field equipment used to collect samples. A trip blank was collected for 1 of the 211 sites; this blank was treated as a source-solution blank for the purposes of this report.

Laboratory Methods

Samples were analyzed for VOCs at the USGS NWQL in Denver, Colorado, by purge & trap gas chromatography with quadrupole mass-spectrometric detection (Connor and others, 1998; NWQL Laboratory Schedule 2020). Samples are stored in the dark at 4°C and analyzed within 14 days of field collection. The quality-assurance program followed by the NWQL is described by Maloney (2005) and Pirkey and Glodt (1998). Laboratory QC samples, including laboratory method blanks, continuing calibration verification checks, reagent spikes, certified standard reference materials, and external blind proficiency samples, are analyzed regularly. The NWQL maintains certification by the National Environmental Laboratory Accreditation Program (NELAP) and other certifications (http://nwql.usgs.gov/Public/lab_cert.shtml).

The NWQL analyzes laboratory instrument blanks (and other quality-control samples) as part of every batch of environmental and field quality-control samples analyzed for VOCs. The purpose of the laboratory instrument blanks is to evaluate the occurrence of potential carry-over between samples during analysis, and to evaluate the presence of potential systemic contamination in the analytical equipment. From May 2004 through September 2010, 2,411 laboratory instrument blanks were analyzed for VOCs (fig. 2C). Results for the VOCs detected in laboratory instrument blanks were obtained from the NWQL (<http://nwqlqc.cr.usgs.gov/>).

The USGS NWQL uses two thresholds for reporting VOC data: the long-term method detection level (LT-MDL) and the laboratory reporting level (LRL). The LT-MDL is determined by using a method (Childress and others, 1999) modified from a procedure reported by the U.S. Environmental Protection Agency for determining the method detection limit (USEPA MDL). The USEPA MDL is the minimum concentration of a substance that can be measured and reported with 99-percent confidence that the concentration is greater than zero; at the MDL, there is less than a 1-percent chance of a false positive (U.S. Environmental Protection Agency, 1997). The USEPA MDL is determined by analyzing at least seven low-level spikes over a relatively short period (“low-level” means less than 5 times the expected MDL concentration). The LT-MDL is designed to capture more of the long-term method variability present in routine laboratory analyses because it is derived from at least 20 measurements of low-level spikes made over an extended period of time (6 to 12 months) by multiple analysts and multiple instruments (Childress and others, 1999). Low-level spikes and blanks are monitored throughout each year, and LT-MDLs are reevaluated at least annually and are updated accordingly. At the LT-MDL, the probability of a false-positive detection (Type I error) is statistically less than or equal to 1 percent.

$$LTMDL = s \times t_{(n-1, 1-\alpha)} \quad (1)$$

where

- n is number of replicate low-level spike determinations (in this case, $n = 24$),
- s is standard deviation of measured concentrations of n low-level spike determination,
- α is level of significance (in this case, $\alpha = 1$ percent, and
- t is Student's t-value for $n - 1$ degrees of freedom and $1 - \alpha$ confidence level (in this case, $t = 2.50$).

The LRL is used to control false-negative (Type II) error and is usually set at two times the LT-MDL for each constituent. The probability of reporting a false negative for a sample that contains a concentration of a constituent greater than or equal to the LRL is predicted to be less than or equal to 1 percent (Childress and others, 1999). The probability of reporting a false negative for a sample that contains a concentration equal to the LT-MDL is 50 percent. Nondetections are reported as <LRL to indicate that the true concentration may be as large as the LRL.

Values below the LRL are reported as “estimated” concentrations, designated with an “E” code. E-coded values have a high likelihood of being greater than zero (detections), but can have a high degree of uncertainty in the precise concentration. For “information-rich” methods, such as the VOC analytical method, the NWQL may report detections with concentrations below the LT-MDL. The VOC method is considered “information-rich” because analyte identity is confirmed by two independent means: chromatographic retention time and mass spectra (Childress and others, 1999). However, detections with concentrations less than the LT-MDL have a greater than 1-percent chance of being false-positive detections.

There are two issues to consider about LT-MDLs and LRLs and interpretation of groundwater-quality data: (1) changes in reporting levels during the period that the samples were analyzed, and (2) definition of acceptable probabilities of false positives and false negatives. Samples discussed in this report were collected from May 2004 through September 2010. During that period, 83 of the 85 VOCs analyzed as part of NWQL Schedule 2020 had at least two different LT-MDLs. For 34 VOCs, the concentration of the maximum LT-MDL was at least twice the concentration of the minimum LT-MDL (table 2). Most notably, the maximum and minimum LT-MDLs for the two most frequently detected VOCs, chloroform and tetrachloroethene, differed by factors of 2 and 2.3, respectively. It is possible that detection frequencies for these VOCs in study units sampled during periods of maximum LT-MDL may not be comparable to those in study units sampled during periods of minimum LT-MDL.

12 VOC Blank Data and Study Reporting Levels, California GAMA PBP, 2004–2010

Table 2. Long-term method detection levels (LT-MDLs) used by the U.S. Geological Survey National Water Quality Laboratory for volatile organic compounds (VOCs), and VOCs detected in groundwater samples and source-solution or field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.

[The five-digit USGS parameter code is used to uniquely identify a specific constituent or property in USGS databases and reports. Abbreviations: µg/L, micrograms per liter; D, detected; –, not detected]

Constituent	USGS parameter code	CAS number ¹	LT-MDL values (µg/L)			Detected	
			Minimum	Median	Maximum	Ground-water	Blanks
Hydrocarbons							
Benzene	34030	71–43–2	0.008	0.01	0.013	D	D
<i>n</i> -Butylbenzene	77342	104–51–8	0.04	0.06	0.07	–	–
<i>sec</i> -Butylbenzene	77350	135–98–8	0.01	0.02	0.03	D	–
<i>tert</i> -Butylbenzene	77353	98–06–6	0.03	0.03	0.04	D	–
Ethylbenzene	34371	100–41–4	0.01	0.015	0.02	D	D
2-Ethyltoluene	77220	611–14–3	0.01	0.02	0.03	D	–
Isopropylbenzene	77223	98–82–8	0.019	0.02	0.021	D	–
4-Isopropyltoluene	77356	99–87–6	0.03	0.04	0.04	D	–
Naphthalene	34696	91–20–3	0.09	0.13	0.2	D	–
<i>n</i> -Propylbenzene	77224	103–65–1	0.018	0.02	0.021	D	–
Styrene	77128	100–42–5	0.015	0.02	0.021	D	D
1,2,3,4-Tetramethylbenzene	49999	488–23–3	0.04	0.07	0.07	D	–
1,2,3,5-Tetramethylbenzene	50000	527–53–7	0.04	0.06	0.09	D	–
1,2,3-Trimethylbenzene	77221	526–73–8	0.03	0.04	0.05	D	–
1,2,4-Trimethylbenzene	77222	95–63–6	0.016	0.02	0.028	D	D
1,3,5-Trimethylbenzene	77226	108–67–8	0.016	0.02	0.022	D	–
Toluene	34010	108–88–3	0.009	0.009	0.03	D	D
<i>m</i> - and <i>p</i> -Xylenes	85795	<i>m</i> :108–38–3 <i>p</i> :106–42–3	0.03	0.04	0.04	D	D
<i>o</i> -Xylene	77135	95–47–6	0.016	0.019	0.02	D	D
Solvents and organic synthesis							
Acetone	81552	67–64–1	1.7	3	3	D	D
Acrylonitrile	34215	107–13–1	0.2	0.4	0.6	–	–
Bromobenzene	81555	108–86–1	0.01	0.011	0.014	–	–
2-Butanone (methyl ethyl ketone, MEK)	81595	78–93–3	0.8	0.8	1	D	D
Chlorobenzene	34301	108–90–7	0.008	0.01	0.014	D	–
Chloroethane	34311	75–00–3	0.03	0.05	0.06	D	–
3-Chloropropene	78109	107–05–1	0.04	0.04	0.25	–	–
2-Chlorotoluene	77275	95–49–8	0.01	0.02	0.02	–	–
4-Chlorotoluene	77277	106–43–4	0.01	0.021	0.03	–	–
Dibromomethane	30217	74–95–3	0.02	0.025	0.025	D	–
1,2-Dichlorobenzene	34536	95–50–1	0.01	0.02	0.024	D	–
1,3-Dichlorobenzene	34566	541–73–1	0.01	0.015	0.02	D	–
<i>trans</i> -1,4-Dichloro-2-butene	73547	110–57–6	0.18	0.3	0.35	–	–
1,1-Dichloroethane	34496	75–34–3	0.018	0.02	0.03	D	–
1,2-Dichloroethane	32103	107–06–2	0.03	0.05	0.07	D	–
1,1-Dichloroethene	34501	75–35–4	0.01	0.011	0.012	D	D
<i>cis</i> -1,2-Dichloroethene	77093	156–59–2	0.01	0.011	0.012	D	–
<i>trans</i> -1,2-Dichloroethene	34546	156–60–5	0.009	0.009	0.016	D	–
Dichloromethane	34423	75–09–2	0.019	0.02	0.03	D	D
Ethyl methacrylate	73570	97–63–2	0.07	0.07	0.09	–	–
Hexachlorobutadiene	39702	87–68–3	0.03	0.05	0.07	–	–
Hexachloroethane	34396	67–72–1	0.07	0.07	0.07	–	–
2-Hexanone (<i>n</i> -Butyl methyl ketone)	77103	591–78–6	0.2	0.23	0.4	–	–
Iodomethane (Methyl iodide)	77424	74–88–4	0.13	0.225	0.4	–	–
1,1-Dichloropropene	77168	563–58–6	0.013	0.015	0.02	–	–

Table 2. Long-term method detection levels (LT-MDLs) used by the U.S. Geological Survey National Water Quality Laboratory for volatile organic compounds (VOCs), and VOCs detected in groundwater samples and source-solution or field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[The five-digit USGS parameter code is used to uniquely identify a specific constituent or property in USGS databases and reports. Abbreviations: µg/L, micrograms per liter; D, detected; –, not detected]

Constituent	USGS parameter code	CAS number ¹	LT-MDL values (µg/L)			Detected	
			Minimum	Median	Maximum	Ground-water	Blanks
Solvents and organic synthesis—Continued							
Isobutyl methyl ketone	78133	108–10–1	0.1	0.18	0.2	D	–
Methyl acrylate	49991	96–33–3	0.2	0.3	0.5	–	–
Methyl acrylonitrile	81593	126–98–7	0.1	0.19	0.2	–	–
Methyl methacrylate	81597	80–62–6	0.1	0.1	0.18	–	–
1,1,1,2-Tetrachloroethane	77562	630–20–6	0.015	0.02	0.02	D	–
Tetrachloroethene (perchloroethene, PCE)	34475	127–18–4	0.013	0.02	0.03	D	D
1,2,3-Trichlorobenzene	77613	87–61–6	0.03	0.06	0.14	–	–
1,2,4-Trichlorobenzene	34551	120–82–1	0.02	0.06	0.06	–	–
1,1,1-Trichloroethane	34506	71–55–6	0.01	0.016	0.02	D	–
1,1,2-Trichloroethane	34511	79–00–5	0.02	0.023	0.032	D	–
1,1,2,2-Tetrachloroethane	34516	79–34–5	0.04	0.05	0.07	–	–
Tetrachloromethane	32102	56–23–5	0.026	0.03	0.04	D	–
Tetrahydrofuran	81607	109–99–9	0.5	0.7	1.1	D	D
Trichloroethene	39180	79–01–6	0.01	0.011	0.019	D	D
Vinyl chloride	39175	75–01–4	0.03	0.04	0.04	D	–
Trihalomethanes							
Bromodichloromethane	32101	75–27–4	0.014	0.017	0.02	D	D
Bromoform	32104	75–25–2	0.04	0.05	0.05	D	–
Chloroform	32106	67–66–3	0.01	0.012	0.02	D	D
Dibromochloromethane	32105	124–48–1	0.05	0.06	0.06	D	–
Fumigants							
Bromomethane	34413	74–83–9	0.1	0.18	0.2	D	–
1,2-Dibromo-3-chloropropane ²	82625	96–12–8	0.17	0.17	0.5	D	–
1,2-Dibromoethane ²	77651	106–93–4	0.018	0.02	0.025	D	–
1,4-Dichlorobenzene	34571	106–46–7	0.01	0.017	0.02	D	–
1,2-Dichloropropane	34541	78–87–5	0.01	0.013	0.015	D	–
1,3-Dichloropropane	77173	142–28–9	0.03	0.03	0.03	–	–
2,2-Dichloropropane	77170	594–20–7	0.02	0.03	0.03	–	–
<i>cis</i> -1,3-Dichloropropene	34704	10061–01–5	0.02	0.03	0.05	–	–
<i>trans</i> -1,3-Dichloropropene	34699	10061–02–6	0.04	0.05	0.07	–	–
1,2,3-Trichloropropane	77443	96–18–4	0.06	0.06	0.09	D	–
Gasoline oxygenates							
Diethyl ether	81576	60–29–7	0.04	0.04	0.06	D	–
Diisopropyl ether	81577	108–20–3	0.03	0.03	0.05	D	–
Ethyl <i>tert</i> -butyl ether (ETBE)	50004	637–92–3	0.015	0.02	0.03	–	–
Methyl <i>tert</i> -butyl ether (MTBE)	78032	1634–04–4	0.05	0.05	0.08	D	–
Methyl <i>tert</i> -pentyl ether	50005	994–05–8	0.02	0.03	0.04	D	–
Naturally occurring							
Carbon disulfide	77041	75–15–0	0.019	0.02	0.03	D	D
Fire retardants							
Bromochloromethane	77297	74–97–5	0.03	0.03	0.06	D	–
Bromoethane	50002	593–60–2	0.05	0.06	0.06	–	–

Table 2. Long-term method detection levels (LT-MDLs) used by the U.S. Geological Survey National Water Quality Laboratory for volatile organic compounds (VOCs), and VOCs detected in groundwater samples and source-solution or field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[The five-digit USGS parameter code is used to uniquely identify a specific constituent or property in USGS databases and reports. Abbreviations: µg/L, micrograms per liter; D, detected; –, not detected]

Constituent	USGS parameter code	CAS number ¹	LT-MDL values (µg/L)			Detected	
			Minimum	Median	Maximum	Ground-water	Blanks
Refrigerants							
Chloromethane	34418	74–87–3	0.05	0.07	0.09	D	–
Dichlorodifluoromethane	34668	75–71–8	0.05	0.07	0.09	D	–
Trichlorofluoromethane	34488	75–69–4	0.04	0.04	0.08	D	D
1,1,2-Trichloro-1,2,2-trifluoroethane	77652	76–13–1	0.017	0.019	0.02	D	–

¹ 1,2-Dibromo-3-chloropropane (DBCP) and 1,2-dibromoethane (EDB) also were analyzed using NWQL Schedule 1306, Low-Level Fumigants, in some study units. The LT-MDLs listed here are for Schedule 2020.

Because the GAMA-PBP generally interprets patterns in water quality from the perspective of an overall dataset—for example, detection frequency is a property of a dataset—rather than by considering individual samples, it is not necessary to censor data based on avoidance of false negatives (Helsel, 2005). For any result, there is a 50-percent probability that the true concentration will be greater than or equal to the measured concentration and a 50-percent probability that it will be less than or equal to the measured concentration. In the absence of sources of contamination bias, at the reporting limit, wherever it is set, the number of samples with measured concentration less than the reporting limit when the true concentration is greater than the reporting limit (false negatives) is expected to be balanced by the number of samples with measured concentration greater than the reporting limit when the true concentration is less than the reporting limit (false positives). Contamination would impart a positive bias, further decreasing the probability of false negatives. In contrast, it may be necessary to censor data based on avoidance of false-positive detections because contamination of groundwater samples during sample collection, handling, or analysis results in positive bias in concentrations and detection frequencies.

The issue of variability in LRLs for VOCs may be addressed in different ways. Moran and others (2006) and Zogorski and others (2006) censored VOC data collected for the NAWQA Program by using a uniform assessment level of 0.02 microgram per liter (µg/L). That concentration was selected because most VOC detections in environmental samples had concentrations greater than 0.02 µg/L, and many of the LT-MDLs were less than 0.02 µg/L. The approach of Moran and others (2006) and Zogorski and others (2006) has the advantages of being simple to implement and leads to a straightforward presentation of results. A second approach is to censor data for each VOC constituent individually, selecting the highest LT-MDL used for that VOC during the study period and applying that LT-MDL as the SRL for that VOC if no higher SRL is warranted. This approach has the advantages

of conforming to common statistical practices for dealing with multiply censored datasets (Helsel, 2005), and preserving a consistent threshold for an acceptable level of false-positive detections for all constituents. This second approach is evaluated in this report.

Data Analysis Methods

Groundwater samples were collected during 2004–2010 from the 32 GAMA-PBP study units by field personnel of the USGS California Water Science Center. These field personnel were a relatively constant group of people, and considerable attention was given to oversight of field activities and use of consistent field methods. Thus, systematic differences among study units in patterns of contamination due to field activities were unlikely. The blanks from the 32 study units were evaluated as if they were collected for one large study. The Data Series Reports for the 32 individual study units (table 1) include evaluation of VOC-blank data for the individual study units. VOC data for groundwater samples in a study unit may be censored on the basis of detections in the field blanks collected in that study unit. Because the number of field blanks collected in each study unit was relatively small (3 to 12), censoring was generally based on the highest concentration measured in the field blanks. As a result, censoring concentrations were different for different study units, which may affect comparison of VOC detection frequencies among study units. The data for all study units were re-evaluated using the SRLs established in this report to have uniform censoring levels for comparison among study units. This re-evaluation was done during preparation of the Scientific Investigations Reports that present the interpretation of the status and understanding of groundwater quality in individual study units or groups of study units.

Evaluation of VOC-blank data was done in three stages: (1) identification of a set of representative quality-control field blanks (QCFBs) to be used for calculation of SRLs,

(2) evaluation of potential sources of extrinsic contamination to blanks and groundwater samples, and (3) selection of appropriate SRLs for VOCs detected in field blanks, and application of those SRLs to the groundwater data.

Identification of Representative Field Blanks

Field blanks are collected by using procedures designed to mimic those used to collect the groundwater samples, and thus are expected to be representative of the potential sources of contamination to the groundwater samples. Small differences between the collection methods for field blanks and groundwater samples, however, may result in exposure of field blanks to sources and processes of contamination that are different from those of the groundwater samples (table 3). Field blanks contaminated by sources and processes not likely to affect groundwater samples might not be representative of the conditions under which groundwater samples were collected; therefore those blanks should not be used in determination of SRLs. To identify a set of representative QCFBs to be used for calculation of SRLs, several questions needed to be answered to determine if field blanks were representative of conditions under which groundwater samples were collected:

- Can the source of contamination be isolated to the certified blank water itself? Compounds with detections reported in the certificates of analysis provided by the NWQL may have a source of contamination that is not representative of sources of contamination to groundwater samples. Many previous QC assessments have assumed that detections of compounds in source-solution blanks indicate contamination by processes not representative of groundwater samples. However, this may be an incorrect assumption because source-solution blanks are processed with several of the same steps as groundwater samples: contact with vials, transportation from the field site to the laboratory, and laboratory analytical processes (table 3). In this study, contamination of the certified blank water itself is assessed with the certificates of analysis. Field blanks with detections of compounds that could be attributed to contamination of the certified blank water itself are not considered representative of groundwater sample collection conditions for those compounds.
- Is the contamination of field blanks the result of a mechanism that is unlikely to affect groundwater samples? The differences in sample collection and handling methods between field blanks and environmental samples (for example, the use of the peristaltic pump; table 3) may result in field blanks being exposed to potential sources of contamination that environmental samples do not encounter. In these cases, the field blanks may not be representative.
- Can the SRL approach be used to address extrinsic contamination for the constituent? There are two general patterns of extrinsic contamination. For many constituents, contamination results in environmental samples and field blanks being contaminated with a small amount of the constituent. The mechanism of contamination may be equally likely to affect field blanks and environmental samples, or it may be more likely to affect field blanks (higher detection frequency in field blanks). In both cases, the concentrations of the constituent imparted to the samples by contamination are relatively low and similar in both sample types. The SRL approach can effectively be applied in these cases because a threshold concentration can be defined; above that threshold, the probability that detections in environmental samples are due to extrinsic contamination is acceptably low. In contrast, for other constituents, contamination results in environmental samples and field blanks being contaminated with either large or small amounts of the constituent. Contaminated environmental samples and field blanks may have higher concentrations of the constituent than present in uncontaminated environmental samples. In this case, the SRL approach cannot be effectively applied because there is no threshold concentration above which concentrations in environmental samples can be considered representative of environmental conditions; the probability of extrinsic contamination in those samples is not acceptably low.
- Are field blanks collected with one sampling equipment configuration representative of conditions under which groundwater samples are collected with a different sampling equipment configuration? Contamination of field blanks and groundwater samples may occur at many steps in the sequence of sample collection, handling, and analysis (table 3). Many of these steps are the same for samples collected with different sampling equipment configurations: for example, all samples come into contact with sample vials, are transported from the field site to the laboratory, and are analyzed in the laboratory. If contamination is related to contact with sample-collection equipment, it is possible that samples collected with different sample-collection equipment configurations may be subject to contamination by the same process, but to different degrees. Because contamination with different VOCs may occur by different mechanisms, field blanks collected with one sampling equipment configuration may be representative of conditions under which groundwater samples were collected with different sampling equipment configurations for some VOCs, but not for others. Statistical tests were used to determine significances of differences between field blanks collected with different equipment configurations.

Table 3. Identification of steps in collection, handling, and analysis of blanks and groundwater samples during which contamination may occur, California GAMA Priority Basin Project.

[Field blanks and groundwater samples were collected with three equipment configurations: short lines (18-inch Teflon sampling line, collection at well head), long lines (25-foot sampling line routed inside mobile lab), monitoring-well equipment (monitoring-well pump plus 25-foot sampling line routed inside mobile lab). **Abbreviations:** all, process applies to all samples of that type; some, process applies to some samples of that type; –, process applies to no samples of that type]

Process	Laboratory instrument blanks	Source-solution blanks	Field blanks			Groundwater samples		
			Short lines	Long lines	Monitoring well	Short lines	Long lines	Monitoring well
Certified blank water								
Laboratory production	all	all	all	all	all	–	–	–
Bottling	–	all	all	all	all	–	–	–
Transit from laboratory to field site	–	all	all	all	all	–	–	–
Vials								
Manufacture and packaging	all	all	all	all	all	all	all	all
Storage and bottle set preparation	–	all	all	all	all	all	all	all
Transit to field site	–	all	all	all	all	all	all	all
Field collection								
Peristaltic pump	–	–	some	all	–	–	–	–
Monitoring-well pump and fittings	–	–	–	–	all	–	–	all
Extra fittings between lines and well	–	–	–	–	–	some	some	–
Contact with long lines and manifold	–	–	–	all	all	–	all	all
Contact with short lines	–	–	all	–	–	all	–	–
Transit of equipment to field site	–	–	all	all	all	all	all	all
Conditions at field site	–	all	all	all	all	all	all	all
Conditions in field vehicle	–	all	all	all	all	all	all	all
Post-collection								
Packing and storage	–	all	all	all	all	all	all	all
Transit from field site to laboratory	–	all	all	all	all	all	all	all
Laboratory handling and analysis	all	all	all	all	all	all	all	all

Definition of Study Reporting Levels (SRLs)

Four potential SRL values were defined for each VOC using three approaches for making quantitative estimates of contamination using the QCFBs: two potential SRL values were defined using a binomial probability method based on one-sided, nonparametric upper confidence limits (Hahn and Meeker, 1991), one was defined as equal to the maximum concentration detected in the field blanks, and one was defined as the maximum laboratory method detection level used during the period samples were analyzed for the project. These four SRL values were compared, and one value was selected for each VOC as the SRL for use with GAMA groundwater data. The SRL is equivalent to a raised reporting limit that can be used in place of the LRL or LT-MDL to reduce the probability of reporting false positives.

Binomial Probability Approach

The first approach for quantitative assessment of blank data is based on binomial probabilities and rank-order statistics. A desired probability of reporting results for groundwater samples without false-positive detections and a confidence level in that probability are defined, then the binomial distribution is used to calculate the number of field blanks in a set of field blanks that must be uncontaminated in order to meet the criteria of the desired probability and confidence level (Martin and others, 1999; Olsen and others, 2010; Bender and others, 2011). If more than the allowed number of field blanks in the set show contamination, then an SRL can be defined by using the ranked concentrations of the field blanks. This approach assumes that contamination has a characteristic concentration, which is generally a range of concentrations that is lower than those observed in the majority of the groundwater samples.

The binomial distribution assigns a probability to achieving a given number of successes in a given number of trials:

$$b(k; n, p) = \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} \quad (2)$$

where

- n is the number of trials (the total number of field blanks collected),
- k is the number of successes (the number of uncontaminated field blanks collected),
- p is the probability of success in each trial (the probability of collecting any one groundwater sample or field blank without contamination), and
- b is the probability of achieving k successes in n trials (the probability of collecting k uncontaminated field blanks in a total of n field blanks collected).

The probability that there will be at least k uncontaminated field blanks among the n field blanks collected is the cumulative probability:

$$\sum_{k=0}^k b(k; n, p) = \sum_{k=0}^k \frac{n!}{k!(n-k)!} p^k (1-p)^{n-k} . \quad (3)$$

Hahn and Meeker (1991) describe a method for determining which ranked field blank corresponds most closely to the upper confidence limit for a given percentile of a set of observations at a given percent of confidence. In the terminology used in this report, the “given percentile of a set of observations” corresponds to p , and the “upper confidence limit” corresponds to $\sum b$. The 90th, 95th, and 99th percentiles and 90- and 95-percent confidence limits are commonly used in QC assessments. Note that the method used by Hahn and Meeker (1991) for calculating the confidence interval is one of many methods, and a more appropriate confidence interval to use may be the Jeffreys interval (Agresti and Coull, 1998; Brown and others, 2001; Belitz and others, 2010). For a small number of samples, the difference between the Jeffreys interval and the interval used by Hahn and Meeker is significant. Using the Jeffreys interval to select the ranked field blank corresponding to the upper confidence limit may result in selection of a lower rank than would the interval used by Hahn and Meeker; thus, the Jeffreys interval may yield an SRL with a lower concentration. For the number of blanks used in this report, the difference is not significant.

Martin and others (1999), Olsen and others (2010), and Bender and others (2011) apply Hahn and Meeker’s method to determine the rank of the field blank corresponding to, for example, the 90th percentile with at least 90-percent confidence. There is at least a 90-percent confidence that the contamination in at least 90 percent of all samples is less than the concentration in the field blank with this rank. For ease of discussion, this concentration is referred to as the “BD-percentile/confidence” concentration, where BD means binomial distribution, the first number is the percentile of interest, and the second number is the percentage of confidence (Olsen and others, 2010). Because ranks are discrete quantities, for a given percentage of confidence, the percentile depends on the number of samples. For example, for datasets of 10, 100, and 1,000 field blanks, the BD-90/90 corresponds to the 98.2, 94.1, and 91.5 percentiles of the datasets, respectively.

BD-95/90 and BD-90/90 concentrations were calculated for the sets of representative field blanks and source-solution blanks, and BD-99/90 concentrations were calculated for the set of laboratory blanks. For the dataset of 167 field blanks used to define SRLs in this study, the BD-90/90 would be the 156th ranked blank, corresponding to the 92.8 percentile of the dataset, and the BD-95/90 would be the 163rd ranked blank, corresponding to the 97.0 percentile of the dataset. Calculations were made using the BINOM.DIST function in Microsoft Excel 2007, which takes the form:

$$CL = \text{BINOM.DIST}(\text{number_s}, \text{trials}, \text{probability_s}, \text{cumulative}) \quad (4)$$

where

- CL is the confidence limit (90 percent);
- number_s is the number of successes in trials, in this case, the specified rank minus 1, where blanks are ranked from highest to lowest concentration with the highest concentration assigned a rank equal to the total number of blanks;
- trials is the number of trials, in this case, the total number of blanks;
- probability_s is the percentile of interest (0.90, 0.95, or 0.99); and
- cumulative is a logical value that determines the form of the function, in this case TRUE, such that BINOM.DIST returns the cumulative distribution function, which is the probability that there are number_s or fewer successes.

Maximum Concentration Approach

The next quantitative approach we consider is defining the maximum concentration measured in field blanks as the SRL. This type of method commonly is used in studies for which the number of blanks collected is too small for meaningful statistically-based assessments. For example, the number of field blanks collected in each GAMA study unit ranged from 3 to 12, which is an insufficient number to define a BD-95/90 or even a BD-90/90 concentration for an individual study unit. Twenty-two field blanks would be needed for the highest concentration blank to correspond to the BD-90/90 concentration; a minimum of 45 field blanks would be needed to define a BD-95/90 concentration. In the absence of other ways of defining an SRL, the highest concentration measured in the field blanks was considered representative of the amount of extrinsic contamination likely to occur in environmental samples. One could make a more conservative estimate by defining the SRL at 5 to 10 times the highest concentration measured in field blanks (for example, Nowell and others, 2011).

The probability that the maximum concentration measured in a set of field blanks is the maximum concentration in the theoretical population of all field blanks may be estimated based on binomial probabilities (Hahn and Meeker, 1991; Helsel, 2005). The estimate used in this report is the Jeffreys interval (Belitz and others, 2010). If 10 field blanks are collected, the probability that the maximum measured concentration is the true maximum concentration is between 72 and 100 percent, at a 90-percent confidence level. If 100 field blanks are collected, then the probability is between 96.9 and 100 percent, and if 1,000 field blanks are collected, then the probability is between 99.7 and 100 percent. The larger the number of field blanks collected, the greater the probability that the highest concentration measured in the field blanks is representative of the highest concentration in the theoretical population of all field blanks.

Maximum LT-MDL Approach

The last approach considered is defining the highest LT-MDL used during the period samples were analyzed for the project (May 2004 through September 2010) as the SRL. As discussed in the section “Laboratory Methods,” using the highest LT-MDL as a censoring threshold is common statistical practice for dealing with multiple censored datasets (Helsel, 2005) and may preserve a consistent threshold for acceptable level of false-positive detections for all constituents. For VOCs detected in field blanks, using the highest LT-MDL as the SRL may provide sufficient protection against false positives if the positive bias associated with extrinsic contamination is small.

Evaluation of Potential Sources of Contamination to Blanks and Groundwater Samples and Selection of Appropriate SRLs

Potential sources of contamination to blanks and groundwater samples primarily were evaluated by comparing detection frequencies of individual VOCs in various groups of blanks and samples. Contamination may occur at many points in the collection, handling, and analysis of blanks and groundwater samples (table 3). Laboratory instrument blanks, source-solution blanks, field blanks collected with different equipment configurations, and groundwater samples collected with different equipment configurations are exposed to different combinations of these potential points of contamination. These points may be divided into four categories: the certified blank water, the vials, field collection processes, and post-collection handling and analysis (table 3). Inferences of contamination mechanisms at each point were based on knowledge of physio-chemical properties of VOCs and knowledge of field and laboratory practices.

Laboratory instrument, source-solution, and field blanks all use the same certified blank water, but the water used for the source-solution and field blanks may have been exposed to sources of contamination associated with bottling the water or with shipping and storing the bottles between the bottling site at the laboratory and the field site. All three types of blanks and the groundwater samples are collected in the same type of vials. The water for laboratory instrument blanks and source-solution blanks is poured directly into the vials. Vials for field blanks and groundwater samples are filled by putting the sampling line down to the bottom of the vial and allowing at least three vial volumes to overflow before withdrawing the sampling line. The vials used for source-solution and field blanks or groundwater samples also may be subject to contamination during storage, packing of bottle sets in preparation for sampling, or transit to the field site.

Source-solution blanks, field blanks, and groundwater samples all are exposed to the ambient conditions in the field vehicle and at the field site, although the degree of potential influence by the ambient conditions may vary depending on whether the sample is collected inside the vehicle or at the well head, and on which sampling vehicle is used. The same equipment is used to collect field blanks and groundwater samples—with the exception of the peristaltic pump that is only used for field blanks and specialized fittings that may be used to fabricate a sampling point on the well head—and all the equipment travels to the field site. Sample-collection equipment is cleaned using the same methods before collection of field blanks and groundwater samples, but there may be differences between equipment configurations because short sampling lines generally are cleaned in the laboratory and the long sampling lines and monitoring-well equipment generally are cleaned at field sites. Samples collected with the three equipment configurations have different amounts

of contact with sampling lines (less contact with short sampling lines and more contact with long sampling lines and monitoring-well equipment), and the amount of water flushed through the lines prior to sample collection generally is greater for groundwater samples than for field blanks. Source-solution blanks, field blanks, and groundwater samples are packed, stored, and shipped together from the field site to the laboratory. All three types of blanks and groundwater samples are analyzed with the same equipment in the laboratory.

The points of possible contamination of blanks and groundwater samples are inferred by comparing detections in different types of samples by using nonparametric statistical tests. For example, if the detection frequency of a VOC in source-solution blanks is greater than in field blanks, one of the sources of contamination to source-solution blanks must be something that is less likely to affect field blanks. Both use the same certified blank water and experience the same post-collection handling and analysis, but field blanks have more contact with sample-collection equipment than do source-solution blanks. That leaves the vials as the likely explanation for higher detection frequency in the source-solution blanks, which is plausible, given the difference in how vials are filled for source-solution blanks and field blanks. Note that the inference that source-solution blanks may be contaminated by the vials does not imply that field blanks do not get contaminated by the vials; both types of blanks may be contaminated by this mechanism, but contamination of the source-solution blanks is more likely.

Potential points of contamination are evaluated separately for the 18 VOCs detected in source-solution blanks and field blanks. Comparison of inferred points of contamination for different VOCs aids in inference of contamination mechanism, which in turn, aids in selection of appropriate SRLs. For example, if the detection frequency of a VOC is greater in field blanks than in source-solution blanks, and greater in field blanks collected with long sampling lines compared to short sampling lines, one might infer that the point of contamination is contact with sampling lines. If concentrations in field blanks and groundwater samples are similar, one might further infer that the field blanks and groundwater samples both may be contaminated with similar amounts of the VOC by contact with sampling lines, and therefore, selection of an SRL yielding extensive censoring of the groundwater data may be most appropriate. In contrast, if no plausible point of contamination can be inferred from the data, and concentrations detected in field blanks are low compared to concentrations detected in groundwater samples, selection of an SRL yielding little or no censoring of the groundwater data may be most appropriate.

The binomial probability approach, BD-95/90, was considered the default approach for determining SRLs in this study. The SRL derived from the BD-95/90 was used unless evaluation of the potential sources of extrinsic contamination indicated that an SRL resulting in more or less censoring of the groundwater data than the BD-95/90 SRL was appropriate.

The BD-95/90, rather than the BD-90/90, was chosen in order to restrict the acceptable probability of false-positive detections. Selecting the BD-95/90 as the SRL is equivalent to defining an acceptable probability of false-positive detections in field blanks of approximately 3 percent, whereas selecting the BD-90/90 as the SRL would be equivalent to defining an acceptable probability of false-positive detections in field blanks of approximately 7 percent.

Statistical Tests Used in Identification of Representative Field Blanks and Evaluation to Infer Potential Sources of Contamination

Nonparametric statistical methods were used to test the significance of differences in detection frequencies or concentrations of a VOC between groups of samples, and of correlations between concentrations of different VOCs. Nonparametric statistics are robust techniques that generally are not affected by outliers and do not require that the data follow any particular distribution (Helsel and Hirsch, 2002). The significance level (p) used for hypothesis testing for this report was compared to a threshold value (α) of 5 percent ($\alpha=0.05$) to evaluate whether the relation was statistically significant ($p<\alpha$). Correlation between concentrations of different compounds was evaluated using Spearman's method to calculate the rank-order coefficient (ρ , rho) and the significance level of the correlation (p).

Significance of differences between concentrations of a single compound between two sample groups was evaluated by using the Wilcoxon rank-sum test. The null hypothesis for the test is that median values of concentration in the two groups are not significantly different from one another. Significance of differences between three or more sample groups was evaluated in two stages: the Kruskal-Wallis test, followed by Tukey's multiple comparison test if the Kruskal-Wallis test yielded a result of significance (Helsel and Hirsch, 2002). The Kruskal-Wallis test evaluates whether any of the groups has a significantly different median concentration than the others, but does not indicate which group is different. The Tukey's multiple comparison test is performed on the rank-transformed concentration data.

Significance of differences between detection frequencies of a single VOC between two sample groups was evaluated by using contingency tables. For a contingency table analysis, the data are recorded as a matrix of counts. One variable is assigned to the columns and the other to the rows, and the entries in the cells of the matrix are the number of observations, O_{ij} , which fall into the i^{th} row and j^{th} column of the matrix. A test statistic is computed by comparing the observed counts (O_{ij}) to the counts expected if the two variables were independent, and significance is determined by comparing the test statistic to the $(1-\alpha)$ quantile of a chi-squared distribution.

Quality-Control Assessment Results

Of the 85 VOCs analyzed, 18 were detected in field blanks or source-solution blanks, and 67 were not detected (table 2). The VOCs detected in blanks may be divided into three groups:

Hydrocarbons	Solvents	Other VOCs
Benzene	acetone	bromodichloromethane
Ethylbenzene	2-butanone	carbon disulfide
Styrene	1,1-dichloroethene	chloroform
Toluene	dichloromethane	trichlorofluoromethane
1,2,4-trimethylbenzene	tetrachloroethene	
<i>m</i> - and <i>p</i> -xylenes	tetrahydrofuran	
<i>o</i> -xylene	trichloroethene	

Field blanks collected for the GAMA Program contained a similar set of VOC contaminants as field blanks collected at groundwater sites by the USGS NAWQA Program, which uses similar field collection, sample handling, and laboratory methods. Eleven VOCs were detected with frequencies greater than 5 percent in NAWQA field blanks collected at production wells: the hydrocarbons benzene, ethylbenzene, toluene, 1,2,4-trimethylbenzene, styrene, *m*- and *p*-xylenes, and *o*-xylene; the solvents acetone and dichloromethane; and the other VOCs carbon disulfide and chloroform (fig. 3; Bender and others, 2011). VOCs detected at greater than 5-percent detection frequency in NAWQA field blanks collected at monitoring wells included the 11 detected in field blanks from production wells, plus tetrahydrofuran, 2-butanone (methyl ethyl ketone, MEK), 1,4-dichlorobenzene, chlorobenzene, 1,2-dichloropropane, tetrachloroethene, bromodichloromethane, and chloromethane. Of these 19 VOCs, 15 were detected in GAMA field blanks, but only 7 (ethylbenzene, toluene, 1,2,4-trimethylbenzene, *m*- and *p*-xylenes, *o*-xylene, acetone, and 2-butanone) had detection frequencies greater than 5 percent (table 4; fig. 3). Thiros and others (2011) suggested that the high detection frequencies of VOCs in field blanks collected for the NAWQA Program may have been due to field crews inconsistently following protocols, particularly failure to use the recommended volume of blank water to rinse sample-collection equipment prior to collection of field blanks.

Identification of VOCs for Which the SRL Approach Can be Applied and of Representative Quality-Control Field Blanks (QCFBs) for Use in Calculation of SRLs

The process of identifying a set of representative QCFBs to be used for calculation of SRLs yielded three results: (1) the certified blank water itself contributed minimally to contamination of field blanks, (2) the SRL approach cannot

be applied to contamination by acetone, 2-butanone, or tetrahydrofuran, and (3) field blanks collected with long and short sampling lines can be combined for the purposes of generating the set of QCFBs for use in calculation of SRLs.

Minimal Contamination from the Certified Blank Water

Between May 2004 and September 2010, 12 lots of certified blank water were available for purchase from the NWQL (universal blank water, lot numbers 80301, 80401, and 80501; organic blank water, lot numbers 80601, 80606, 80702, 80801, 80803, 80804, 80901, 81002, and 81004). Certificates of analysis for these lots of certified blank water are available from the USGS NWQL (<http://www.nwql.cr.usgs.gov/qas.shtml?obw>). Eleven of the 12 lots had certificates of analysis indicating that no VOCs were detected. Lot 80301 was the only lot with two certificates of analysis—one produced at the beginning and one produced at the end of the time period it was available for purchase (all other lots only had certificates produced at the beginning). The second certificate for lot 80301 (February 2004) reported acetone at a concentration of 2.2 µg/L; the LT-MDL in effect during February 2004 was 3 µg/L.

On the basis of the certificates of analysis, certified blank water may have been a potential source of contamination of field blanks or source-solution blanks by acetone, but not for any of the other VOCs. For the other 17 VOCs detected in field blanks or source-solution blanks, processes or conditions encountered at the field site, during shipping or storage of blank water or vials or samples, or at the laboratory must have been responsible for introducing the VOCs into the blanks.

Acetone, 2-Butanone, and Tetrahydrofuran Contamination Associated with Methanol

The VOCs associated with the methanol used to clean field equipment provide an example of contamination to which the SRL approach cannot effectively be applied. Moreover, some of the inferred mechanisms by which field blanks may be contaminated by methanol are unlikely to affect groundwater samples.

Inadvertent Field Test of Contamination by Methanol

The pattern of VOC detections observed in the field blank collected on June 25, 2007, led to an unusual opportunity to demonstrate the importance of the rigorous procedures for cleaning equipment after samples are collected (Fram and others, 2009). During sampling, three vials are filled in the field for each VOC sample or blank, and the laboratory (the NWQL) randomly selects one to be analyzed for VOCs and reserves the other two for reruns that may be necessary if there are problems with the analysis of the first vial or if the project

Table 4. Detection frequencies in field, source-solution, and laboratory blanks and in groundwater samples for the 18 volatile organic compounds (VOCs) and tentatively identified compounds (TICs) detected in field or source-solution blanks, California GAMA Program, Priority Basin Project, May 2004 through September 2010.

[Quality-control field blanks (QCFBs) are a subset of all field blanks and consist of the field blanks collected at production wells and inferred not to be contaminated with the methanol used to clean equipment. **Abbreviations:** n, number]

	Detection frequency (percent)								
	Field blanks				Source-solution blanks (n=109)	Laboratory blanks (n=2,411)	Groundwater samples		
	All (n=211)	Production well (n=189)	Monitoring well (n=22)	QCFB (n=167)			All (n=2,026)	Production well (n=1,859)	Monitoring well (n=167)
Hydrocarbons									
Benzene	1.4	1.1	4.5	0	0	1.6	1.6	1.2	6.0
Ethylbenzene	10	10	14	6.0	1.8	0.1	0.9	0.6	4.2
Styrene	2.4	2.6	0	0	0	0.2	0.1	0.2	0
Toluene	36	33	59	28	41	4.2	7.7	6.0	26
1,2,4-Trimethylbenzene	7.1	5.8	18	6.0	6.4	0.1	11	11	8.4
<i>m</i> - and <i>p</i> -Xylenes	15	14	27	9.0	6.4	0.04	1.9	1.2	9.6
<i>o</i> -Xylene	9.5	9.0	14	5.4	1.8	0.04	0.7	0.4	4.2
Solvents									
Acetone	9.5	7.9	23	1.2	5.5	2.1	0.4	0.3	1.8
2-Butanone	9.5	9.0	14	0	0.9	0.04	0.4	0.3	2.4
1,1-Dichloroethene	0	0	0	0	0.9	0	3.4	3.6	0.6
Dichloromethane	1.9	2.1	0	0.6	0.9	0.7	1.5	1.5	1.2
Tetrachloroethene	1.9	1.6	4.5	1.8	0	0.1	13	13	6.6
Tetrahydrofuran	0.9	0.5	4.5	0	0	0.04	1.2	0.8	5.4
Trichloroethene	1.4	1.1	4.5	0.6	0	0.7	6.2	6.7	1.2
Other VOCs									
Bromodichloromethane	0.5	0.5	0	0	0	0	6.3	6.7	2.4
Carbon disulfide	2.8	3.2	0	3.0	3.7	1.6	4.3	3.8	9.6
Chloroform	4.7	2.6	23	1.8	0.9	0.2	27	27	18
Trichlorofluoromethane	0.5	0.5	0	0.6	0.9	0	2.0	2.2	0
TICs	17	11	73	6.0	19	0.7	14	13	31

(GAMA) requests a rerun to verify a result. Under normal circumstances, the three vials collected for a sample or a blank would yield comparable results. Highly unusual conditions occurred when the June 25, 2007, field blank was collected and resulted in the three vials having markedly different VOC results.

In the field notes for the site at which the unusual field blank was collected, the field crew recorded that they thought they might not have rinsed the peristaltic pump used to pump the blank water from the source bottles through the sampling equipment and into the sample vials for the field blank after the cleaning steps, which usually involve a methanol wash (which was done) and blank-water rinse (which was likely omitted). The three VOC vials for the field blank were the first sample containers to be filled during sample collection; therefore, the VOC results from the first of these vials would be the most affected by any contaminants from residual methanol in the lines or pump. The collection order was not marked on the three vials.

The NWQL notified GAMA project staff upon noticing a high number of VOC detections and an unusual chromatogram for this field blank. Information in the field notes led to a hypothesis that residual methanol may have been the source, and the remaining two vials were analyzed to test this hypothesis. Methanol is a polar organic solvent and would be expected to readily dissolve other polar organic compounds (if present), as well as (to a lesser degree) less polar and nonpolar organic compounds. Although the methanol used for cleaning is labeled as 99.9 percent pure, this level of purity does not preclude the presence of other organic constituents at microgram-per-liter concentrations. In addition, methanol may be exposed to airborne contaminants while being transferred into the containers used to transport and store it safely in field vehicles and mobile laboratories, and while being used for cleaning. Thus, the methanol likely had opportunities to accumulate organic contaminants.

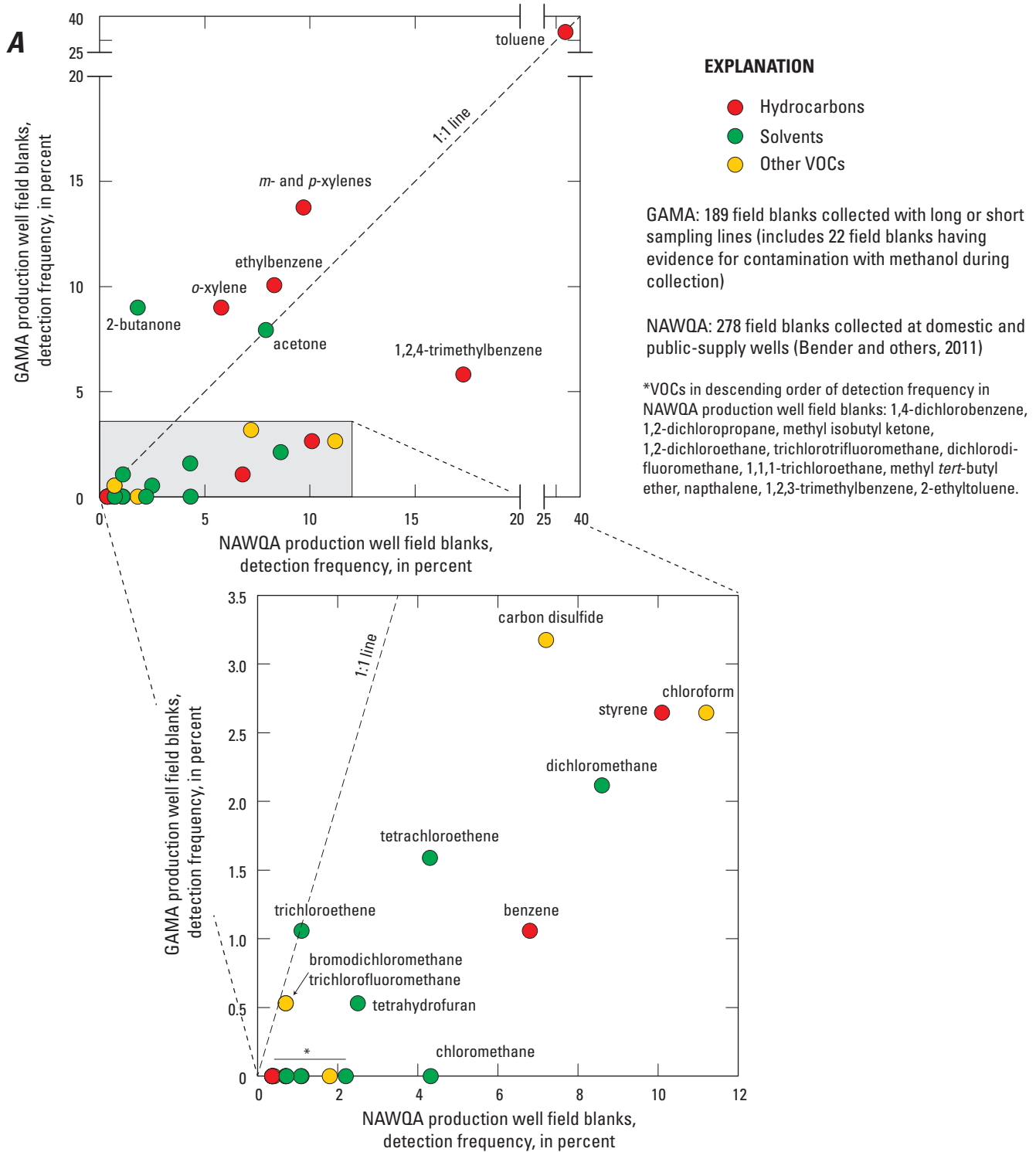


Figure 3. Detection frequencies in field blanks collected at production wells by the National Water-Quality Assessment (NAWQA) Program and detection frequencies in (A) all field blanks collected with long and short sampling lines by the GAMA Priority Basin Project, and (B) quality-control field blanks (QCFBs) collected with long and short sampling lines and inferred to be without contamination by the methanol used to clean field equipment.

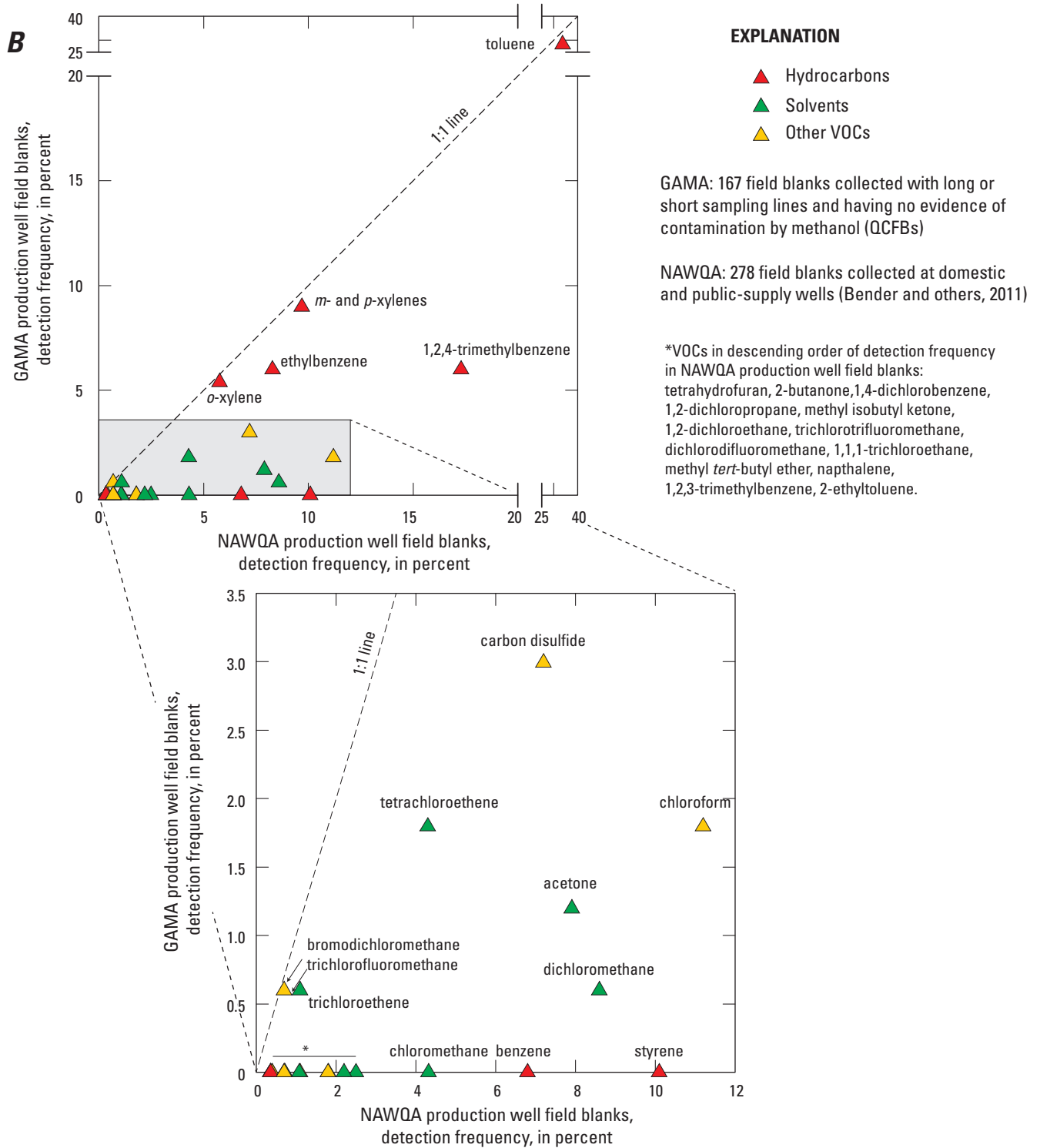


Figure 3.—Continued

Analyses of the three vials yielded different results. For the purposes of discussion, the vials were numbered based on the size of an unusually broad peak present on the chromatograms for all three vials from this field blank (fig. 4); this peak generally is not present on chromatograms for groundwater or surface-water samples (Donna Rose, U.S. Geological Survey National Water Quality Laboratory, written commun., 2007). On the basis of comparison between retention times for identified VOCs on the chromatogram and retention times for a larger suite of VOCs (J&W Scientific, 1998), this large, broad peak was inferred to correspond to methanol. This inferred methanol peak was not identified on the basis of the mass spectra because of the masses of the primary ions that would be produced from methanol are below the range of masses scanned by the mass spectrometer (Connor and others, 1998).

Results for the first, second, and third vials showed a progressive decrease in the number and concentration of VOCs detected (table 5). Three solvents (2-butanone, acetone, and tetrahydrofuran) were detected in the first and second vials, and only 2-butanone was detected in the third vial (table 5). These three solvents are polar organic compounds with high solubility in methanol and relatively high vapor pressures. The methanol purchased for cleaning is certified 99.9 percent pure methanol, with a maximum of 0.001 percent carbonyl compounds, which means that the methanol could have as much as a total of 10,000 µg/L of carbonyl compounds, such as acetone and 2-butanone. In addition, 2-butanone, acetone, and tetrahydrofuran are components of common products, including PVC cement, varnishes, and cleaners, that may be encountered in the field. Thus, it is not unexpected to find these constituents as contaminants in the methanol carried by the mobile laboratories.

In addition, the NWQL reported an unusually high number of tentatively identified compounds (TIC) in the chromatogram of the first vial, and fewer TICs in the chromatograms for the second and third vials (table 5). TICs are constituents not included in the 85 VOCs analyzed on NWQL schedule 2020. TICs are tentatively identified on the basis on their retention times and their mass spectra. The presence of a large number of TICs suggests some VOCs in the sample may have come from a source that usually does not contribute VOCs to groundwater or surface-water samples. NWQL schedule 2020 was designed to include most VOCs encountered in groundwater or surface-water samples (Connor and others, 1998).

Thiros and others (2011) report similar results for VOC contamination in blanks collected after insufficient rinsing of field sample-collection equipment. Field and equipment blanks contaminated with methanol contained high concentrations of acetone, 2-butanone, and tetrahydrofuran (8–800 µg/L), low concentrations of hydrocarbons (less than 1 µg/L), and a high number of TICs.

On the basis of these results, residual methanol from cleaning of equipment was inferred to be the source of the VOC detections in the three vials of the June 25, 2007, field blank. The progressive changes in the size of the inferred

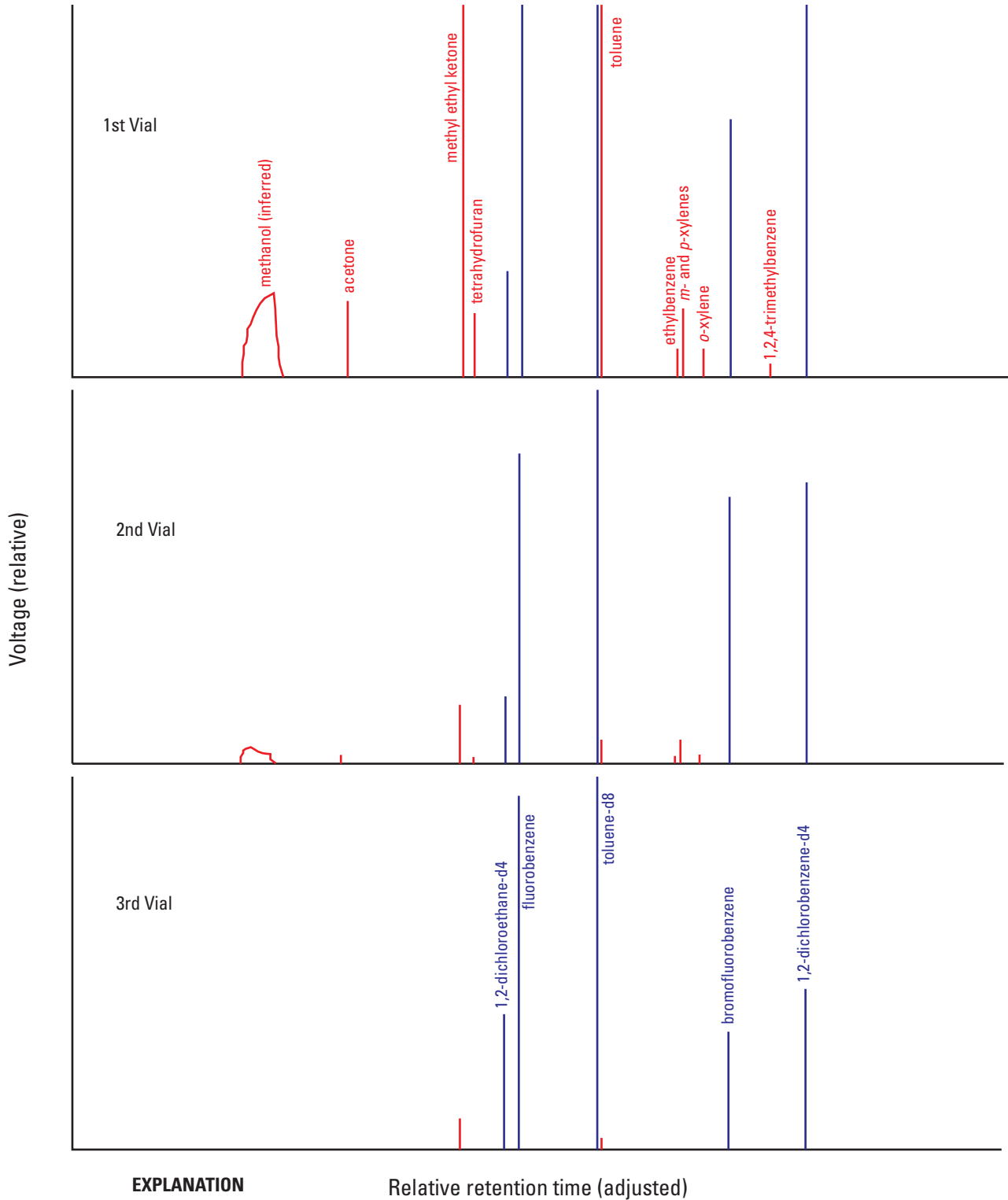
Table 5. Volatile organic compounds (VOCs) detected in a field blank analyzed in triplicate and determined to be affected by residual methanol from equipment cleaning, California GAMA Priority Basin Project, May 2004 through September 2010.

[The three vials were collected sequentially. TICs, tentatively identified compounds; E, estimated because of a higher degree of uncertainty than higher concentrations reported for the same compound; µg/L, micrograms per liter; –, not detected]

Constituent	Concentration (µg/L)		
	Vial #1	Vial #2	Vial #3
Solvents			
Acetone	30.3	E3.4	–
2-Butanone	155	16.4	E4.1
Tetrahydrofuran	4.36	E0.64	–
Hydrocarbons			
Toluene	0.12	E0.02	E0.02
Ethylbenzene	E0.07	E0.01	–
<i>m</i> - and <i>p</i> -Xylenes	E0.20	E0.06	–
<i>o</i> -Xylene	E0.08	E0.02	–
Styrene	E0.05	–	–
1,2,4-Trimethylbenzene	E0.02	–	–
Other VOCs			
TICs	13	0	1

methanol peak, the number of TICs, and the number and concentration of VOCs detected from the first to the second to the third vial are inferred to reflect the progressive decrease in the amount of methanol in the blank water as the pump was flushed with more blank water. (Results from the third vial were used to represent the field blank and are included in table A2.) The association of 2-butanone, acetone, tetrahydrofuran, and TICs appears to be indicative of contamination of field blanks with residual methanol used for cleaning of equipment.

Rinsing of field equipment during collection of a field blank appears sufficient to prevent methanol contamination of a groundwater sample collected immediately following collection of a field blank contaminated with methanol. The volume of blank water passing through the pump during collection of the three VOC vials was less than 1 liter; thus, the progressive decrease in the amount of methanol in the three vials suggests that the methanol was being rinsed out of the pump rapidly. Sample bottles filled after collection of the VOC vials would be expected to have little or no contamination from methanol. The groundwater sample collected immediately following the inadvertent methanol contamination test described in this report had no detections of VOCs (Fram and others, 2009; sample TMART-01). The groundwater sample collected immediately following collection of the field blank contaminated with methanol described by Thiros and others (2011) had no detections of VOCs that were detected in the contaminated field blank.



EXPLANATION Relative retention time (adjusted)

— Surrogate compounds Chromatograms were adjusted slightly so that the relative retention times for the surrogate compounds and the relative voltage for the toluene-d8 peak were the same for all three vials. Only peaks for surrogate compounds and identified volatile organic compounds (VOCs) are shown. Peaks for unidentified VOCs are not shown.

— Identified VOCs

Figure 4. Three vials of a field blank affected by methanol, California GAMA Priority Basin Project, June 25, 2007.

Acetone, 2-Butanone, and Tetrahydrofuran Contamination in Field Blanks

Occurrences of acetone, 2-butanone, tetrahydrofuran, and TICs in the full set of 211 field blanks suggest that 26 (12 percent) may have been affected by contamination from the methanol used to clean equipment. Fifteen (7.1 percent) had detections of acetone with concentrations greater than 2 µg/L (maximum 29 µg/L) (fig. 5), and 20 (9.5 percent) had detections of 2-butanone with concentrations ranging from 0.5 to 124 µg/L (fig. 6). A threshold of greater than 2 µg/L of acetone was used to indicate potential contamination from methanol because the highest concentrations measured in the source blank water, laboratory instrument blanks, and source-solution blanks were approximately 2 µg/L. The only two detections of tetrahydrofuran in field blanks occurred in field blanks that also had detections of 2-butanone and acetone (fig. 7; table A2). The 26 field blanks inferred to be contaminated with methanol had significantly higher numbers of TICs than the 185 field blanks without 2-butanone or acetone detections (table 6). The number of TICs was significantly positively correlated with 2-butanone concentration (Spearman's rho=0.63, p=0.001) and with acetone concentration (Spearman's rho=0.53, p=0.005).

The frequency of this inferred contamination with methanol was significantly greater in field blanks collected with monitoring-well equipment or long sampling lines compared to field blanks collected with short sampling lines (Kruskal-Wallis test, p=0.004). Eighteen percent (4 of 22) of the field blanks collected with monitoring-well equipment, 19 percent (15 of 77) of the field blanks collected with long sampling lines, and 6.2 percent (7 of 112) of field blanks collected with short sampling lines were inferred to have methanol contamination. The differences in frequency of contamination with methanol may be explained by differences between methods used to collect field blanks with the three configurations of sampling lines and by the differences in efficiency of rinsing the three configurations.

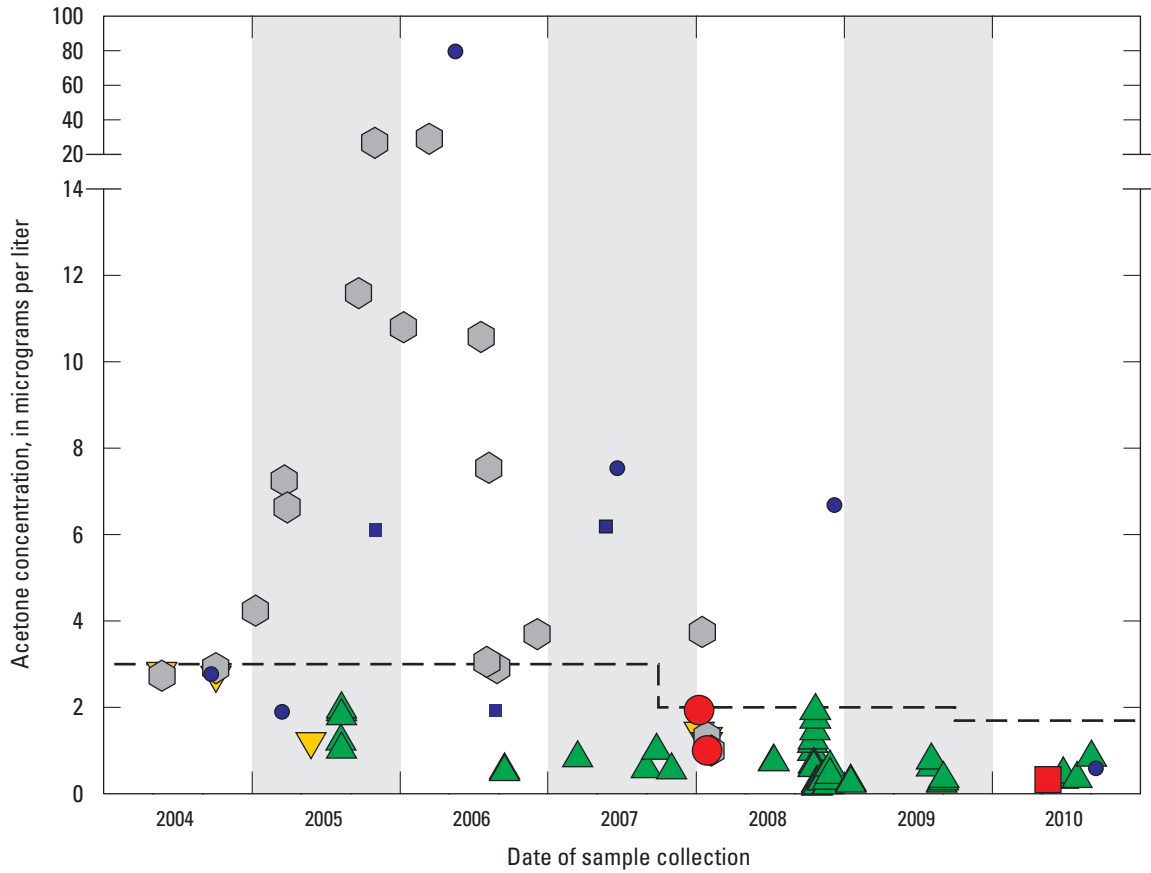
The USGS National Field Manual for the Collection of Water-Quality Data (<http://water.usgs.gov/owq/FieldManual/>) recommends that sampling equipment be rinsed with 8 liters of certified blank water after the methanol wash step, and that an additional 6 liters of certified blank water be pumped through the equipment prior to collecting a field blank. In a test of field methods for collection of VOCs, Thiros and others (2011) verified that this protocol was sufficient for removing residual methanol from sampling equipment: none of the field blanks collected for their study contained quantifiable concentrations of 2-butanone, acetone, or tetrahydrofuran. Thiros and others (2011) concluded that high detection frequencies of VOCs in field blanks collected for the NAWQA Program likely indicated that field crews did not always use the recommended amount of certified blank water to rinse sample-collection equipment before collecting field blanks. Field blanks

collected for the GAMA Program had lower detection frequencies of VOCs than those collected by the NAWQA Program, suggesting that GAMA field crews followed the recommended rinsing protocols more consistently than did NAWQA field crews. Nevertheless, it is possible that some field blanks were collected after rinsing with less than 14 liters of certified blank water.

The portable peristaltic pump used to pump blank water through the equipment in order to collect the field blank is not used for collection of groundwater samples. The peristaltic pump is also used for pumping the series of cleaning solutions through sampling equipment after collection of groundwater samples, and does come in contact with methanol. Use of a dedicated peristaltic pump for collection of blanks may reduce the chance of contamination (although even a dedicated pump would be cleaned between uses with the same procedure). The second possibility is insufficient rinsing of the sample-collection equipment with blank water after the methanol wash step and prior to collection of field blanks. In contrast, hundreds of liters of groundwater pass through the sampling equipment prior to sample collection because of the time required to purge a well and wait for the field parameter readings to stabilize prior to commencement of sample collection. These differences result in a much greater likelihood that the field blanks come in contact with the methanol used to clean field equipment.

Acetone, 2-Butanone, and Tetrahydrofuran Contamination in Groundwater Samples

The detection frequencies of 2-butanone and acetone in the 2,026 groundwater samples were 0.4 percent each, which are much lower than the detection frequencies in the field blanks (table 4). Fifteen of the 2,026 groundwater samples had detections of 2-butanone and (or) acetone, and 7 of these 15 also had detections of tetrahydrofuran. An additional 17 groundwater samples had a detection of tetrahydrofuran without detections of 2-butanone or acetone. Of these 32 groundwater samples, 28 had no detections of solvents other than acetone or 2-butanone or tetrahydrofuran. Of the 32 groundwater samples, 11 (34 percent) were collected with monitoring-well equipment, which is significantly higher than the percentage of all groundwater samples collected with monitoring-well equipment (8.2 percent) (contingency table test, p<0.001). The association between 2-butanone and acetone detections and the significantly greater detection frequency in samples collected with monitoring-well equipment in the groundwater samples and the field blanks suggests that contamination with methanol may have affected a small number of groundwater samples. The overall detection frequency in groundwater samples was less than in field blanks because the peristaltic pump was not used for groundwater samples and because of the additional amount of rinsing that generally occurs during collection of groundwater samples.



EXPLANATION

Sample type (only detections are shown)

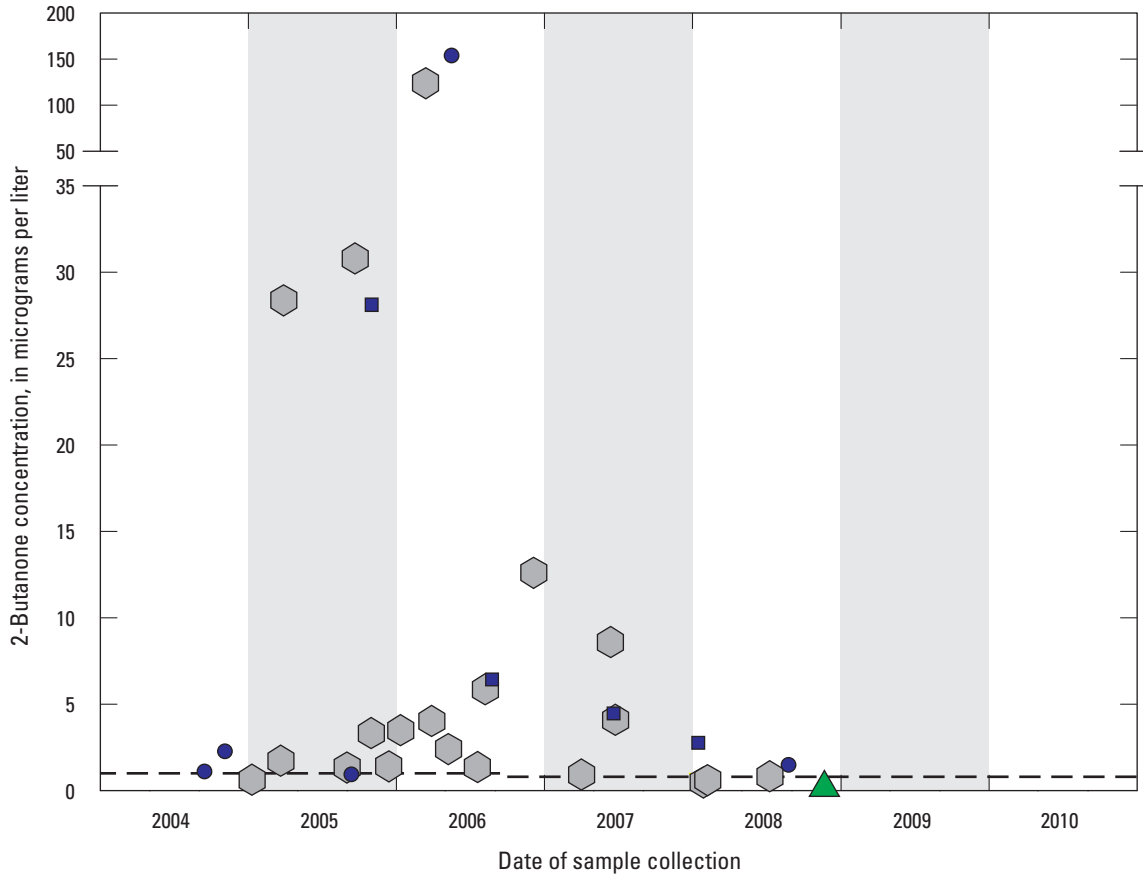
- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- ⬡ Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Threshold

- - - Long-term method detection level (LT-MDL)

The study reporting level (SRL) approach was not applied to acetone because there is no threshold concentration above which concentrations in groundwater can be distinguished from concentrations in field blanks. All detections in groundwater are rejected, and the samples are considered "not analyzed" for acetone.

Figure 5. Concentrations of acetone detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

Sample type (only detections are shown)

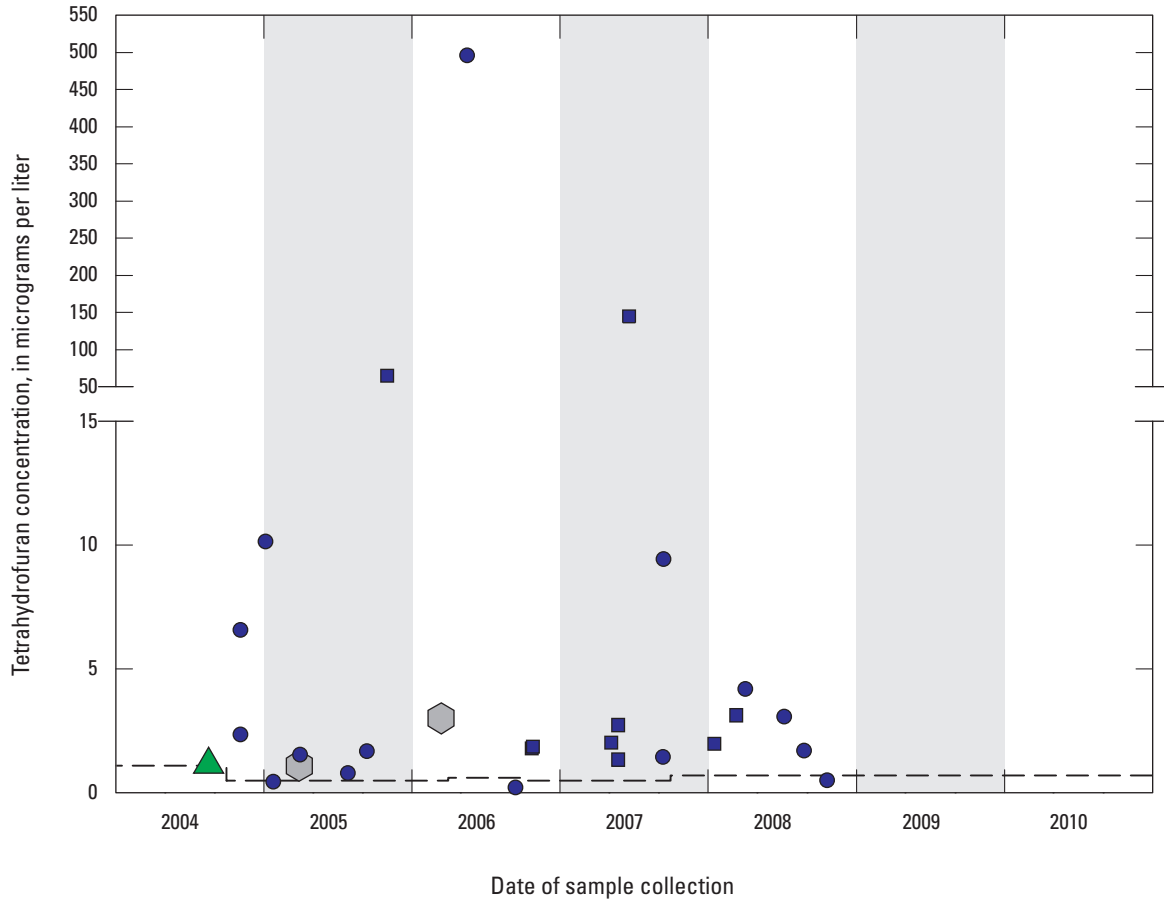
- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- ⬡ Field blank contaminated by methanol (n=26)
- ◇ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Threshold

- - - Long-term method detection level (LT-MDL)

The study reporting level (SRL) approach was not applied to 2-butanone because there is no threshold concentration above which concentrations in groundwater can be distinguished from concentrations in field blanks. All detections in groundwater are rejected, and the samples are considered "not analyzed" for 2-butanone.

Figure 6. Concentrations of 2-butanone detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Threshold

- - Long-term method detection level (LT-MDL)

The study reporting level (SRL) approach was not applied to tetrahydrofuran because there is no threshold concentration above which concentrations in groundwater can be distinguished from concentrations in field blanks. All detections in groundwater are rejected, and the samples are considered "not analyzed" for tetrahydrofuran.

Figure 7. Concentrations of tetrahydrofuran detected in field blanks, source-solution blanks, laboratory instrument blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

Table 6. Detection frequencies for the 17 VOCs and the TICs detected in field blanks and results of statistical tests for differences between subsets of the field blanks, California GAMA Priority Basin Project, May 2005 through September 2010.

[A result of significant difference on a statistical test is as a p-value less than the threshold value (α) of 0.05. For cases with a result of significance on the Kruskal-Wallis test, Tukey's multiple comparison test was applied to determine which sample groups were significantly different. **Sampling equipment configurations:** M, monitoring-well equipment; L, long sampling lines; S, short sampling lines. **Other abbreviations:** VOCs, volatile organic compounds; TICs, tentatively identified compounds; n, number; <, less than; >, greater than; ns, not significant]

	Detection frequency (percent)		p-value (Wilcoxon test, methanol-affected to unaffected)	Three configurations of unaffected field blanks, detection frequency (percent)			p-value (Kruskal-Wallis test, three configurations)	Configurations with significant differences
	Methanol-affected field blanks (n = 26)	Unaffected field blanks (n = 185)		Monitoring-well equipment (M) (n = 18)	Long sampling lines (L) (n = 62)	Short sampling lines (S) (n = 105)		
Hydrocarbons								
Benzene	12	0	<0.001	0	0	0	ns	ns
Ethylbenzene	42	5.9	<0.001	5.6	15	1.0	0.002	L > S
Styrene	19	0	<0.001	0	0	0	ns	ns
Toluene	77	30	<0.001	50	31	27	ns	ns
1,2,4-Trimethylbenzene	7.7	7.0	ns	17	11	2.9	0.036	M > S, L > S
<i>m</i> - and <i>p</i> -Xylene	50	10	<0.001	22	18	3.8	0.002	M > S, L > S
<i>o</i> -Xylene	38	5.4	<0.001	5.6	13	1.0	0.004	L > S
Solvents								
Acetone	65	1.6	<0.001	5.6	1.6	1.0	ns	ns
2-Butanone	77	0	<0.001	0	0	0	ns	ns
Dichloromethane	12	0.5	<0.001	0	0	1.0	ns	ns
Tetrachloroethene	3.8	1.6	ns	0	3.2	1.0	ns	ns
Tetrahydrofuran	7.7	0	<0.001	0	0	0	ns	ns
Trichloroethene	7.7	0.5	0.004	0	1.6	0	ns	ns
Other VOCs								
Bromodichloromethane	3.8	0	0.007	0	0	0	ns	ns
Carbon disulfide	3.8	2.7	ns	0	3.2	2.9	ns	ns
Chloroform	15	3.2	0.006	17	3.2	1.0	0.002	M > L, M > S
Trichlorofluoromethane	0	0.5	ns	0	0	1.0	ns	ns
TICs	46	12	<0.001	72	8.1	4.8	<0.001	M > L, M > S

In addition, 2-butanone, acetone, and tetrahydrofuran are the primary ingredients in the cements used to join polyvinyl chloride (PVC) piping, and PVC piping may be used in the distribution system connected to the well. The groundwater sample with the highest concentrations (80 µg/L of acetone, 154 µg/L of 2-butanone, and 495 µg/L of tetrahydrofuran) was collected from a well where the owner had just connected a PVC line to the wellhead to create a sampling port, and a strong odor of PVC cement was recorded in the field notes for the site (Ferrari and others, 2008). It is highly probable that the detections were the result of contamination from PVC cement and were not representative of the groundwater in the aquifer. The presence of PVC piping with relatively fresh connections was noted at a few other sites from which the groundwater samples had detections of 2-butanone, acetone, and (or) tetrahydrofuran (Fram and others, 2009). However, the presence or absence of these conditions is not routinely recorded in the field notes, thus, it is not possible to assess how many of the detections of these compounds in groundwater could be due to contamination from PVC cement contacting the groundwater during sample collection.

The relative concentrations of the three solvents imparted by contamination from the two known sources (methanol and PVC cement) do not appear to follow a characteristic pattern. The groundwater sample with the highest concentrations of all three solvents does not lie at the end of a trend in the concentration data for other samples and blanks containing the solvents. Two other groundwater samples from sites with documented presence of new PVC cement contained only tetrahydrofuran (Fram and others, 2009; study unit M5). The order of the three solvents in the list of ingredients in different brands of PVC cement varies, suggesting that the relative amounts of the three solvents vary. Field blanks containing methanol generally were characterized by the presence of 2-butanone and acetone, with lesser amounts of tetrahydrofuran (table 5), although the data do not fall on a smooth trend. The concentrations of the acetone, 2-butanone, and tetrahydrofuran contaminants in the methanol may be variable, which makes sense, as different containers of methanol may have different histories of exposure to sources of contamination.

SRLs for Acetone, 2-Butanone, and Tetrahydrofuran

The contamination patterns of acetone, 2-butanone, and tetrahydrofuran are not amenable to the SRL approach. The highest concentrations of all three VOCs in groundwater samples (greater than 100 µg/L) and in field blanks occurred in samples collected at sites having confirmed presence of known sources of extrinsic contamination—fresh PVC cement at well sites and methanol in field blanks. Seven field blanks contained greater than 10 µg/L of one or more of the three VOCs. In contrast, the maximum concentration for all other VOCs detected in field blanks was 0.69 µg/L. The observations that field blanks can contain high concentrations of acetone, 2-butanone, and tetrahydrofuran, and that contamination from PVC cement at well sites can produce

high concentrations of these three VOCs in groundwater samples, indicate that it is not possible to define a threshold concentration above which detections in groundwater have an acceptable probability of being representative of aquifer conditions rather than due to contamination. Therefore, SRLs cannot be defined for these three VOCs.

Because SRLs cannot be defined and no quantitative QC assessment can be made, it is not possible to evaluate whether detections of 2-butanone, acetone, and tetrahydrofuran in groundwater samples represent aquifer conditions or extrinsic contamination. For the GAMA Program, groundwater samples with reported detections of these three VOCs are defined as having no data available for these three VOCs. This is achieved by changing the data-quality-indicator code (DQI) in NWIS to “Q,” for “reviewed and rejected” and by adding the following result-level remark: “Upon careful review, these data have been rejected per Fram and others, 2012, USGS SIR 2012-5139.” Data for groundwater samples having non-detections of 2-butanone, acetone, and tetrahydrofuran are not similarly rejected. Extrinsic contamination produces a positive bias; therefore, a non-detection indicates both the absence of contamination and the absence of detectable concentrations of the VOC in groundwater. Note that “not analyzed” is not the same as “not detected.” Rejecting all reported detections of these three VOCs means that detection frequencies for these VOCs in groundwater cannot be defined.

Differences Between Sample-Collection Equipment Configurations

Because the frequency of contamination attributable to methanol was significantly different in field blanks collected with different sampling equipment configurations, it was prudent to assess whether there were significant differences for other constituents. Of the 185 field blanks without methanol contamination, 18 were collected with monitoring-well equipment, 62 were collected with long sampling lines, and 105 were collected with short sampling lines. Significant differences between the field blanks collected using the three equipment configurations were found for hydrocarbons, chloroform, and TICs (table 6).

Field blanks collected with long sampling lines had significantly greater concentrations of *m*- and *p*-xylenes, *o*-xylene, ethylbenzene, and 1,2,4-trimethylbenzene than field blanks collected with short sampling lines, and field blanks collected with monitoring-well equipment had significantly greater concentrations of *m*- and *p*-xylenes and 1,2,4-trimethylbenzene than field blanks collected with short sampling lines (table 6). However, detection frequencies of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene were much greater in blanks (of any configuration) than in the groundwater samples (table 4); thus these differences between sample-collection equipment configurations are not considered relevant for the quality-control assessment of the groundwater VOC data.

Chloroform was the most frequently detected VOC in groundwater samples (27 percent; [table 4](#)), thus the quality-control assessment for chloroform is vitally important and could have a noticeable effect on the interpretation of the groundwater-quality data. Chloroform concentrations were significantly greater in field blanks collected with monitoring-well equipment than in field blanks collected with either long or short sampling lines, and there was no significant difference between field blanks collected with the long and with the short sampling lines ([table 6](#)).

TICs usually are not used in the interpretation of the groundwater-quality data; however, they may be an indicator of the presence of contamination by VOCs not generally present in groundwater. The occurrence of TICs in field blanks collected with monitoring-well equipment was significantly more frequent than the occurrence in field blanks collected with either long or short sampling lines.

Quality-Control Field Blanks (QCFBs)

Of the 211 field blanks, 167 were included in the set of QCFBs that was used to calculate SRLs. The 26 field blanks with evidence of contamination by methanol and 18 other field blanks collected with monitoring-well equipment were excluded from the set of QCFBs.

Field blanks collected with monitoring-well equipment had significantly more detections of chloroform, toluene, 1,2,4-trimethylbenzene, and *m*- and *p*-xylenes than field blanks collected with long or short sampling lines ([table 6](#)). However, with only 18 field blanks collected with monitoring-well equipment, SRLs can be established with far less confidence than for the set of 167 QCFBs: The 18th-ranked monitoring-well field blank corresponds to the BD-95/56. In the absence of more quantitative estimates, the SRLs determined from the QCFBs were also applied to groundwater samples collected with monitoring-well sampling equipment, except in the case of chloroform where detections of chloroform in monitoring-well field blanks suggested that an SRL with a higher concentration was warranted.

Evaluation of Potential Sources of Contamination, Selection of SRLs, and Application of SRLs to Groundwater Data for VOCs Detected in Blanks

The 15 VOCs that were detected in field or source-solution blanks and considered to be amenable to the SRL approach were divided into groups on the basis of chemical

class and inferred mechanism of contamination. For each group, the following topics are discussed: (1) inferred mechanism(s) of contamination, (2) comparison of SRLs determined by the different methods, (3) selection of an appropriate SRL (if any) and results of application of that SRL to the groundwater data, and (4) comparison to SRLs determined from NAWQA VOC field-blank data by Bender and others (2011).

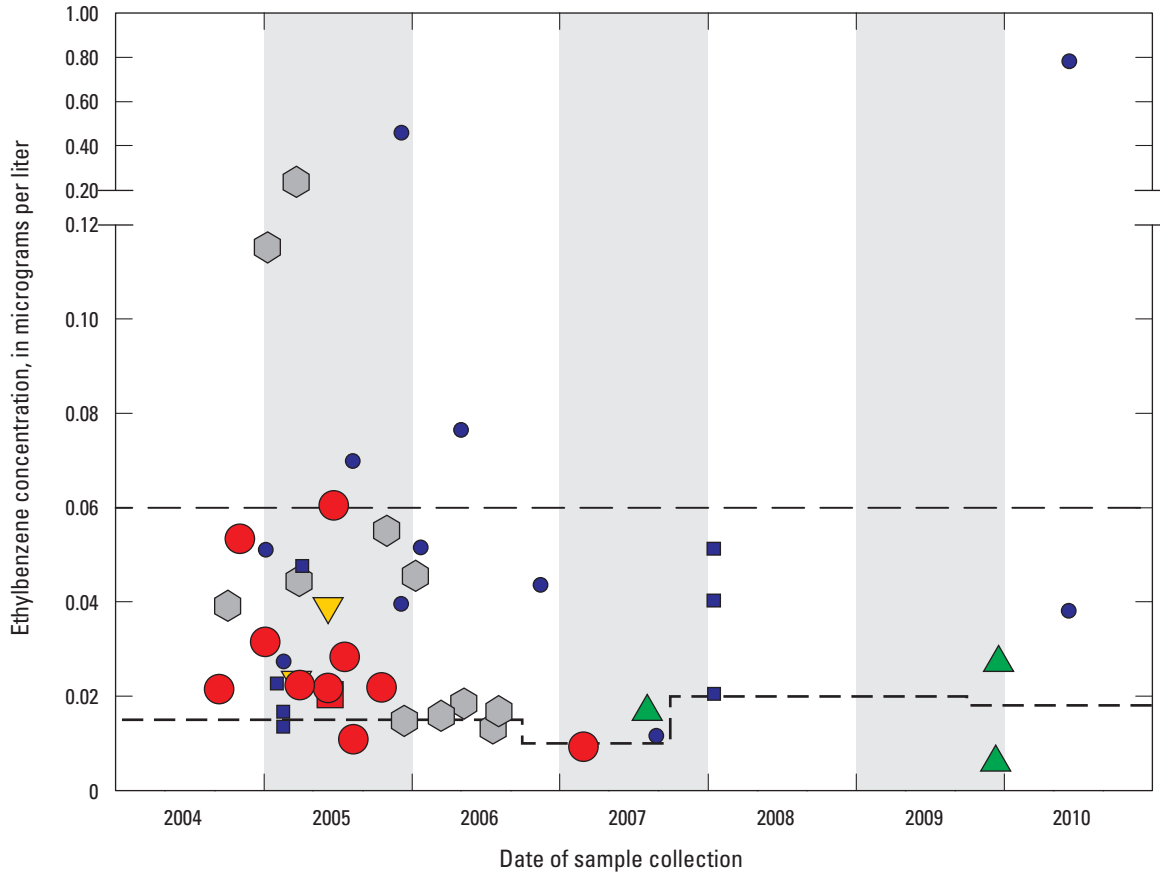
SRLs were implemented in NWIS by changing the reported value to “<SRL,” where “SRL” is the value of the SRL for that VOC, and by adding the following result-level remark: “Upon careful review, these data have been censored per Fram and others, 2012, USGS SIR 2012-5139. Bench chemist values can be obtained from NWQL.”

Hydrocarbons

Chemically, the seven hydrocarbons detected in blanks all are benzene rings with 0 to 3 aliphatic hydrocarbon substituents. All are components of gasoline and other petroleum-based fuels, materials, and combustion products. They are divided into three groups for discussion based on similarities in inferred mechanisms of contamination.

Ethylbenzene, *m*- and *p*-Xylenes, *o*-Xylene, Benzene, and Styrene

Ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene had higher detection frequencies in QCFBs and source-solution blanks than in groundwater samples, whereas the detection frequencies of benzene and styrene were lower in the QCFBs and source-solution blanks than in groundwater samples ([table 4](#); [figs. 8–12](#)). These five hydrocarbons are present in fuels used in and exhaust produced by operation of vehicles and generators, and emissions from fuel combustion generally are the dominant source of these hydrocarbons in ambient air (for example, Daisey and others, 1994; Monod and others, 2001). Although it is also possible that these compounds could enter the blanks and the groundwater samples through entirely different avenues, this is unlikely to be the case. Correlations among the five hydrocarbons and the ratios of hydrocarbon species in blanks and groundwater samples were examined to evaluate the hypothesis that fuel vapors or exhaust were the source of contamination.



EXPLANATION

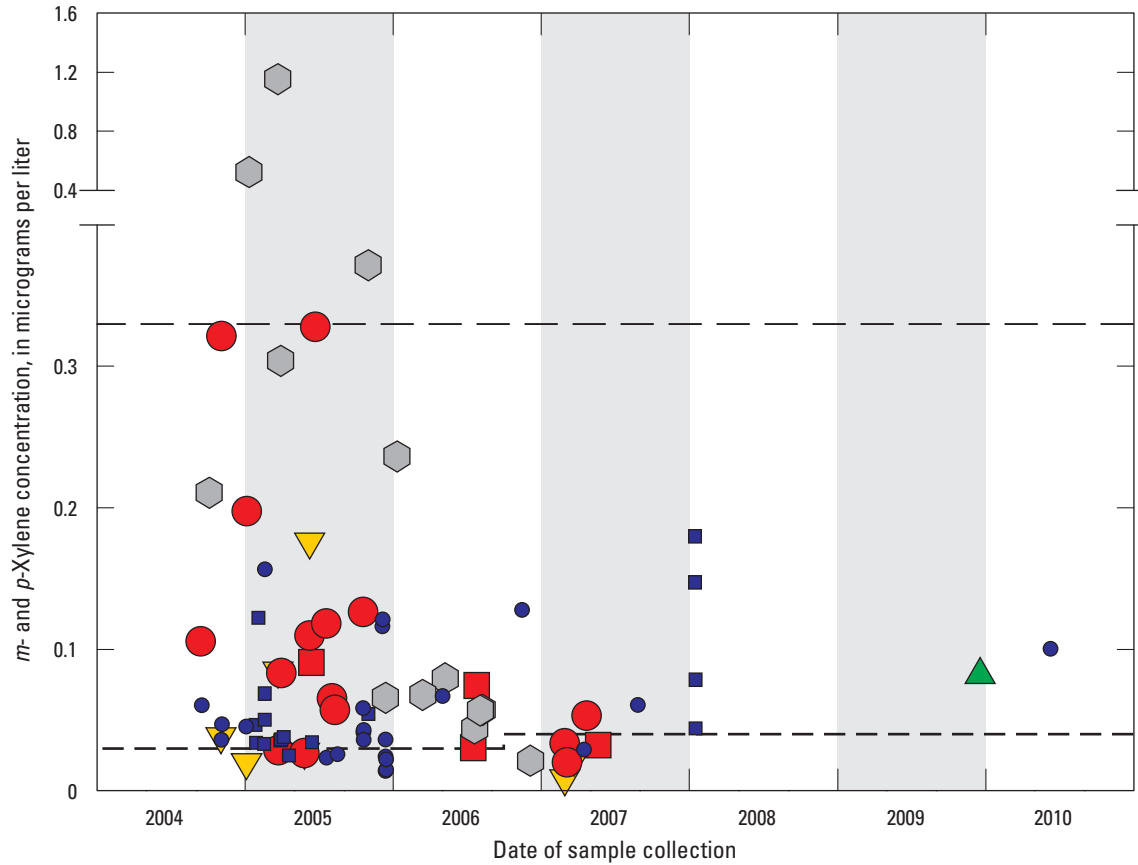
Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- ⬡ Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Thresholds

- - - Long-term method detection level (LT-MDL)
- — — Study reporting level (SRL)

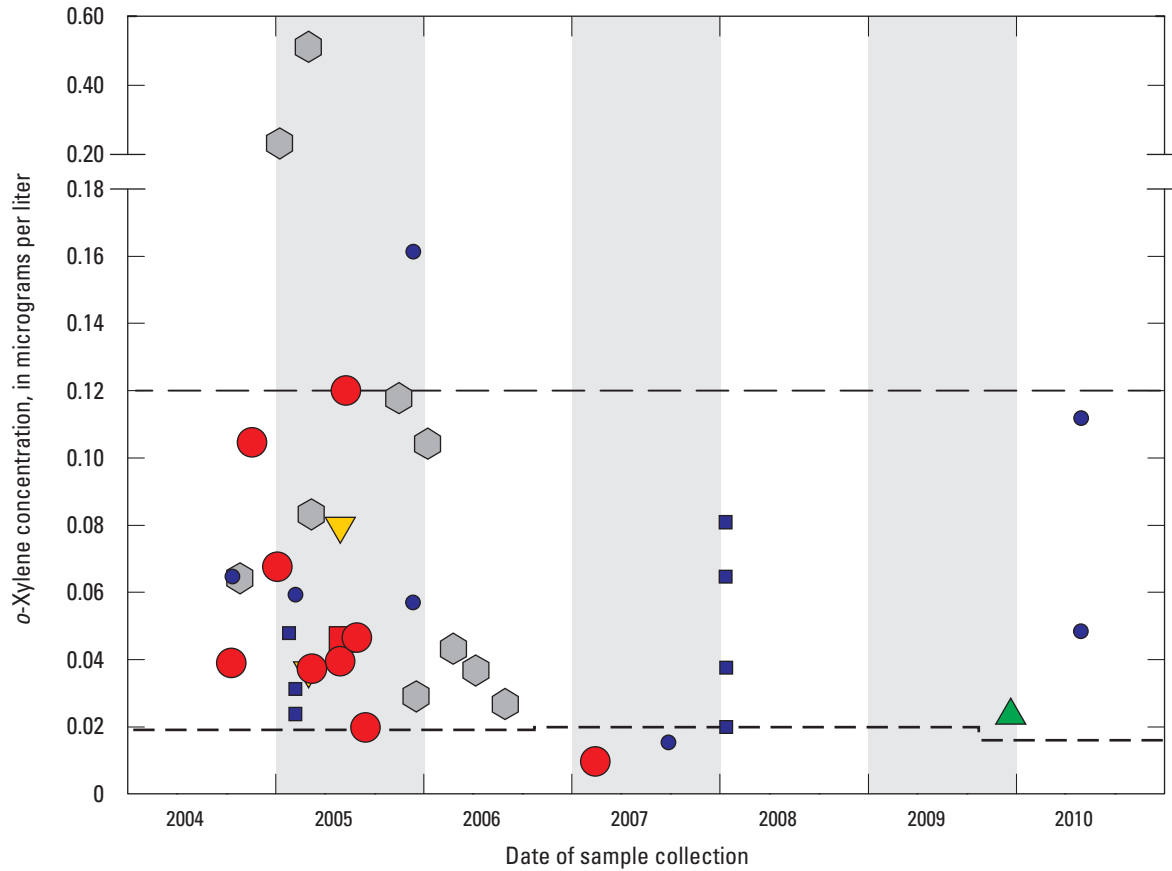
Figure 8. Concentrations of ethylbenzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

- Sample type (only detections are shown)**
- Quality-control field blank (QCFB, n=167)
 - Monitoring-well field blank (n=18)
 - ⬡ Field blank contaminated by methanol (n=26)
 - ▼ Source-solution blank (n=109)
 - ▲ Laboratory instrument blank (n=2,411)
 - Groundwater—long or short lines (n=1,859)
 - Groundwater—monitoring well (n=167)
- Thresholds**
- - - Long-term method detection level (LT-MDL)
 - Study reporting level (SRL)

Figure 9. Concentrations of *m*- and *p*-xylenes detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

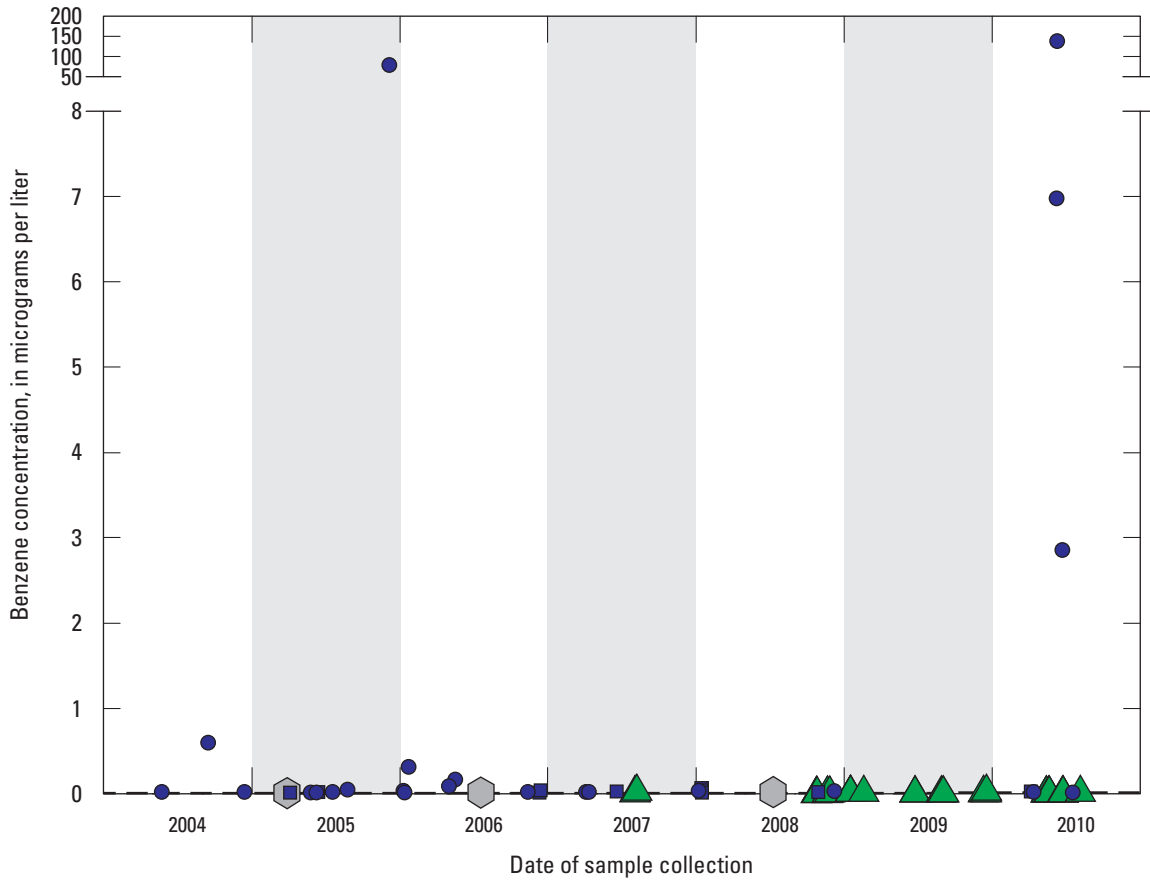
Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- ⬡ Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Thresholds

- - - Long-term method detection level (LT-MDL)
- — — Study reporting level (SRL)

Figure 10. Concentrations of *o*-xylene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

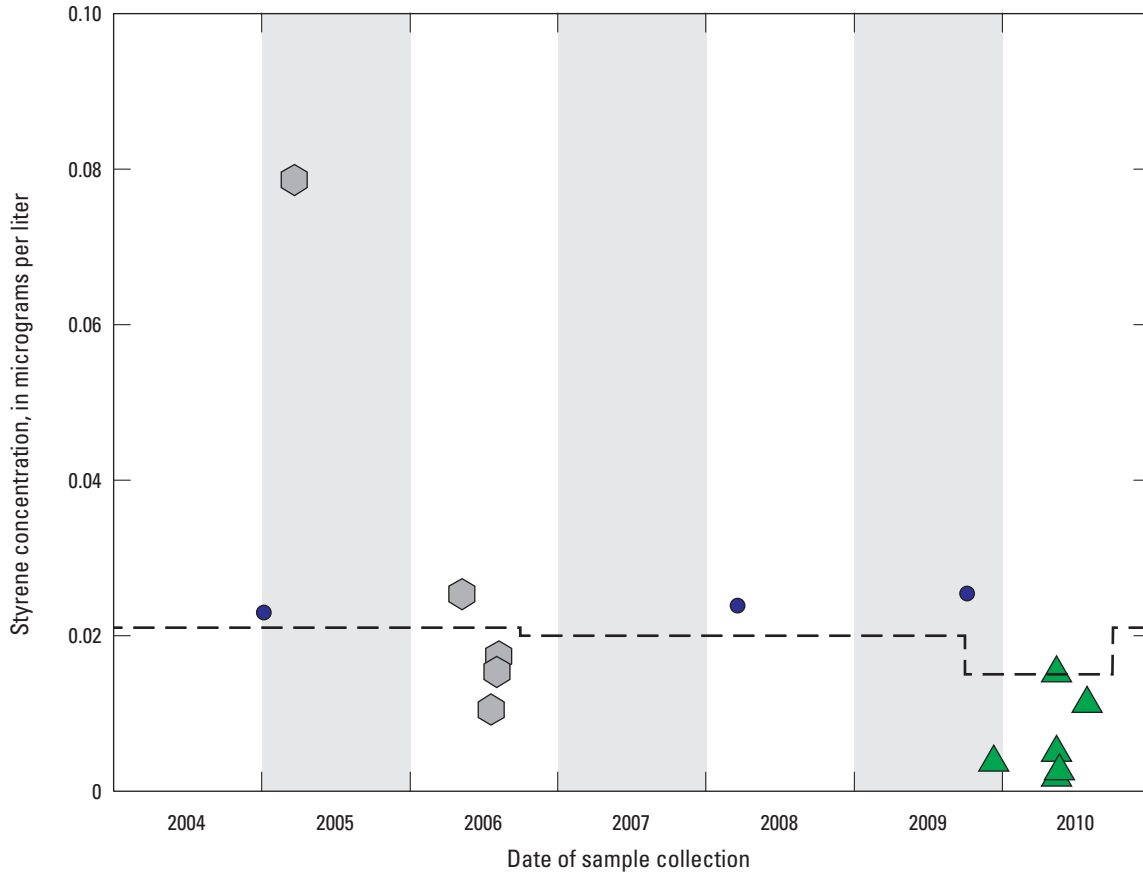
Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Threshold

- - Long-term method detection level (LT-MDL)
- A study reporting level (SRL) was not needed for benzene.

Figure 11. Concentrations of benzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—long or short lines (n=1,859)
- Groundwater—monitoring well (n=167)

Threshold

- - Long-term method detection level (LT-MDL)
- A study reporting level (SRL) was not needed for styrene.

Figure 12. Concentrations of styrene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

Inferred Mechanisms of Contamination

Concentrations of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene in the blanks are significantly correlated with one another ($p < 0.001$ for Spearman's rho tests between each pair). Concentrations of the three compounds in the QCFBs, source-solution blanks, field blanks from monitoring wells, and field blanks affected by methanol contamination all lie on the same linear correlations that correspond to ethylbenzene/*m*- and *p*-xylenes and *o*-xylene/*m*- and *p*-xylenes ratios of approximately 0.2 and 0.4, respectively (fig. 13A,B). These ratios are similar to those found in vehicle exhaust and ambient urban air (Daisey and others, 1994; Monod and others, 2001). These relations suggest that the QCFBs, source-solution blanks, field blanks from monitoring wells, and field blanks affected by methanol contamination are all subject to contamination from the same source of hydrocarbons, which is likely vehicle exhaust fumes.

Most groundwater samples containing ethylbenzene, *o*-xylene, and *m*- and *p*-xylenes had ratios of hydrocarbons similar to those observed in field and source-solution blanks (fig. 13A,B), suggesting that the groundwater samples may have been contaminated with the same source of hydrocarbons as the blanks—vehicle exhaust fumes. VOCs from vehicle exhaust fumes also could have been present in the aquifer due to recharge of recent precipitation; however, other information about the groundwater samples suggests that the ethylbenzene, *o*-xylene, and *m*- and *p*-xylenes were unlikely to have been the result of aquifer conditions. Of the groundwater samples with hydrocarbon ratios similar to those in the blanks or detection of low concentration of *m*- and *p*-xylenes without detections of ethylbenzene or *o*-xylene, 45 percent had tritium activities less than 1 TU, suggesting absence of significant amounts of modern recharge. Of those with tritium activities greater than 1 TU, 60 percent were from sites with less than 20 percent urban land use in the area within 500 meters of the well site, suggesting absence of significant sources of vehicle exhaust fumes. In the dataset as a whole, percentage of urban land use around the well site was not correlated with detection of ethylbenzene, *o*-xylene, or *m*- and *p*-xylenes in groundwater samples (Wilcoxon rank-sum test, $p > 0.05$).

Five groundwater samples had ethylbenzene/*m*- and *p*-xylenes and (or) *o*-xylene/*m*- and *p*-xylenes ratios greater than 1, which suggests a different source of hydrocarbons. The two samples with the highest ratios were collected from the same site (TLR-07) in 2005 and 2010 in study unit V7 (southeast San Joaquin Valley; Burton and Belitz, 2008), and also contained greater than 75 µg/L of benzene. That area of the southeast San Joaquin Valley has extensive oil and gas production, thus the source of the hydrocarbons in groundwater may be the petroleum deposits. Hydrocarbons

in natural petroleum deposits or anthropogenic sources of petroleum products (such as spills and leaks) will dissolve in groundwater. The dissolved hydrocarbons are then subject to biodegradation under aquifer conditions, and they biodegrade at different rates; thus, hydrocarbon ratios in groundwater may differ from those in petroleum.

Concentrations of benzene and styrene in the blanks were correlated with concentrations of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene ($p < 0.001$ for styrene and $p < 0.001$ to 0.003 for benzene, Spearman's rho test), and the ratios of benzene and styrene to *m*- and *p*-xylenes in field blanks were similar to the ratios in ambient air (fig. 13C,D). The detection frequencies of benzene and styrene in blanks, however, were much lower than those of the other hydrocarbons (table 4). The median detected concentrations of benzene and styrene in field blanks were less than or equal to the maximum LT-MDL; the median detected concentrations of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene in field blanks were greater than the maximum LT-MDL. This suggests that although the ambient air with vehicle exhaust may contaminate sampling equipment (or the methanol) with all five hydrocarbons, the resulting concentrations of benzene and styrene commonly may be below detection levels. All six field blanks containing benzene and styrene were contaminated with methanol, and five of the six blanks (83 percent) also had detections of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene (table A2).

Among groundwater samples with detections of benzene or styrene, the detection frequency of ethylbenzene, *m*- and *p*-xylenes, or *o*-xylene (33 percent) was significantly lower than in the blanks (contingency table test, $p = 0.021$). Furthermore, the ratios between benzene or styrene and *m*- and *p*-xylenes in groundwater samples were not the same as the ratios in blanks (fig. 13C,D). These ratios suggest that the detections of styrene and benzene in groundwater likely were not caused by contamination.

The relative detection frequencies of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene hydrocarbons in laboratory instrument blanks, source-solution blanks, the various subsets of field blanks, and groundwater samples (tables 4, 6) provided data for developing a hypothesis about the mechanism of contamination from vehicle exhaust. The presence of hydrocarbons in source-solution blanks indicates that potential sources of contamination are the source blank water, laboratory processes, the vials, or something encountered during travel, either before or after sample collection. The absence of detections on the certificates of analysis for the source blank water suggests that the source blank water itself is not the source of contamination, and the much lower detection frequencies in laboratory instrument blanks suggest that laboratory processes are not the source.

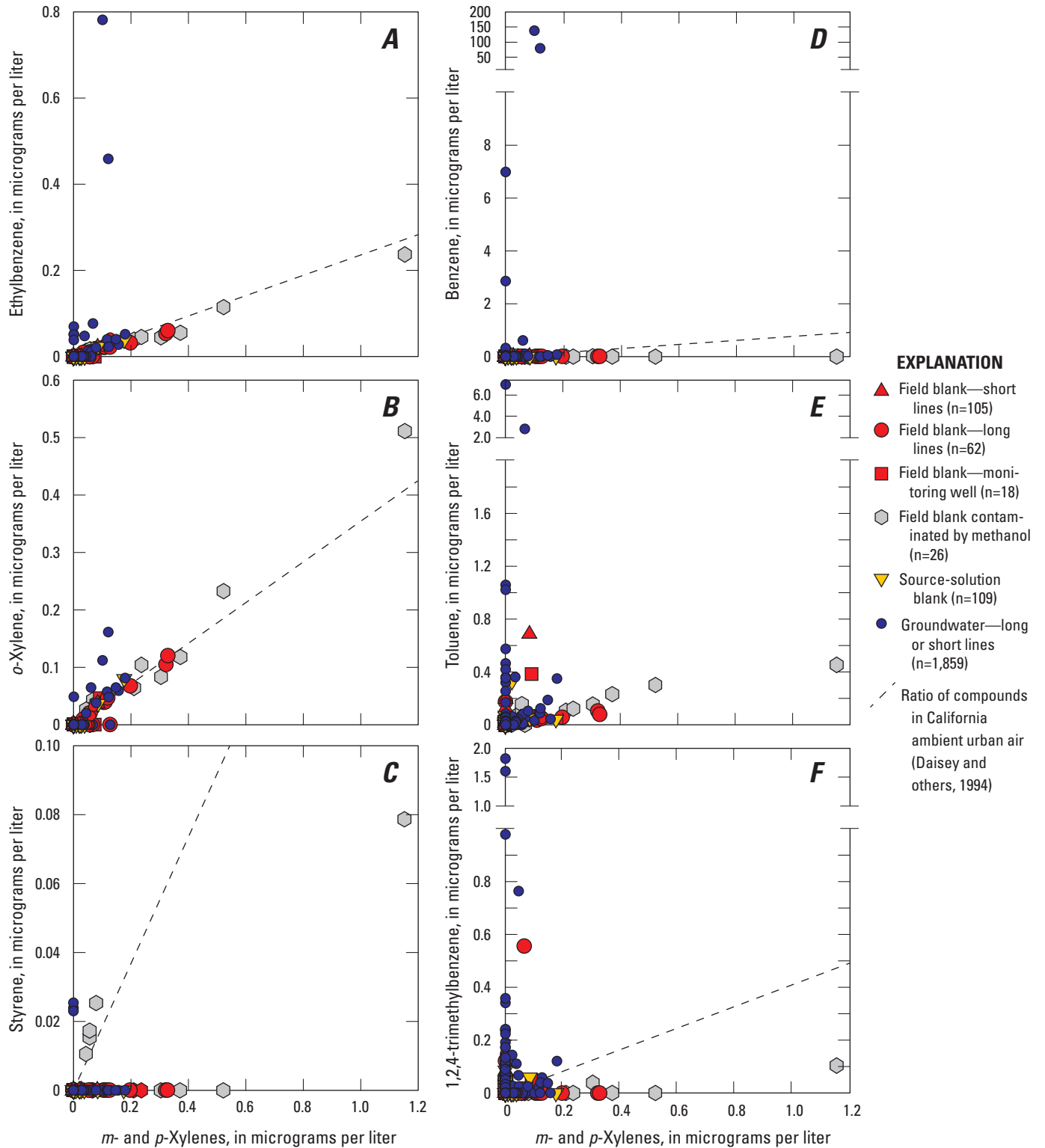


Figure 13. Relations between *m*- and *p*-xylenes and (A) ethylbenzene, (B) *o*-xylene, (C) styrene, (D) benzene, (E) toluene, and (F) 1,2,4-trimethylbenzene detected in field blanks, source-solution blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010.

The fact that the detection frequencies in groundwater samples are less than in source-solution blanks suggests that processes occurring during travel after sample collection are not the source. That leaves the vials and processes occurring during transit of the source blank water to the field site as potential sources of contamination to the source-solution blanks. Both the vials and the source blank water may be exposed to fuel exhaust or vapors from fuel used in vehicles during transit or storage. The bottles of source blank water tend to be tightly sealed, and caps on the unused VOC vials generally are loosely attached. This difference in capping may point to the vials as the problem, but there is no way to be certain with this dataset.

The potential sources of contamination to field blanks are the same as those for source-solution blanks, with the addition of contact with sample-collection equipment. Detection frequencies of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene were significantly higher in field blanks than in source-solution blanks (table 4), indicating that contact with sample-collection equipment was a source of contamination. Detection frequencies of the three hydrocarbons were significantly higher in QCFBs collected with long sampling lines compared to those collected with short sampling lines (table 6), indicating that more contact with field equipment yields more contamination. Detection frequencies of the three hydrocarbons were significantly higher in field blanks affected by methanol compared to those not affected by methanol (table 6); however, the concentrations of hydrocarbons in the inadvertent field test of methanol contamination (table 5) were similar to the concentrations in QCFBs (figs. 8–10). This suggests that the methanol itself was not the source of the hydrocarbons. The purpose of the methanol rinse is to wash organic compounds off of the sample-collection equipment; many organic compounds, including hydrocarbons, are more soluble in methanol than they are in water.

If the methanol is effective for removing hydrocarbons from the field collection equipment, then why did field blanks with no evidence for contamination with methanol still have relatively high frequencies of contamination with hydrocarbons (table 6)? This observation may be explained by the timing of the methanol rinse. To reduce the use of methanol by field crews, sample-collection equipment was cleaned in the laboratory (where fume hoods are available to limit exposure) whenever possible. Sets of clean sample-collection equipment may be exposed to fuel exhaust or vapor from fuel used in vehicles during travel in the field vehicles. According to protocols, sample-collection equipment and peristaltic pumps that were last cleaned in the laboratory would require rinsing with 6 liters of certified blank water in the field before collection of a field blank. It is possible that rinsing with 6 liters of blank water may not be sufficient to remove hydrocarbons that sorbed onto the clean equipment during transit to the field site. The lower detection frequencies

in the groundwater samples compared to the field blanks suggest that the additional amount of rinsing of equipment and vials that occurs during collection of groundwater samples was more effective for removing the hydrocarbons.

SRLs for Ethylbenzene, *m*- and *p*-Xylenes, *o*-Xylene, Benzene, and Styrene

The different methods for calculating SRLs yield SRLs for ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene that would result in vastly different amounts of censoring to the groundwater data (table 7). On the basis of the inferred mechanisms of contamination for field blanks and groundwater samples, a large portion of the detections in groundwater samples may be the result of contamination, suggesting that SRLs that result in censoring of a large portion of the groundwater data may be more appropriate. However, the hydrocarbon ratios suggest that hydrocarbons in a few of the groundwater samples are derived from a distinct source; thus, some detections of hydrocarbons in groundwater samples likely do reflect hydrocarbon occurrence in the aquifer rather than contamination, and these data should not be censored.

The SRLs derived from the maximum concentration in the QCFBs, 0.06 µg/L, 0.33 µg/L, and 0.12 µg/L, were selected for ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene, respectively (table 8). These SRLs result in censoring nearly all of the groundwater data for ethylbenzene and *o*-xylene and all of the groundwater data for *m*- and *p*-xylenes (table 8; figs. 8–10). Detections of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene occurred in 11 of the 32 study units (N3, N6, S1, S2, S3, V1, V3, V4, V5, V7, and V9; table 9), and of the 71 total detections, 66 were censored by application of the SRLs (table 8).

Four groundwater samples contained concentrations of ethylbenzene greater than the SRL. Ethylbenzene/*m*- and *p*-xylenes and *o*-xylene/*m*- and *p*-xylenes ratios in these samples were considerably higher than the ratios calculated for field blanks (fig. 13A,B). Three of these four samples had additional characteristics suggesting geogenic sources of hydrocarbons: benzene and hydrocarbons were the only VOCs detected, groundwater samples had tritium < 1 TU, and the wells were relatively deep (Landon and Belitz, 2012).

In contrast, if the BD-95/90, BD-90/90, or maximum LT-MDL SRLs had been selected, many detections in groundwater samples with concentrations and ratios of hydrocarbons indistinguishable from those in the field blanks would have been retained as detections representative of aquifer conditions. Thirty groundwater samples had detections of ethylbenzene, *m*- and *p*-xylenes, or *o*-xylene censored by application of SRLs equal to the highest concentration measured in QCFBs; these detections would not have been censored had the BD-90/90 values been selected as the SRLs.

Table 7. Values of study reporting levels (SRLs) for the 18 VOCs detected in field blanks or source-solution blanks determined from the set of 167 quality-control field blanks using four methods, and changes in detection frequencies in the set of 2,026 groundwater samples with application of the different SRLs, California GAMMA Priority Basin Project, May 2004 through September 2010.

[LT-MDL, long-term method detection level; BD-95/90, 90-percent upper confidence limit of the 95th percentile; BD-90/90, 90-percent upper confidence limit of the 90th percentile; QCFB, quality-control field blanks; µg/L, micrograms per liter; %, percent; -, not detected; NA, not applicable]

	Detection frequency in 2,026 groundwater samples (percent)		BD-90/90		BD-95/90		Maximum QCFB		Maximum LT-MDL	
	90th percentile (µg/L)	SRL BD-90/90 (µg/L)	Detection frequency after application of SRL (percent)	95th percentile (µg/L)	SRL BD-95/90 (µg/L)	Detection frequency after application of SRL (percent)	SRL maximum QCFB (µg/L)	Detection frequency after application of SRL (percent)	SRL maximum LT-MDL (µg/L)	Detection frequency after application of SRL (percent)
Hydrocarbons										
Benzene	-	-	no change	-	-	no change	-	no change	0.013	1.4
Ethylbenzene	-	-	no change	0.022	0.022	0.7	0.060	0.2	0.02	0.7
Styrene	-	-	no change	-	-	no change	-	no change	0.021	no change
Toluene	0.036	0.048	1.6	0.060	0.104	0.8	0.686	0.2	0.03	2.6
1,2,4-Trimethylbenzene	-	-	no change	0.035	0.069	3.9	0.556	0.2	0.028	8.4
<i>m</i> - and <i>p</i> -Xylenes	-	0.033	1.5	0.083	0.118	0.3	0.328	0	0.04	1.1
<i>o</i> -Xylene	-	-	no change	0.020	0.040	0.4	0.120	0.05	0.02	0.6
Solvents										
Acetone ¹	0.4	-	NA ¹	-	-	NA ¹	2 1.938	NA ¹	3	0.2
2-Butanone ¹	0.4	-	NA ¹	-	-	NA ¹	-	NA ¹	1	0.4
1,1-Dichloroethene	3.4	-	no change	-	-	no change	-	no change	0.012	no change
Dichloromethane	1.5	-	no change	-	-	no change	0.028	1.1	0.03	1.0
Tetrachloroethene	13	-	no change	-	-	no change	0.148	5.1	0.03	9.6
Tetrahydrofuran ¹	1.2	-	NA ¹	-	-	NA ¹	-	NA ¹	1.1	1.0
Trichloroethene	6.2	-	no change	-	-	no change	0.093	3.8	0.019	6.0
Other VOCs										
Bromodichloromethane	6.3	-	no change	-	-	no change	-	no change	0.02	6.2
Carbon disulfide	4.3	-	no change	-	0.056	1.7	³ 0.092	1.2	0.03	3.3
Chloroform	27	-	no change	-	-	no change	0.127	9.3	0.02	23
Trichlorofluoromethane	2.0	-	no change	-	-	no change	0.100	1.2	0.08	1.4

¹ The SRL approach cannot be applied to acetone, 2-butanone, and tetrahydrofuran. Detections in groundwater samples reported by the laboratory were reviewed and rejected.

² Maximum concentrations of acetone in the source-solution blanks and laboratory blanks were 2.842 µg/L and 1.957 µg/L, respectively.

³ Maximum concentrations of carbon disulfide in the source-solution blanks and laboratory blanks were 0.089 µg/L and 0.490 µg/L, respectively.

Table 8. Study reporting levels (SRLs) and number of data censored by application of the SRLs, California GAMA Priority Basin Project, May 2004 through September 2010.

[SRL method: BD-95/90, field blank having rank corresponding to the upper 90-percent confidence interval of the 95th percentile determined using the binomial distribution; max QCFB, maximum concentration in the set of quality-control field blanks; max LT-MDL, maximum long-term method detection level used during period samples were analyzed. **Other abbreviations:** NA, not applicable; n, number; µg/L, micrograms per liter]

Constituent	SRL	SRL method	Detection frequency (percent)			
			Long and short sampling lines (n = 1,859)		Monitoring-well equipment (n = 167)	
			Original	SRL applied	Original	SRL applied
Hydrocarbons						
Benzene	No SRL	BD-95/90	1.2	1.2	6.0	6.0
Ethylbenzene	SRL = 0.06 µg/L	max QCFB	0.6	0.2	4.2	0
Styrene	No SRL	BD-95/90	0.2	0.2	0	0
Toluene	SRL = 0.69 µg/L	max QCFB	6.0	0.2	26	0.6
1,2,4-Trimethylbenzene	SRL = 0.56 µg/L	max QCFB	11	0.2	8.4	0.6
<i>m</i> - and <i>p</i> -Xylenes	SRL = 0.33 µg/L	max QCFB	1.2	0	9.6	0
<i>o</i> -Xylene	SRL = 0.12 µg/L	max QCFB	0.4	0.1	4.2	0
Solvents						
Acetone	Report all detections as “not analyzed”	NA ¹	0.3	0	1.8	0
2-Butanone	Report all detections as “not analyzed”	NA ¹	0.3	0	2.4	0
1,1-Dichloroethene	No SRL	BD-95/90	3.6	3.6	0.6	0.6
Dichloromethane	No SRL	BD-95/90	1.5	1.5	1.2	1.2
Tetrachloroethene	No SRL	BD-95/90	13	13	6.6	6.6
Tetrahydrofuran	Report all detections as “not analyzed”	NA ¹	0.8	0	5.4	0
Trichloroethene	No SRL	BD-95/90	6.7	6.7	1.2	1.2
Other VOCs						
Bromodichloromethane	No SRL	BD-95/90	6.7	6.7	2.4	2.4
Carbon disulfide	SRL = 0.03	LT-MDL	3.8	3.0	9.6	6.6
Chloroform	No SRL for long or short lines; SRL = 0.02 µg/L for monitoring wells	BD-95/90 LT-MDL	27	27	18	14.4
Trichlorofluoromethane	No SRL	BD-95/90	2.2	2.2	0	0

¹The SRL approach was not applied to acetone, 2-butanone, or tetrahydrofuran because there is no threshold concentration above which concentrations in groundwater samples can be considered representative of environmental conditions (see text for discussion).

Of these 30 samples, 8 (27 percent) had detections of benzene and at least two of the other four characteristics suggestive of geogenic sources of hydrocarbons (elevated ethylbenzene/*m*- and *p*-xylenes or *o*-xylene/*m*- and *p*-xylenes ratios, no VOCs other than hydrocarbons and carbon disulfide detected, tritium < 1 TU, and deep wells). However, concentrations of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene in these 8 samples were indistinguishable from concentrations in the other 22 samples that showed no relations between detections of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene and presence or absence of detections of other VOCs, groundwater age, well depth, or land use.

SRLs defined on the basis of the maximum concentration in the QCFBs may not be robust because collection of additional field blanks may result in an increase in the maximum concentration. Because of the relatively large number of QCFBs, however, the probability that additional field blanks collected under the same conditions would yield a higher concentration is relatively small. For 167 field blanks, the probability that the maximum measured concentration is the true maximum concentration is 98.6 to 100 percent, at a 90-percent confidence level.

Table 9. Raw detection frequencies by study unit of volatile organic compounds (VOCs) before and after application of study reporting limits (SRLs), California GAMMA Priority Basin Project, May 2004 through September 2010.

[Detection frequencies are not area-weighted; they are raw detection frequencies indicating the percentage of detections among the total number of groundwater samples. Thus, original detection frequencies may not be the same as those reported for grid well networks in the Data Series Reports for individual study units. Study unit names given in [table 1](#). Detection frequencies of zero are indicated by the – symbol]

Study unit	Number of samples	Ethylbenzene		1,2,4-Trimethylbenzene		Toluene		<i>m</i> - and <i>p</i> -Xylenes		<i>o</i> -Xylene		Acetone		2-Butanone		Tetrahydrofuran		Carbon disulfide		Chloroform		
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	
Desert study units																						
D1	57	–	–	3.5	–	40	–	–	–	–	–	–	–	–	–	–	–	–	–	–	37	37
D2	59	–	–	12	–	5.1	1.7	–	–	–	–	–	–	–	–	3.4	–	–	–	–	29	29
D3	35	–	–	–	–	29	–	–	–	–	–	–	–	–	–	–	–	–	–	–	23	23
D4	28	–	–	14	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	14	14
D5	52	–	–	23	5.8	5.8	–	–	–	–	–	1.9	–	–	–	–	–	–	–	–	27	27
Mountain study units																						
M1	83	–	–	4.8	–	3.6	–	–	–	–	–	–	–	–	–	1.2	–	–	–	–	22	22
M2	75	–	–	6.7	–	8.0	–	–	–	–	–	–	–	–	–	2.7	–	–	–	–	12	12
M3	50	–	–	–	–	4.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	14	14
M4	30	–	–	–	–	6.7	–	–	–	–	–	3.3	–	–	–	3.3	–	–	–	–	17	17
M5	53	–	–	40	–	3.8	–	–	–	–	–	–	–	–	–	3.8	–	–	–	–	30	30
M6 ¹	72	–	–	61	–	1.4	–	–	–	–	–	1.4	–	–	–	–	–	–	–	–	13	13
North and Central Coast study units																						
N1	30	–	–	30	–	3.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	27	27
N2	28	–	–	36	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	25	25
N3	108	0.9	–	17	–	5.6	–	3.7	–	1.9	–	0.9	–	–	1.9	–	–	–	–	–	17	17
N4	79	–	–	–	–	7.6	–	–	–	–	–	2.5	–	–	1.3	–	–	–	–	–	27	27
N5	54	–	–	–	–	1.9	–	–	–	–	–	–	–	–	1.9	–	–	–	–	–	19	19
N6	97	1.0	1.0	7.2	–	4.1	–	1.0	–	–	–	–	–	–	1.0	–	–	–	–	–	22	22
N7	70	–	–	26	–	5.7	–	–	–	–	–	–	–	–	–	1.4	–	–	–	–	16	16
South Coast study units																						
S1	53	–	–	–	–	13	1.9	1.9	–	–	–	–	–	–	–	1.9	–	–	–	–	17	15
S2	69	1.4	–	2.9	–	5.8	1.4	1.4	–	–	–	–	–	–	–	1.4	–	–	–	–	45	45
S3	52	–	–	1.9	–	5.8	–	1.9	–	–	–	–	–	–	–	–	–	–	–	17	15	79
S4	99	–	–	19	–	5.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	72	72
S5	58	–	–	–	–	6.9	–	–	–	–	–	–	–	–	–	–	–	–	–	1.7	31	31

Table 9. Raw detection frequencies by study unit of volatile organic compounds (VOCs) before and after application of study reporting units (SRLs), California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[Detection frequencies are not area-weighted; they are raw detection frequencies indicating the percentage of detections among the total number of groundwater samples. Thus, original detection frequencies may not be the same as those reported for grid well networks in the Data Series Reports for individual study units. Study unit names given in [table 1](#). Detection frequencies of zero are indicated by the – symbol]

Study unit	Number of samples	Ethylbenzene		1,2,4-Trimethylbenzene		Toluene		<i>m</i> - and <i>p</i> -Xylenes		<i>o</i> -Xylene		Acetone		2-Butanone		Tetrahydrofuran		Carbon disulfide		Chloroform			
		Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final	Initial	Final		
Central Valley study units																							
V1	66	4.5	–	6.1	–	7.6	–	6.1	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
V2	87	–	–	10	–	1.1	–	–	–	–	–	1.1	–	–	–	–	–	–	–	–	–	–	
V3	87	1.1	–	1.1	–	14	–	5.7	–	–	–	1.1	–	–	–	–	–	–	–	–	–	–	
V4	75	6.7	–	9.3	1.3	35	–	11	–	5.3	–	–	–	–	–	–	–	–	–	–	–	–	
V5	78	1.3	1.3	2.6	–	3.8	1.3	1.3	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
V6	35	–	–	5.7	–	2.9	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
V7	101	3.0	2.0	5.0	–	5.0	–	13	–	3.0	1.0	–	–	–	–	–	–	–	–	–	–	–	
V8	50	2.0	–	4.0	–	4.0	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	
V9	56	1.8	–	1.8	–	1.8	–	–	–	1.8	–	–	–	–	–	–	–	–	–	–	–	–	
All	2,026	0.9	0.2	11	0.2	7.7	0.2	1.9	–	0.7	0.05	0.4	–	0.4	–	0.4	–	1.2	–	4.3	3.3	27	26

¹An additional 18 samples were collected for study unit M6 in October 2010.

Bender and others (2011) also reported detection frequencies of ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene in field blanks collected at production wells and at monitoring wells greater than detection frequencies in groundwater samples collected at those site types. Field blanks collected at production wells by the GAMA Program (this study) and by the NAWQA Program (Bender and others, 2011) had similar detection frequencies for each of these three VOCs (fig. 3). However, the SRLs calculated by Bender and others (2011) have much lower concentrations (fig. 14) because they used the BD-90/90 method to calculate SRLs. For the 278 production well field blanks used by Bender and others (2011), the BD-90/90 corresponds to the 258th-ranked field blank, which yielded SRLs of 0.008 µg/L for ethylbenzene and 0.02 µg/L for *m*- and *p*-xylenes (the method yielded no SRL for *o*-xylene because the 258th-ranked field blank was a non-detection). These SRLs result in little censoring of groundwater data. Application of the BD-90/90 method to the 167 QCFBs in this study would have resulted in (1) no SRLs for ethylbenzene or *o*-xylene (table 7) because the 156th-ranked field blank was a non-detection, and (2) an SRL of 0.033 µg/L for *m*- and *p*-xylenes. The BD-90/90 method does not yield an SRL if the detection frequency in the field blanks is less than approximately 7 percent.

Benzene and styrene were detected in laboratory instrument blanks and in field blanks affected by methanol (tables 4, 6; figs. 11, 12). Neither was detected in the QCFBs; therefore, none of the four methods for determining SRLs yielded concentrations. The BD-99/90 for benzene in laboratory instrument blanks was 0.006 µg/L, which was lower than all of the concentrations detected in groundwater samples (fig. 11). No SRLs are recommended for benzene or styrene on the basis of detections in the blanks (table 8).

Toluene

Toluene, like ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene, was detected more frequently in blanks than in groundwater samples; it is discussed separately, however, because the patterns of toluene detections differed from those of the other hydrocarbons. Toluene was the most frequently detected VOC in laboratory instrument blanks, source-solution blanks, and field blanks (table 4; fig. 15).

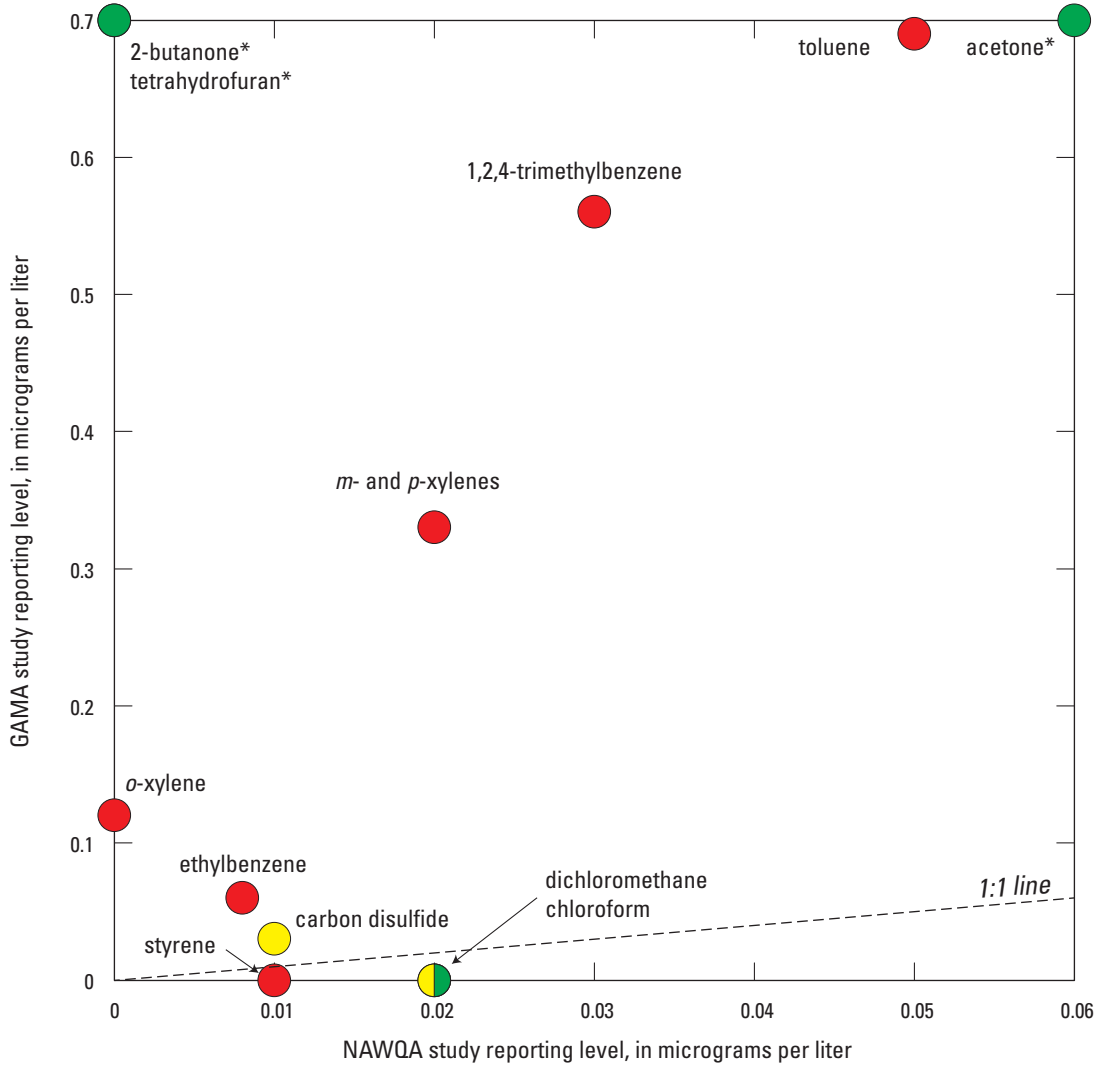
Inferred Mechanisms of Contamination

The relations between toluene and other hydrocarbons and of the relative detection frequencies of toluene in laboratory instrument blanks, source-solution blanks, the various subsets of field blanks, and groundwater samples suggest that there are multiple sources of contamination for toluene. Although toluene concentrations in blanks were significantly correlated to concentrations of ethylbenzene,

m- and *p*-xylenes, and *o*-xylene in blanks ($p < 0.001$ for Spearman's rho tests), the relations were not dominated by single linear correlations as they were among ethylbenzene and the xylenes (fig. 13E). Contamination of equipment and vials by vehicle exhaust of fuel fumes may result in contamination of blanks and groundwater samples by toluene along with ethylbenzene and the xylenes; however, additional significant sources of toluene contamination are required to account for the relative detection frequencies.

Unlike ethylbenzene and the xylenes, toluene was detected less frequently in QCFBs (28 percent) than in source-solution blanks (41 percent) (table 4), and there was no significant difference in toluene occurrence between QCFBs collected with long and short sampling lines (table 6). This suggests that contact with field equipment was not the dominant source of contamination by toluene. The presence of toluene in laboratory instrument blanks (4.2 percent) indicates that there was a source of contamination in laboratory processes. The detection frequency of toluene in source-solution blanks was significantly higher than in laboratory instrument blanks, suggesting that either the vials or processes occurring during transit to the field site also are sources of contamination. The detection frequency in groundwater samples (7.7 percent) was significantly lower than in source-solution blanks or field blanks, indicating that processes occurring during transit after sample collection could not have been a large source of contamination. These observations suggest that the primary sources of contamination were toluene that enters the bottles of source blank water after the initial certificates of analysis are produced and toluene that was present in the vials at the time of purchase and (or) that entered the vials during transit to the field.

Contamination of blanks by toluene derived from contact with field equipment is discernible when the blank data are divided into different concentration ranges. Of the 320 total field blanks and source-solution blanks, 121 have detections of toluene (tables A2, A3). Two-thirds of the toluene detections had concentrations less than 0.03 µg/L (a value equal to the maximum LT-MDL, table 7), and one-third had concentrations between 0.03 µg/L and 0.69 µg/L. The group of field and source-solution blanks with higher toluene concentrations had hydrocarbon ratios and relations between detection frequencies and sample-collection equipment configurations similar to those observed for field blanks contaminated with ethylbenzene, *o*-xylene, and *m*- and *p*-xylenes. The group with higher toluene concentrations had a significantly higher detection frequency of *m*- and *p*-xylenes (68 percent) compared to the group with lower toluene concentrations (12 percent detection frequency of *m*- and *p*-xylenes; contingency table tests, $p < 0.001$). Toluene and *m*- and *p*-xylene concentrations had a strong linear correlation in the group with higher toluene concentrations (fig. 13D).



EXPLANATION

- Hydrocarbons
- Solvents
- Other VOCs

*For GAMA, all detections of acetone, 2-butanone, and tetrahydrofuran in groundwater samples are censored. For NAWQA, acetone's SRL is 1 microgram per liter, and 2-butanone and tetrahydrofuran have no SRLs. [NAWQA SRLs are the SRLs determined for public-supply and domestic wells by Bender and others (2011).]

Figure 14. Concentrations of study reporting levels (SRLs) established from field blanks collected for the California GAMA Priority Basin Project, May 2004 through September 2010, and SRLs established from field blanks collected at production wells for the National Water-Quality Assessment (NAWQA) Program (Bender and others, 2011).

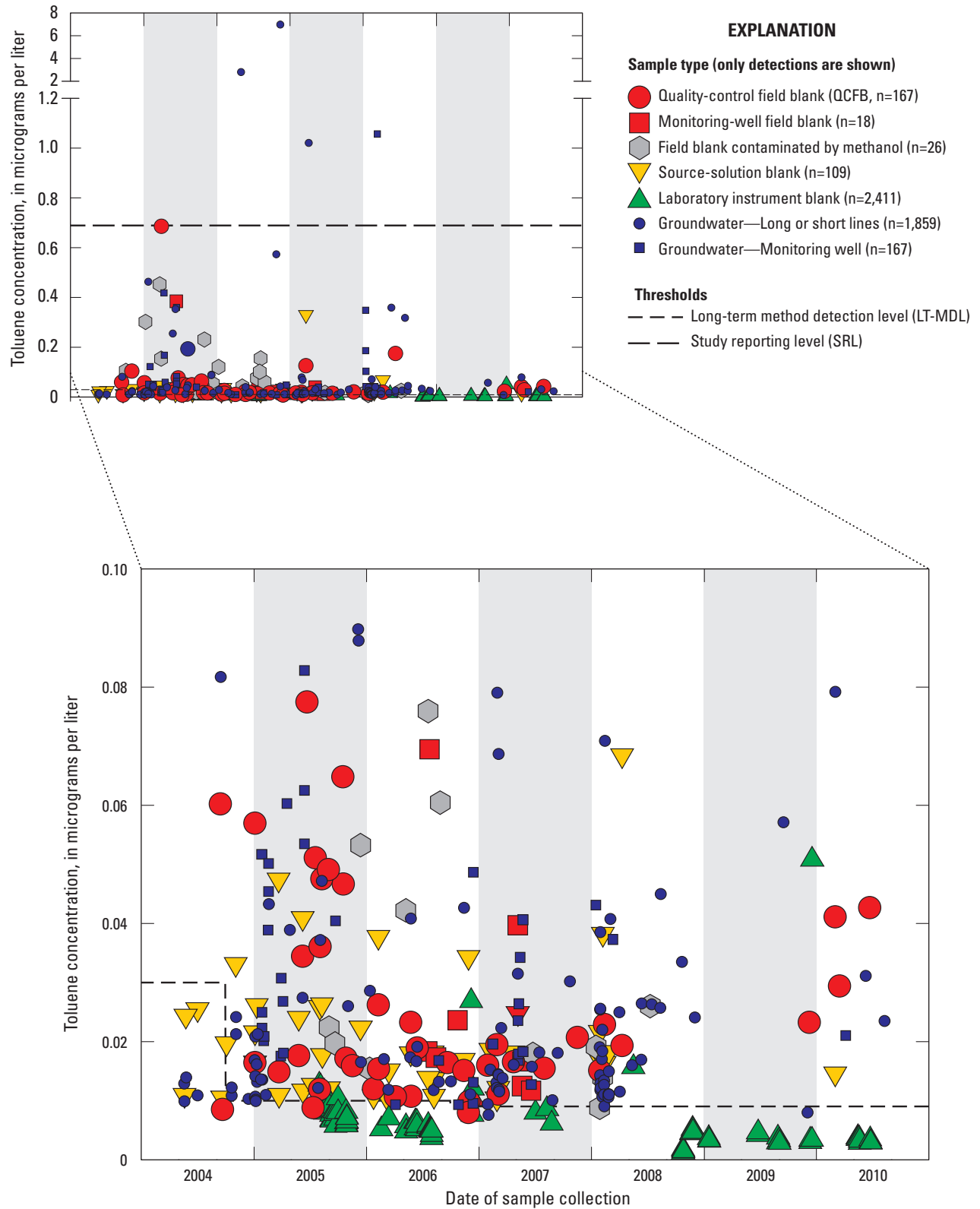


Figure 15. Concentrations of toluene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

The ratio was slightly higher than observed in ambient urban air ([fig. 13E](#)), suggesting that there may be a systematic fractionation. The group with higher toluene concentrations also had a significantly higher proportion of field blanks (80 percent field blanks, 20 percent source-solution blanks) compared to the group with the lower toluene concentrations (54 percent field blanks) (contingency test, $p=0.006$), suggesting that contact with field equipment increased contamination with toluene over the contamination present in source-solution blanks. The detection frequency of toluene with a concentration greater than $0.03 \mu\text{g/L}$ was significantly greater in QCFBs collected with long sampling lines compared to short sampling lines, and in field blanks contaminated with methanol compared to QCFBs (contingency table tests, $p=0.013$ and $p<0.001$, respectively). This is similar to the pattern observed for ethylbenzene, *o*-xylene, and *m*- and *p*-xylenes ([table 6](#)), suggesting that higher concentrations of toluene contamination in field blanks likely have the same origin as contamination with ethylbenzene, *o*-xylene, and *m*- and *p*-xylenes—exposure of the water or sampling equipment to fuel exhaust vapors.

In contrast, the group of blanks with lower concentrations of toluene appeared to be contaminated by toluene from a different source(s). There were no significant differences in detection frequency of toluene with concentrations less than $0.03 \mu\text{g/L}$ between methanol-contaminated field blanks compared to QCFBs (contingency table test, $p=0.42$), or between QCFBs collected with long sampling lines compared to short sampling lines (contingency table test, $p=0.78$). These patterns are consistent with the source of contamination being the vials and the source-blank water, as inferred from comparison of detection frequencies in laboratory instrument blanks, source-solution blanks, field blanks, and groundwater samples.

SRL for Toluene

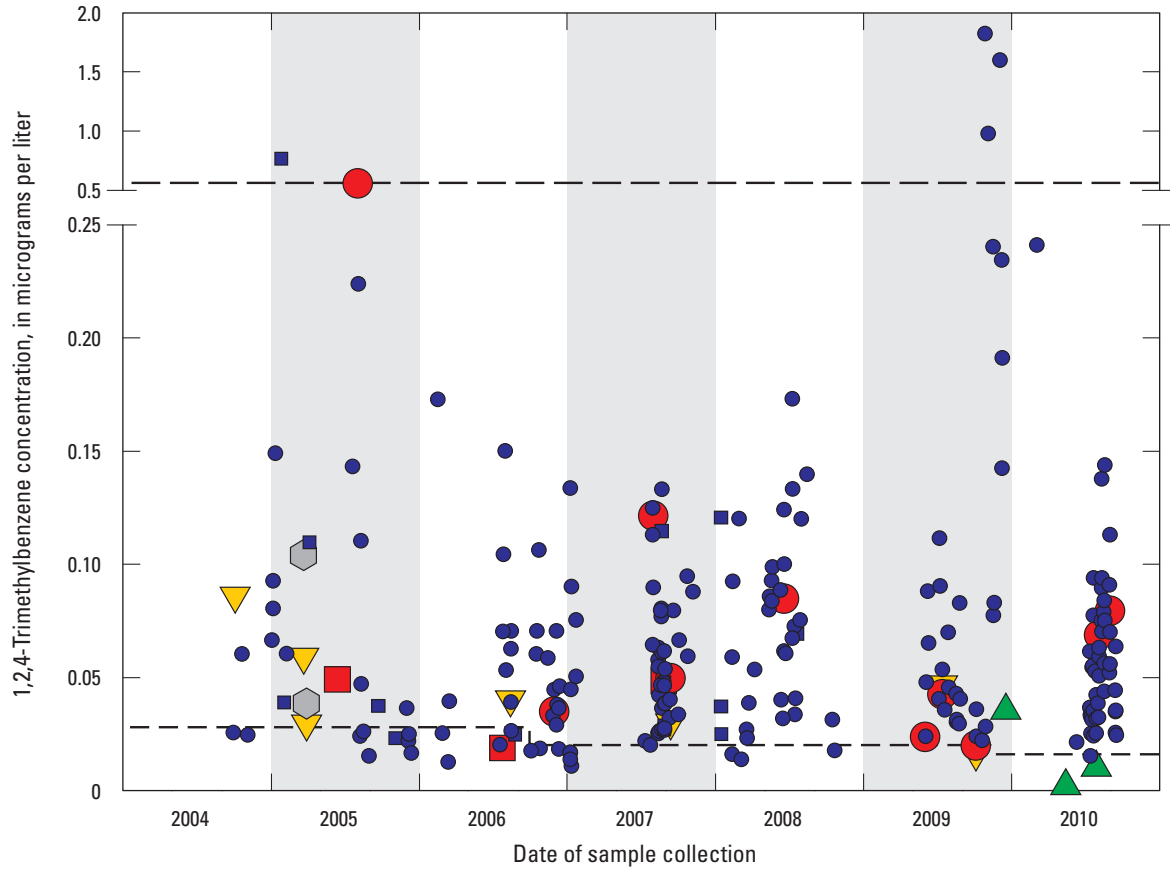
The detection frequency of toluene in groundwater without censoring is 7.7 percent. On the basis of the inferred mechanisms of contamination for field blanks and groundwater samples, a large portion of the detections in groundwater samples may be the result of extrinsic contamination, suggesting that an SRL that results in censoring of a large portion of the groundwater data may be most appropriate. However, the highest concentration measured in groundwater samples was 10 times higher than the highest concentration measured in field blanks, suggesting that at least some of the detections in groundwater are likely to represent intrinsic, rather than extrinsic contamination.

SRLs derived from the four methods all result in substantial reduction in the detection frequency of toluene in groundwater samples ([table 7](#)). If an SRL were calculated using the maximum QCFB method, detection frequency in groundwater samples would decrease from 7.7 to 0.2 percent, and if the maximum LT-MDL method were used, the detection frequency would be 2.6 percent. The detection frequencies that resulted by using SRLs computed from the BD-95/90 and BD-90/90 were 0.8 and 1.6 percent, respectively. Given the multiple potential sources of extrinsic toluene contamination and the likelihood that some of the detections in groundwater are indicative of intrinsic contamination, the SRL based on the QCFB method— $0.69 \mu\text{g/L}$ —was selected ([table 8](#)). Of the 156 toluene detections in groundwater samples, 152 were censored by application of the SRL.

Bender and others (2011) also reported detection frequencies of toluene in field blanks collected at production wells and at monitoring wells greater than detection frequencies in groundwater samples collected at those site types. The detection frequency in field blanks collected at production wells was 34 percent, which is similar to the detection frequency observed in field blanks collected for GAMA ([fig. 3](#)); however, the SRL calculated by Bender and others (2011) had a much lower concentration than the SRL selected during this study ([fig. 14](#)). Bender and others (2011) used the BD-90/90 method to calculate the SRL of $0.05 \mu\text{g/L}$ for data from production wells; the BD-90/90 method applied to the QCFBs in this study would have yielded an SRL with nearly the same concentration ([table 7](#)).

1,2,4-Trimethylbenzene

The occurrence patterns of 1,2,4-trimethylbenzene in blanks and groundwater samples were quite different from the patterns observed for any of the other hydrocarbons. The 1,2,4-trimethylbenzene concentration was not significantly correlated with concentrations of toluene or *m*- and *p*-xylenes ($p>0.05$, Spearman's rho tests; [fig. 13F](#)). Fifty-nine percent of blanks and 49 percent of groundwater samples containing 1,2,4-trimethylbenzene had no other detections of VOCs. Detections of 1,2,4-trimethylbenzene commonly occurred in clusters in time ([fig. 16](#)). Detection frequency in groundwater samples (11 percent) was greater than in QCFBs (6.0 percent) or source-solution blanks (6.4 percent) ([table 4](#)), and the ranges of concentrations measured in the groundwater samples and blanks were similar ([fig. 13F](#)).



EXPLANATION

Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- ⬡ Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—Long or short lines (n=1,859)
- Groundwater—Monitoring well (n=167)

Thresholds

- - - Long-term method detection level (LT-MDL)
- — — Study reporting level (SRL)

Figure 16. Concentrations of 1,2,4-trimethylbenzene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

Inferred Mechanisms of Contamination

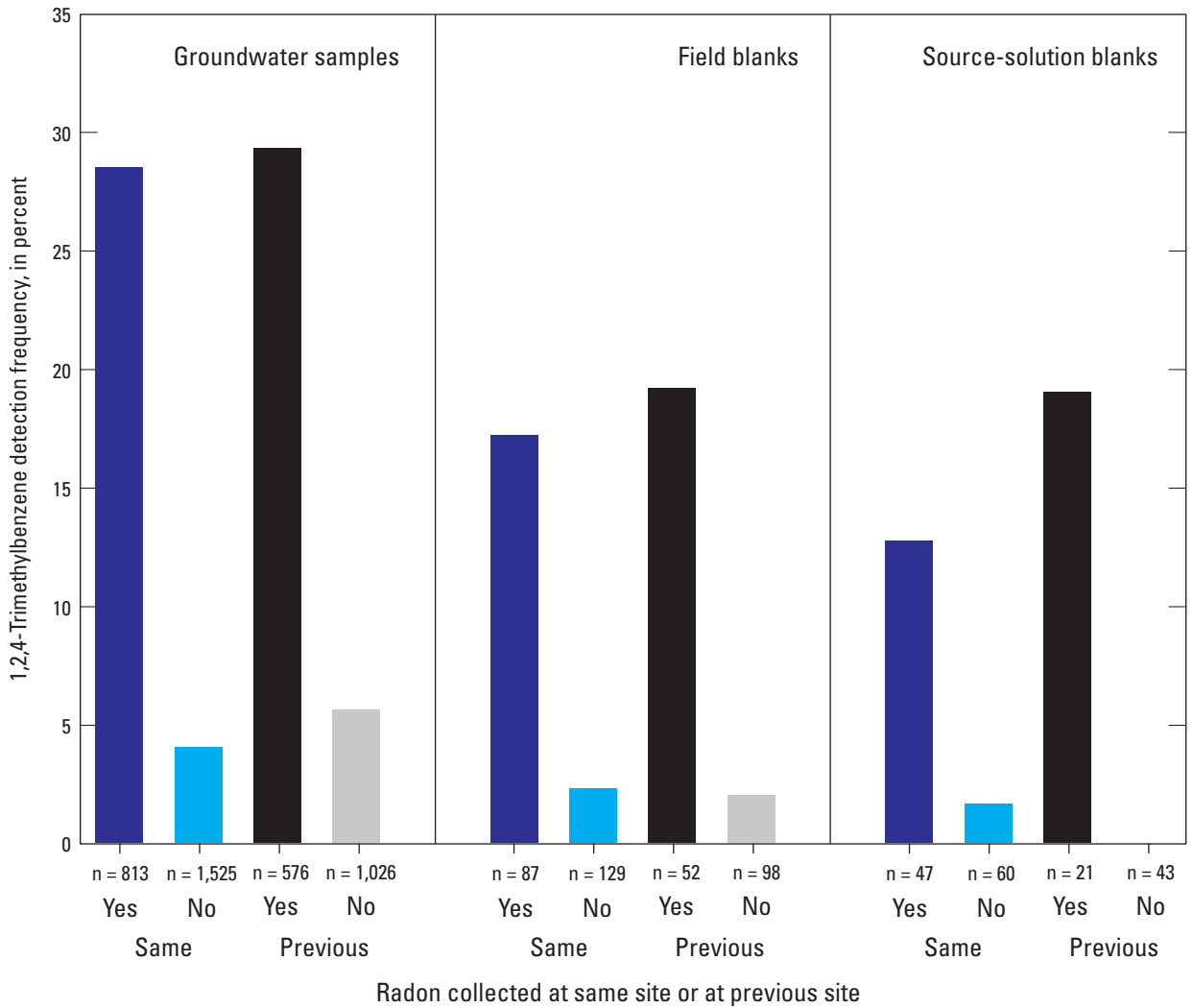
An understanding of the probable source of contamination was useful for selecting an appropriate recommended SRL for 1,2,4-trimethylbenzene. As with the other hydrocarbons, the relative detection frequencies in laboratory instrument blanks, source-solution blanks, the various subsets of field blanks, and groundwater samples provided data as to the likely source of contamination with 1,2,4-trimethylbenzene. The detection frequencies of 1,2,4-trimethylbenzene in source-solution blanks and QCFBs were not significantly different ([table 4](#)), suggesting that contact with field sample-collection equipment was not a source of contamination. However, QCFBs collected with monitoring-well equipment and QCFBs collected with long sampling lines had significantly greater occurrence of 1,2,4-trimethylbenzene than QCFBs collected with short sampling lines ([table 6](#)), suggesting that contact with field sample-collection equipment was a source of contamination. 1,2,4-Trimethylbenzene was the only hydrocarbon that did not have significantly greater occurrence in field blanks contaminated with methanol ([table 6](#)), suggesting that unlike the other hydrocarbons, the occurrence of 1,2,4-trimethylbenzene in field blanks was not related to the amount of rinsing of sampling equipment that occurred during collection of the field blanks. These seemingly contradictory observations suggest that contamination with 1,2,4-trimethylbenzene was caused by a difference between sample collection with short sampling lines and sample collection with long sampling lines or monitoring-well equipment that was not related to increased contact with equipment.

One difference between sites sampled with short sampling lines and sites sampled with long sampling lines or monitoring-well equipment is that samples for radon-222 analysis were more likely to be collected with the latter two equipment types. The scintillation media in the vials used to collect radon-222 samples is a mixture of mineral oil and 1,2,4-trimethylbenzene (Horton, 1983; Whittaker and others, 1989; Vitz and Martin, 1991). Therefore, samples collected with long sampling lines or monitoring-well equipment were more likely to be collected under conditions where a potential source of 1,2,4-trimethylbenzene was present than were samples collected with short sampling lines.

Radon-222 samples were not collected at all sites sampled for the GAMA-PBP. Radon-222 samples were collected at 616 (30 percent) of the 2,026 sites sampled (see references in [table A1](#) for data). In most study units for which radon-222 samples were collected, they were only collected at sites where samples for the larger suite of analytes were collected. Samples for radon-222 were not collected at sites sampled for only the core suite of analytes. Most sites at which the larger suite of analytes were collected were sampled with long sampling lines or monitoring-well equipment, and most sites at which only the core suite of analytes were collected were sampled with short sampling lines. Long sampling lines or monitoring-well equipment were used at 82 percent of the sites at which a sample for radon-222 was collected. Samples for radon-222 were collected at 37 percent of the sites at which field blanks were collected. These data indicate that a potential source of contamination of 1,2,4-trimethylbenzene—the vials used to collect radon-222 samples—were more likely to be present at sites where long sampling lines or monitoring-well equipment was used, which may account for the higher occurrence of 1,2,4-trimethylbenzene in field blanks collected with long sampling lines compared to short sampling lines.

Further examination of the correlations between collection of radon-222 samples and occurrence of 1,2,4-trimethylbenzene provided additional evidence that collection of radon-222 samples is responsible for contamination of groundwater samples and blanks by 1,2,4-trimethylbenzene. The detection frequency of 1,2,4-trimethylbenzene in groundwater samples from sites where a sample for radon-222 was collected (29 percent) was significantly greater than the detection frequency in groundwater samples from sites where a sample for radon-222 was not collected (4.1 percent) (contingency table test, $p < 0.001$) ([fig. 17A](#)). The detection frequency of 1,2,4-trimethylbenzene in field and source-solution blanks collected at sites where radon-222 samples were collected (16 and 13 percent, respectively) also were significantly greater than the detection frequency in field and source-solution blanks from sites where radon-222 samples were not collected (2.4 and 1.6 percent, respectively) (contingency table tests, $p < 0.001$ and $p = 0.019$) ([fig. 17A](#)). There were no significant differences in detection frequencies between field blanks and source-solution blanks.

A



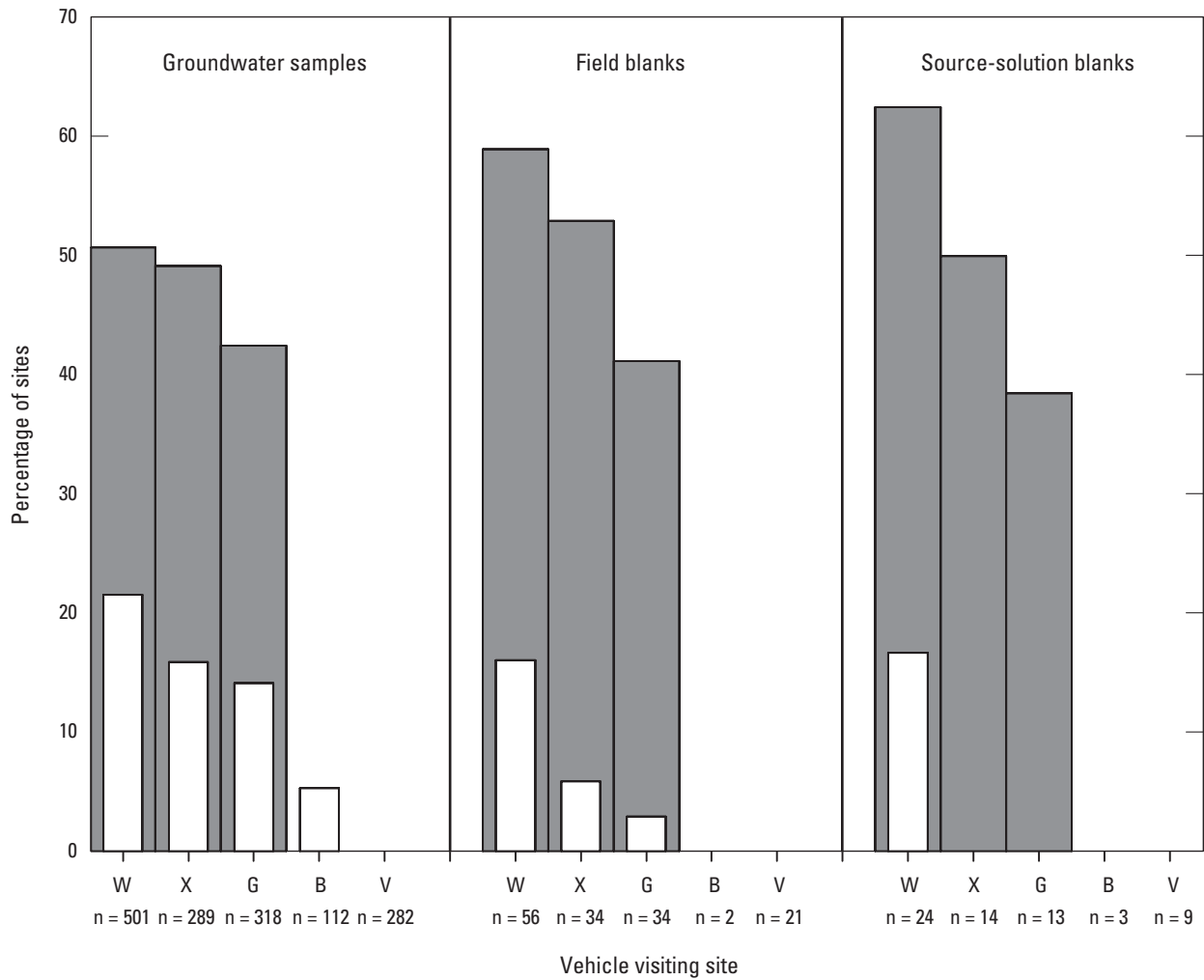
EXPLANATION

Radon collected at site
 YES [Dark Blue] NO [Light Blue]
 Radon collected at previous site
 YES [Black] NO [Grey]

The number of sites in each category at which groundwater samples, field blanks, or source-solution blanks were collected is given below the bar.

Figure 17. Relations between detection frequencies of 1,2,4-trimethylbenzene in groundwater samples and blanks and (A) whether or not samples for analysis of radon-222 were collected at the same site or previous site, and (B) which GAMA field vehicle visited the site, California GAMA Priority Basin Project, May 2004 through September 2010.

B

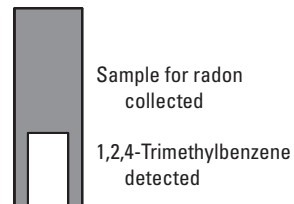


EXPLANATION

USGS-GAMA vehicles

- W = White lab
- X = X-Lab
- G = Green Lab
- B = Blue Lab
- V = Van

Percentage of sites



Five field vehicles were used to visit sites and collect samples for the California GAMA Priority Basin Project between May 2004 and September 2010. The number of sites visited by each vehicle for collection of groundwater samples, field blanks, or source-solution blanks is given below the vehicle letter code.

Figure 17.—Continued

The detection of 1,2,4-trimethylbenzene in groundwater samples and in blanks also had similar relations to whether or not radon-222 samples had been collected at a previous site visited by a particular sampling vehicle. The GAMA-PBP uses five different sampling vehicles, and the identity of the vehicle was recorded for nearly all sites visited between October 2005 and September 2010. Nearly all of the detections of 1,2,4-trimethylbenzene in groundwater samples and all of the detections in field blanks and source-solution blanks occurred at sites visited by three of the vehicles, the X-Lab, the White Lab, or the Green Lab ([fig. 17B](#)). The other two vehicles (the Blue Lab and the Van Lab) were never used at sites where samples were collected for radon-222, and although 24 percent of the groundwater samples were collected in these two vehicles, only 2.9 percent of the 1,2,4-trimethylbenzene detections in groundwater samples occurred in samples collected using these two vehicles. The six detections of 1,2,4-trimethylbenzene in groundwater samples that were collected in the Blue Lab were collected during two different weeks (one week in study unit V2, one week in study unit V7), and in both cases, groundwater samples collected in the White Lab in the same study unit during the same week had detections of 1,2,4-trimethylbenzene.

How and when does the 1,2,4-trimethylbenzene from the radon-222 vials reach the VOC vials? The VOC sample is collected and vials are sealed at the beginning of the sample collection sequence, and the radon-222 sample is collected near the end of the sample collection sequence. At sites sampled with long sampling lines or monitoring-well equipment, VOCs are collected inside the field vehicle, and radon is collected outside at the well head. Furthermore, field blanks and source-solution blanks are not collected for radon-222. Thus, direct exposure of VOC samples at the field site to the 1,2,4-trimethylbenzene in the radon-222 sample vial used at the same field site is unlikely.

The correlation between 1,2,4-trimethylbenzene occurrence and sampling vehicle ([fig. 17B](#)) and whether or not a sample for radon-222 was collected at the previous site ([fig. 17A](#)) suggest that radon-222 sampling can cause contamination of field vehicles with 1,2,4-trimethylbenzene. 1,2,4-Trimethylbenzene is highly soluble in the mineral oil and would be expected to volatilize gradually, potentially contaminating the vehicle over time. The fact that detection frequencies of 1,2,4-trimethylbenzene were not significantly different between field blanks and source-solution blanks may suggest that the 1,2,4-trimethylbenzene was present in the atmosphere in the vehicle and entered the blank water by partial equilibration between the blank water and the atmosphere. The kits used for radon sampling are stored in the vehicle, and gloves that may have come in contact with the scintillation fluid during collection of the radon samples

generally are disposed of inside the vehicle. Field personnel had not been told that the scintillation fluid may present a contamination problem.

SRL for 1,2,4-Trimethylbenzene

The methods for calculating SRLs yield SRLs for 1,2,4-trimethylbenzene that would result in vastly different amounts of censoring to the groundwater data ([table 7](#)). Application of the BD-90/90 method would result in no censoring of the groundwater data, and at the other extreme, use of the maximum concentration measured in the QCFBs as the SRL would result in reducing the detection frequency in groundwater samples from 11 to 0.2 percent. Because of the strong association between 1,2,4-trimethylbenzene contamination in blanks and groundwater samples and presence of materials connected with collection of samples for radon-222, it is likely that a large portion of the detections in groundwater samples may be the result of contamination. This suggests that an SRL that results in censoring of a large portion of the groundwater data may be most appropriate.

The SRL derived from the maximum concentration in the QCFBs, 0.556 µg/L, was selected ([table 8](#)) and results in censoring nearly all of the groundwater data for 1,2,4-trimethylbenzene ([table 8](#); [fig. 16](#)). Uncensored detections of 1,2,4-trimethylbenzene occurred in 216 groundwater samples distributed across 25 of the 32 study units ([table 9](#)). After application of the SRL, there are only four detections in two study units.

Other information about the four groundwater samples having detections of 1,2,4-trimethylbenzene after application of the SRL suggests that these four detections also may be the result of extrinsic contamination and not representative of aquifer conditions. Three of the samples were collected in the Green Lab (during study unit D5 data collection). All 52 sites for study unit D5 were sampled by using the Green Lab or the X-Lab, and samples for radon-222 were collected at 46 percent of the sites. In addition to the three samples with detections of 1,2,4-trimethylbenzene in groundwater with concentrations above the SRL, eight samples had detections with concentrations below the SRL that were censored by application of the SRL. The vehicle used for one sample was not recorded (study unit V4). Among the four groundwater samples with 1,2,4-trimethylbenzene concentrations greater than the SRL, one had no other VOCs detected, two had detections of toluene at concentrations less than the SRL, and two had detections of low concentrations of chloroform. This suggests that the detections of 1,2,4-trimethylbenzene with concentrations greater than the SRL likely also are the result of extrinsic contamination. Even though these four detections would not be censored by application of the SRL, it may be appropriate to censor the detections on the basis of the additional information about the samples.

Bender and others (2011) also reported detection frequencies of 1,2,4-trimethylbenzene in field blanks collected at production wells and at monitoring wells greater than detection frequencies in groundwater samples collected at those site types. The detection frequency in field blanks collected at production wells was 17 percent, which is considerably higher than the detection frequency observed in field blanks collected for the GAMA-PBP (fig. 3); however, the SRL calculated by Bender and others (2011) had a much lower concentration than the SRL selected in this study (fig. 14). Bender and others (2011) used the BD-90/90 method to calculate the SRL of 0.03 µg/L for data from production wells; the BD-90/90 method applied to the QCFBs in this study would have yielded no SRL because the detection frequency of 1,2,4-trimethylbenzene in the QCFBs was less than 7 percent. Approximately 54 percent of the 9,000 groundwater sites sampled by the NAWQA Program have data for radon-222 (U.S. Geological Survey, 2012). Information concerning relations between field vehicles used at sites at which samples for radon-222 were collected and occurrence of 1,2,4-trimethylbenzene in blanks and groundwater samples is not available.

Chlorinated Organic Solvents

Dichloromethane and 1,1-dichloroethene were detected in source-solution blanks, and dichloromethane, tetrachloroethene, and trichloroethene were detected in QCFBs (table 4; figs. 18–21). The detection frequencies of all four solvents in groundwater samples were greater than the detection frequencies in QCFBs (table 4).

Dichloromethane, 1,1-Dichloroethene, and Trichloroethene

The detection frequencies of dichloromethane and trichloroethene in the QCFBs were similar to the detection frequencies in the laboratory instrument blanks (table 4), and the concentrations detected in the QCFBs were within the range of concentrations detected in the laboratory instrument blanks (figs. 18, 21). These similarities suggest that laboratory sources of these two VOCs are sufficient to account for the observed detections in the QCFBs. Concentrations of dichloromethane and trichloroethene in field blanks affected by methanol were significantly greater than concentrations in field blanks not affected by methanol (table 6). Dichloromethane and trichloroethene are both highly soluble in methanol; thus their presence in field blanks contaminated by methanol is not surprising.

Because the detection frequencies of dichloromethane and trichloroethene in the QCFBs are less than 1 percent and the detected concentrations are low compared to most of the concentrations detected in groundwater samples, it is not

necessary to censor the dichloromethane and trichloroethene data on the basis of detections in blanks. Application of the BD-95/90 method yields the result of no SRL for either VOC (table 7) because the detection frequencies of the two VOCs in the QCFBs are less than 3 percent. For the 167 QCFBs, the BD-95/90 method selects the 163rd-ranked blank as the SRL; if the detection frequency in the QCFBs is less than 3 percent, the 163rd-ranked blank is a non-detection.

1,1-Dichloroethene was not detected in the QCFBs (table 4; fig. 19). Therefore, no SRL was defined.

Tetrachloroethene

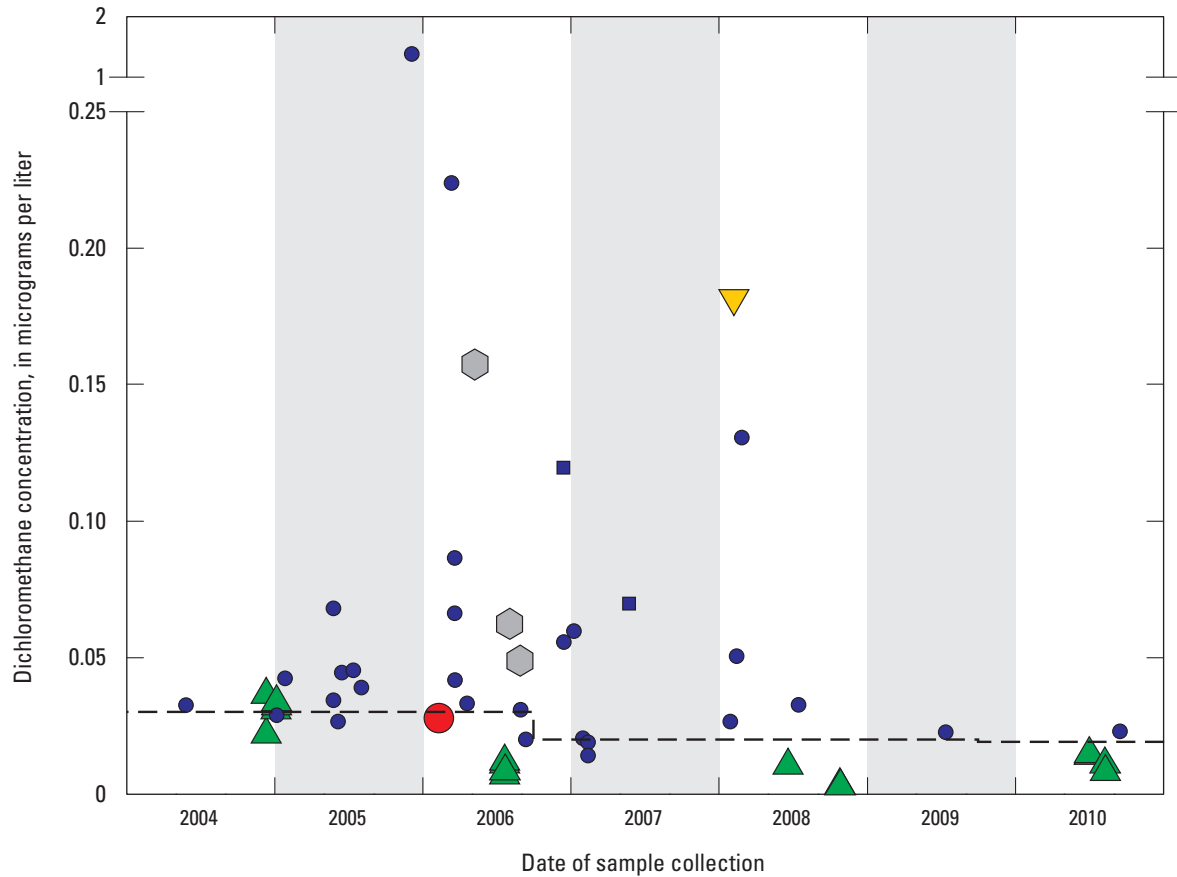
The detection frequency of tetrachloroethene in the QCFBs was significantly greater than in the laboratory instrument blanks (table 4; contingency table test, $p < 0.001$; fig. 20), indicating that there is a source of contamination beyond processes occurring during laboratory analysis. However, detection frequencies in the QCFBs and source-solution blanks were not significantly different (table 4; contingency table test, $p = 0.16$), suggesting that contact with field sample-collection equipment is not a major source of extrinsic contamination. Given the low detection frequency of tetrachloroethene in the QCFBs (1.8 percent), and the lack of definitive pattern of detection frequencies pointing to a likely source of contamination, no censoring of the data for tetrachloroethene in groundwater samples appears to be needed. Application of the BD-95/90 method yields the result of no SRL for tetrachloroethene (table 7).

Other VOCs

The remaining four VOCs detected in blanks belong to three classes of VOCs and have been lumped together as the group “other VOCs” for convenience. Trichlorofluoromethane is a refrigerant, bromodichloromethane and chloroform are trihalomethanes, and carbon disulfide is naturally occurring and is used in industrial organic syntheses. The four VOCs are divided into three groups for discussion on the basis of patterns of detection in blanks.

Bromodichloromethane and Trichlorofluoromethane

Bromodichloromethane was detected in one field blank contaminated with methanol (fig. 22), and trichlorofluoromethane was detected in one QCFB and one source-solution blank collected at the same site (fig. 23). The detection frequencies in groundwater samples were greater than in blanks (table 4). Given the low detection frequencies in QCFBs for bromodichloromethane and trichlorofluoromethane (0 and 0.6 percent, respectively), no SRLs are needed for bromodichloromethane or trichlorofluoromethane. Application of the BD-95/90 method yields no SRLs for either VOC (table 7).



EXPLANATION

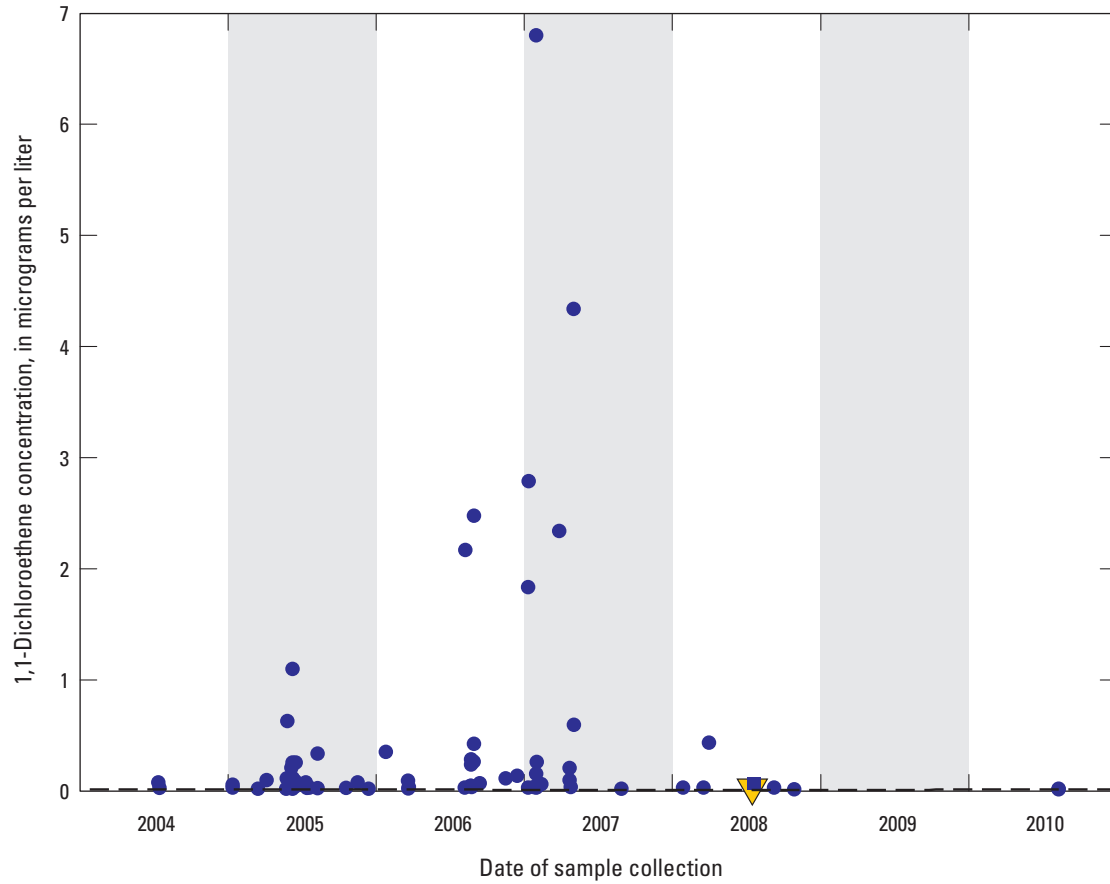
Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- ▲ Laboratory instrument blank (n=2,411)
- Groundwater—Long or short lines (n=1,859)
- Groundwater—Monitoring well (n=167)

Threshold

- — — Long-term method detection level (LT-MDL)
- A study reporting level (SRL) was not needed for dichloromethane.

Figure 18. Concentrations of dichloromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

Sample type (only detections are shown)

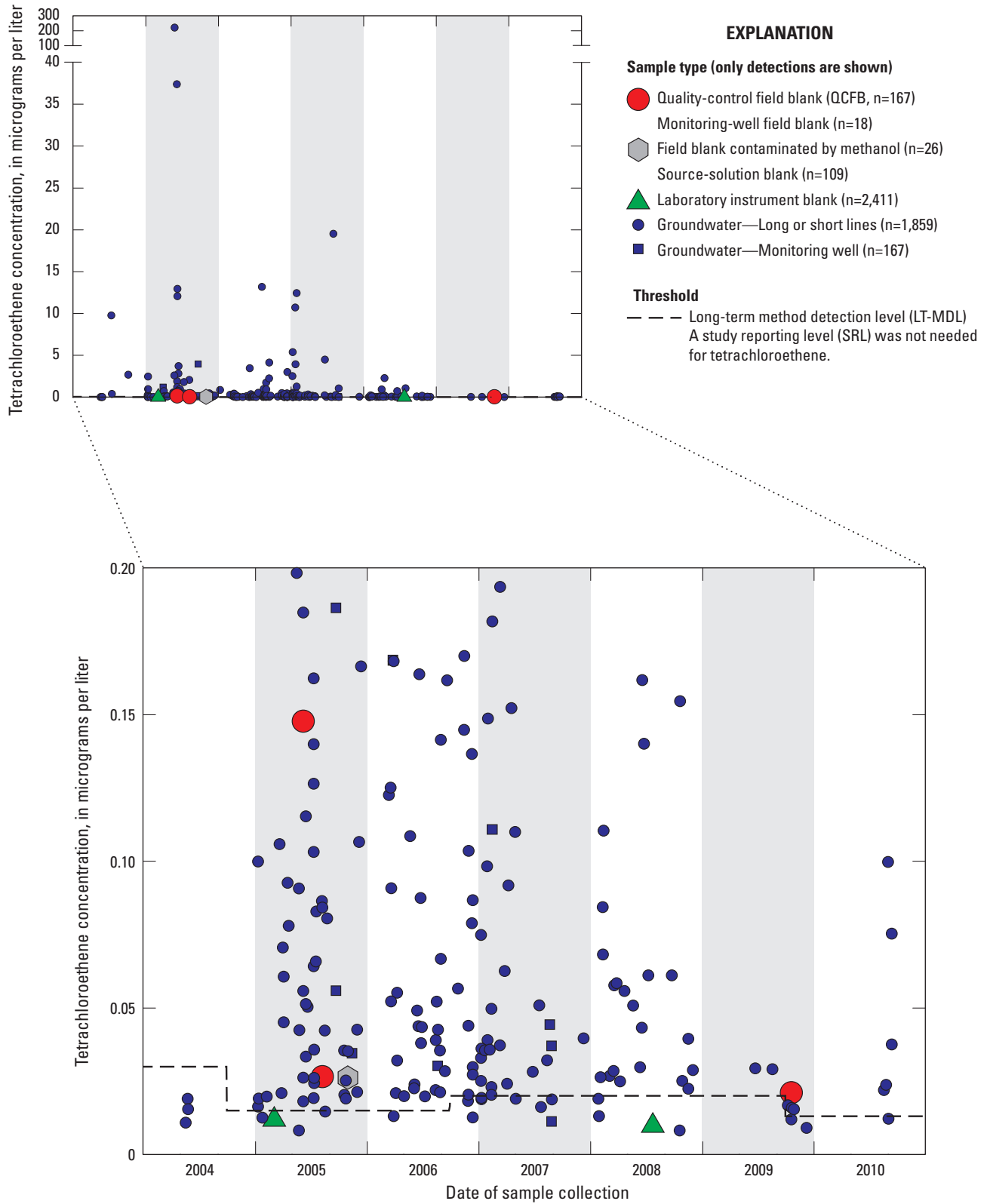
- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—Long or short lines (n=1,859)
- Groundwater—Monitoring well (n=167)

Threshold

- — — Long-term method detection level (LT-MDL)

A study reporting level (SRL) was not needed for 1,1-dichloroethene.

Figure 19. Concentrations of 1,1-dichloroethene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



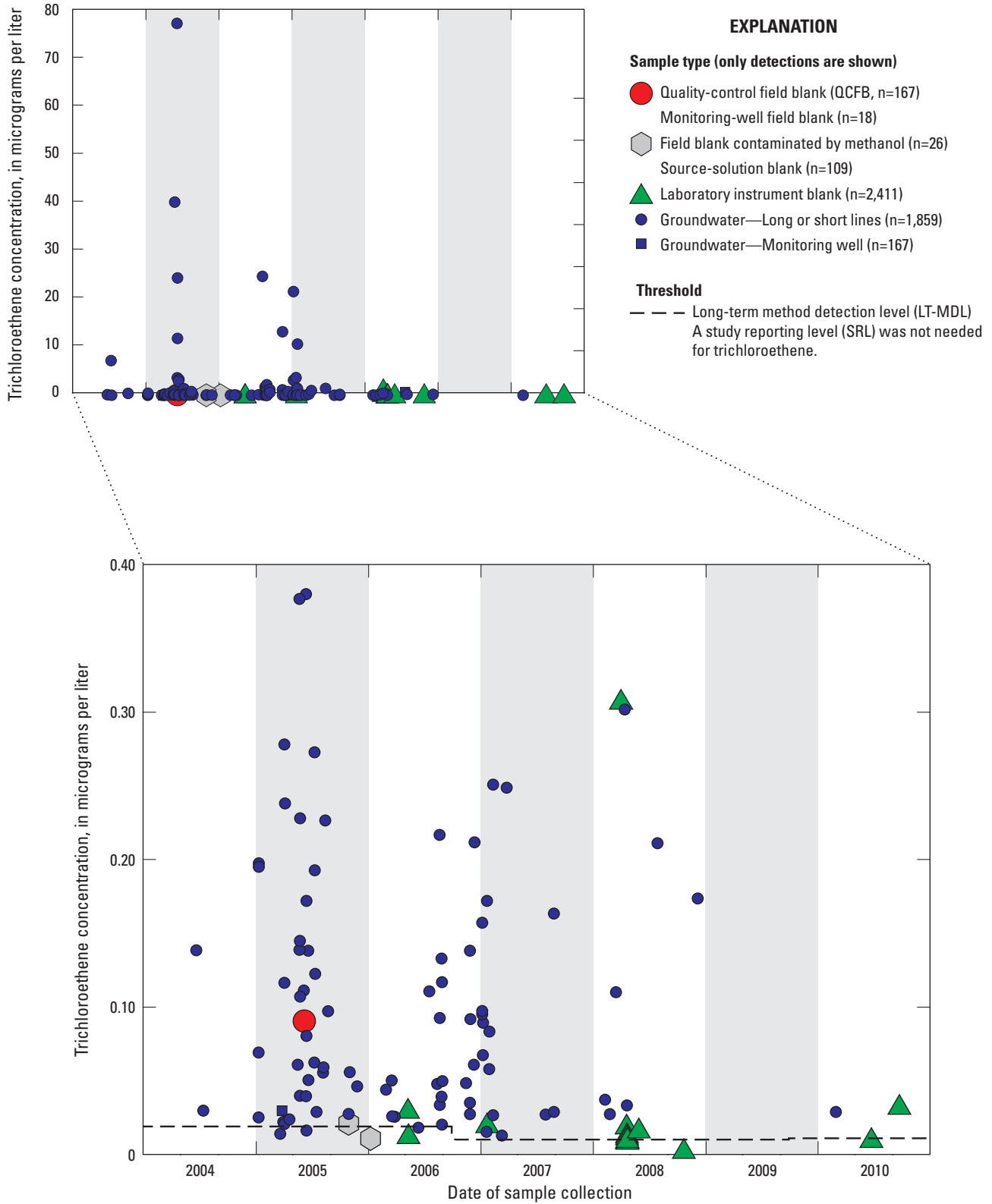
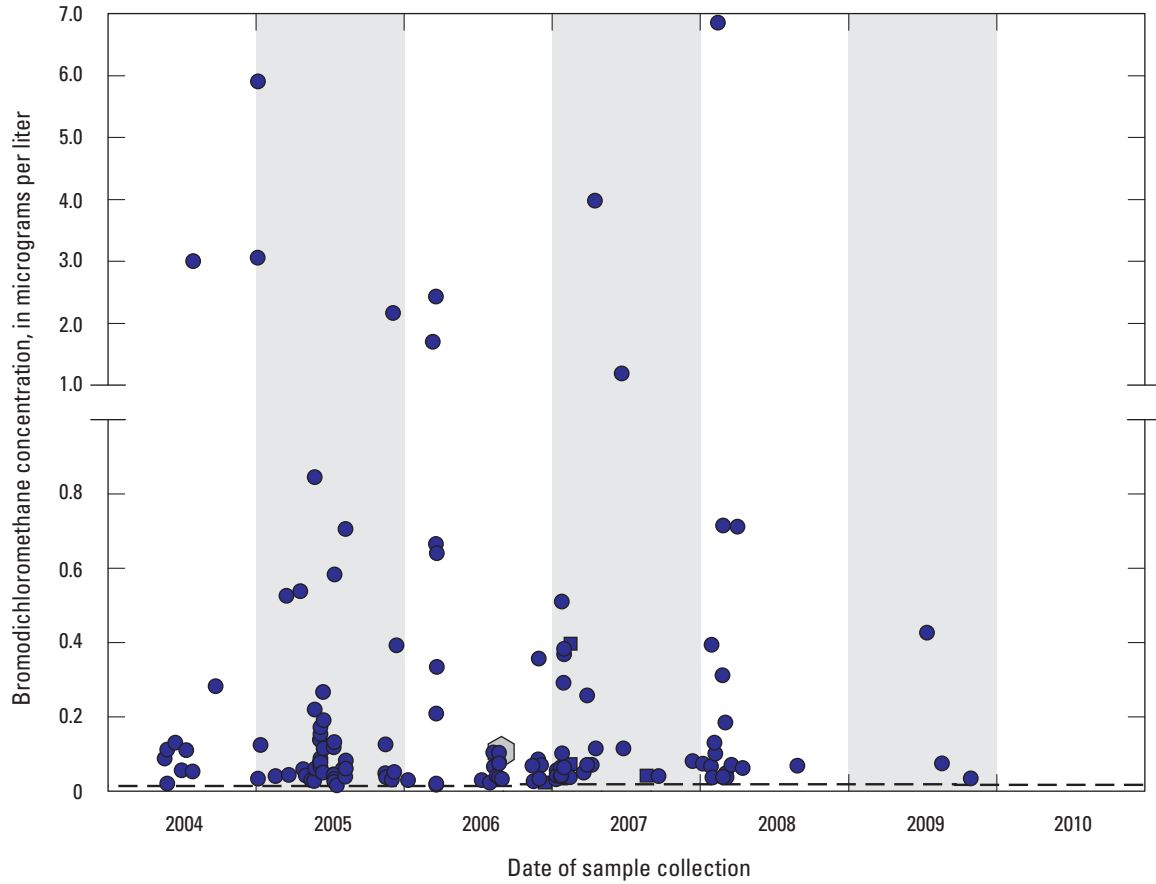


Figure 21. Concentrations of trichloroethene detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

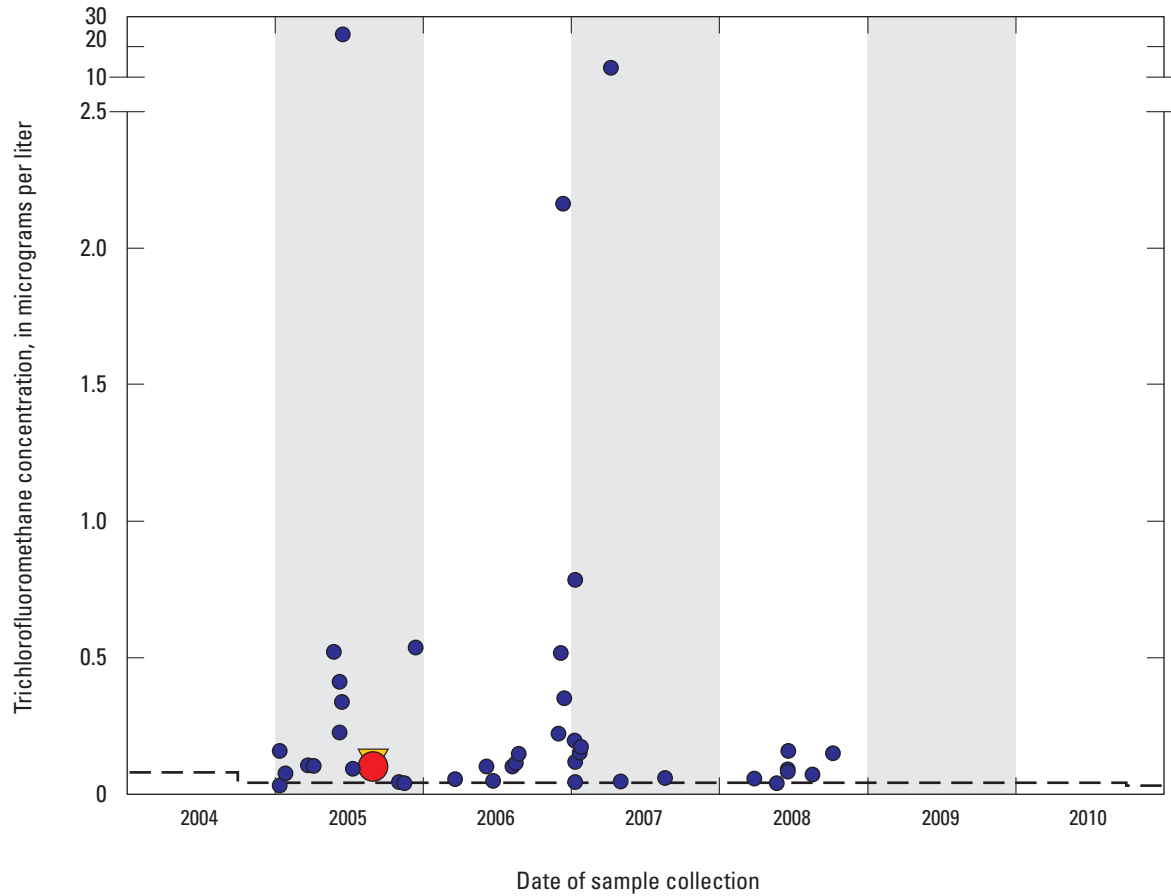
Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—Long or short lines (n=1,859)
- Groundwater—Monitoring well (n=167)

Threshold

- — — Long-term method detection level (LT-MDL)
- A study reporting level (SRL) was not needed for bromodichloromethane.

Figure 22. Concentrations of bromodichloromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.



EXPLANATION

Sample type (only detections are shown)

- Quality-control field blank (QCFB, n=167)
- Monitoring-well field blank (n=18)
- Field blank contaminated by methanol (n=26)
- ▼ Source-solution blank (n=109)
- Laboratory instrument blank (n=2,411)
- Groundwater—Long or short lines (n=1,859)
- Groundwater—Monitoring well (n=167)

Threshold

- — — Long-term method detection level (LT-MDL)
- A study reporting level (SRL) was not needed for trichlorofluoromethane.

Figure 23. Concentrations of trichlorofluoromethane detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

Carbon Disulfide

Carbon disulfide has anthropogenic and natural sources. It has been an important industrial chemical since the 1800s, primarily because of its ability to solubilize fats, rubber, phosphorous, and other substances (Agency for Toxic Substances and Disease Registry, 1996). The most important current industrial uses are in the manufacturing of rayon, cellophane, and carbon tetrachloride. Carbon disulfide was used as a fumigant, primarily for insect control in stored grain, until registration was cancelled in 1985 (U.S. Environmental Protection Agency, 1985). Natural microbial reduction of sulfate produces carbon disulfide in soils, marshes, stratified lakes, and other anaerobic environments, and carbon disulfide is emitted to the atmosphere from the oceans and from volcanic eruptions (for example, Chin and Davis, 1993; Devai and DeLaune, 1995; Agency for Toxic Substances and Disease Registry, 1996).

Inferred Source of Contamination

Comparisons of detection frequencies and concentrations of carbon disulfide in laboratory instrument blanks, source-solution blanks, and field blanks suggest that there are sources of contamination during analysis of samples in the laboratory and in sample collection or handling in the field. The detection frequency in laboratory instrument blanks (1.6 percent) was lower than in other types of blanks (table 4); however, the differences were not statistically significant (contingency table tests, $p > 0.05$), and the concentrations detected in all three types of blanks were similar (fig. 24).

There were no significant differences in detection frequencies of carbon disulfide between source-solution blanks (3.7 percent), methanol-affected field blanks (3.8 percent), field blanks collected with long sampling lines (3.2 percent), or field blanks collected with short sampling lines (2.9 percent) (tables 4, 6), indicating that contact with field sampling equipment likely was not the source of contamination during sample collection and handling.

On the basis of results from two sets of laboratory experiments, the likely source of contamination by carbon disulfide is the nitrile gloves used by both laboratory and field personnel. Soaking a nitrile glove in 1,000 mL of blank water for 20 minutes yielded 38 $\mu\text{g/L}$ carbon disulfide in the water (Worthington and others, 2007). In a separate experiment, soaking four types of nitrile gloves used by field or laboratory personnel in blank water for 24 hours leached 800 to 11,600 micrograms per gram ($\mu\text{g/g}$) of carbon disulfide from the gloves (Lisa Olsen and Donna Rose, U.S. Geological Survey, written commun., 2011). One glove (approximately 10 grams) soaked in 1,000 mL of water would yield 80 to 1,160 $\mu\text{g/L}$ carbon disulfide in the water. The carbon disulfide leached from gloves in these experiments may be sufficient to account for the low concentrations observed in field and

source-solution blanks (0.01 $\mu\text{g/L}$ to 0.09 $\mu\text{g/L}$). If blank water dripping off a glove contained 100 $\mu\text{g/L}$ of carbon disulfide, then the median detected concentration observed in field blanks and source-solution blanks (0.056 $\mu\text{g/L}$) would correspond to a mixture of 0.056 percent drip water and 99.944 percent source-blank water. This is equivalent to approximately $\frac{1}{2}$ drop of drip water in a 40-mL VOC vial.

SRL for Carbon Disulfide

The occurrence pattern of carbon disulfide in groundwater samples is largely consistent with the pattern expected for the occurrence of carbon disulfide from natural sources; therefore, selection of an SRL that results in little censoring of the data may be most appropriate. Carbon disulfide can form naturally under anoxic conditions by reaction between organic matter and dissolved sulfide (for example, Devai and DeLaune, 1995). The detection frequency of carbon disulfide in groundwater samples considered anoxic (10 percent) was significantly greater than the detection frequency in groundwater samples considered oxic (1.5 percent) (contingency table test, $p < 0.001$). [For the purposes of this report, samples are considered anoxic if dissolved oxygen concentration was less than 1 milligram per liter (mg/L) or if iron concentration was greater than 100 $\mu\text{g/L}$ or if manganese concentration was greater than 50 $\mu\text{g/L}$. Anoxic samples were not further classified because of insufficient data: of the 2,026 groundwater samples, 1,783 had dissolved oxygen data, 1,315 had iron and manganese data, and 1,243 had data for dissolved oxygen and for iron and manganese.]

The methods for determining SRLs yield SRLs that result in censoring of vastly different amounts of the groundwater data. The BD-90/90 method does not yield an SRL because the detection frequency of carbon disulfide in the QCFBs is less than 7 percent, and therefore would result in no censoring of the groundwater data. The other methods yield SRLs ranging from 0.056 $\mu\text{g/L}$ (BD-95/90) to 0.092 $\mu\text{g/L}$ (maximum QCFB) (table 7).

Application of the BD-95/90 as the SRL would reduce the detection frequency to 5.0 percent in anoxic samples and 0.08 percent in oxic samples. However, many of the detections censored by application of this SRL appear to be representative of aquifer conditions. Of the 18 oxic groundwater samples having carbon disulfide less than 0.056 $\mu\text{g/L}$, 11 samples (61 percent) had detections of chlorinated solvents and 11 samples were from wells surrounded by more than 50 percent urban land use, which are factors that are correlated with industrial sources of carbon disulfide to groundwater. Many detections in groundwater samples appear to be representative of aquifer conditions; however, these detections would be censored by the application of an SRL as high as 0.056 $\mu\text{g/L}$.

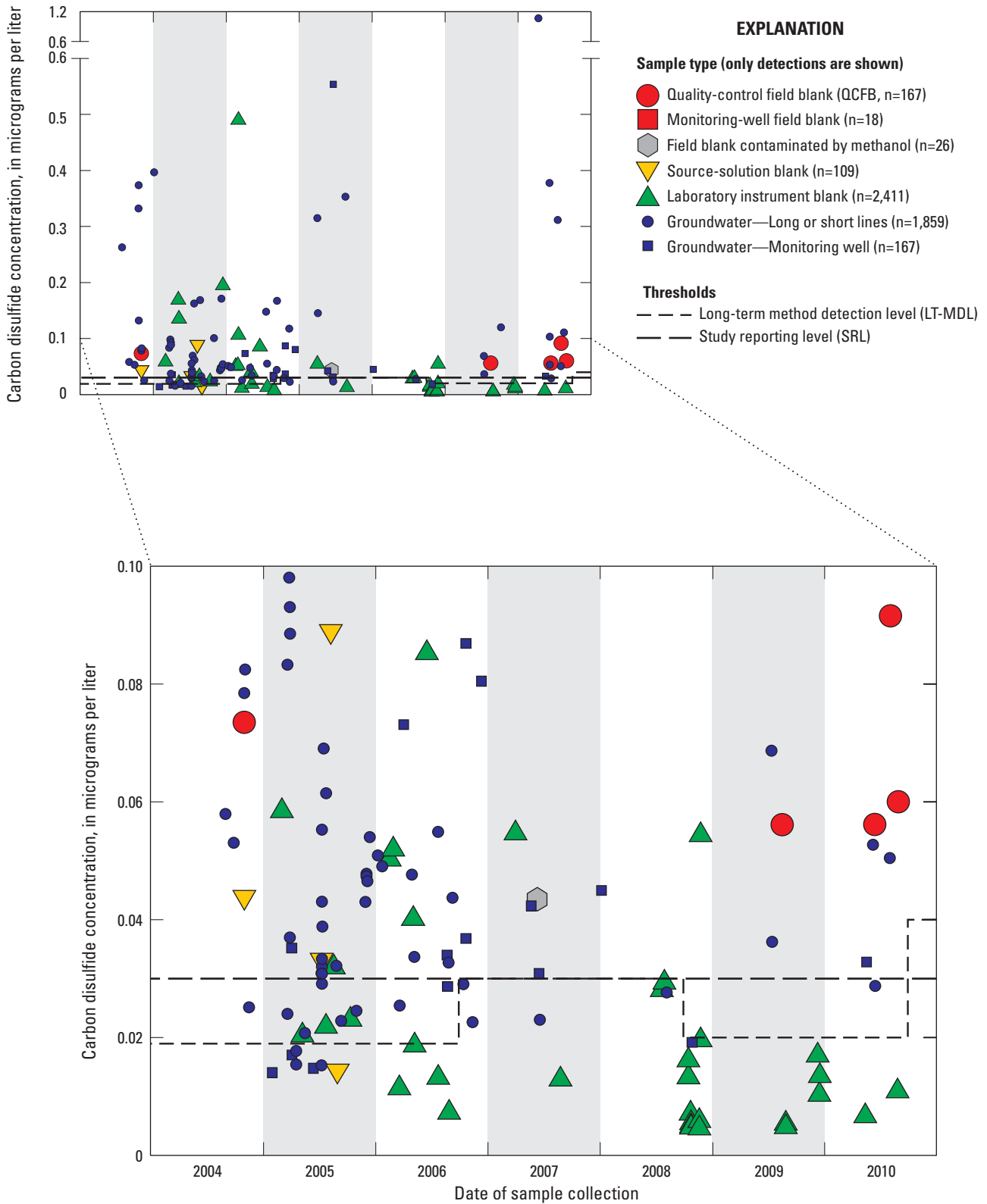


Figure 24. Concentrations of carbon disulfide detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

The results for the laboratory instrument blanks indicate that an SRL is needed for carbon disulfide. The BD-99/90 for carbon disulfide in the laboratory instrument blanks was 0.022 µg/L, which is higher than the LT-MDL for some periods of time between May 2004 and September 2010 (fig. 24). A BD-99/90 concentration greater than the LT-MDL may indicate that the set of samples used to establish the LT-MDL was not representative of the true variability, which would result in the LT-MDL having been too low a concentration. The SRL for carbon disulfide (0.03 µg/L) was defined as the highest concentration LT-MDL used for carbon disulfide between May 2004 and September 2010. Application of this SRL reduced the overall detection frequency in groundwater samples from 4.3 percent to 3.3 percent (tables 7, 8). Detection frequencies in anoxic and oxic samples decreased to 8.4 percent and 0.9 percent, respectively.

The detection frequencies of carbon disulfide in field blanks (7.2 percent) and groundwater samples (approximately 8 percent) collected at production wells by the NAWQA Program (Bender and others, 2011) were greater than the detection frequencies observed in this study (3.2 and 3.8 percent, respectively; table 4; fig. 3). The SRL calculated by Bender and others (2011) had a lower concentration than the SRL selected in this study (fig. 14). Bender and others (2011) used the BD-90/90 method to calculate the SRL of 0.01 µg/L for data from production wells; the BD-90/90 method applied to the QCFBs in this study would have yielded no SRL because the detection frequency of carbon disulfide in the QCFBs was less than 7 percent.

Chloroform

The trihalomethane chloroform was the most frequently detected VOC in groundwater samples (27 percent; table 4). Chloroform was detected in 1.8 percent of the QCFBs (table 4), and the patterns of detection of chloroform in field blanks, source-solution blanks, and laboratory instrument blanks are consistent with the primary source of contamination being the tap water used to rinse field equipment. Most tap water has been disinfected with chlorine solutions during the drinking-water treatment process. Chlorine solutions can react with organic matter present in the water, forming trihalomethanes and other halogenated disinfection byproducts.

Inferred Source of Contamination

The occurrence of chloroform was significantly higher in field blanks contaminated with methanol (15 percent) than in ones not contaminated with methanol (3.2 percent) (table 6). Among the field blanks not contaminated with methanol, the occurrence of chloroform was significantly greater in field blanks collected at monitoring wells (17 percent) compared to field blanks collected with long sampling lines (3.2 percent) or short sampling lines (1.0 percent). The lines used for the

monitoring-well sampling equipment are longer and more complex than those used for the long and short sampling lines sampling configurations. There may be higher probability that a small amount of tap water would remain in the equipment even after rinsing with a sufficient amount of blank water to remove the methanol. The median detected concentration of chloroform in field blanks was 0.038 µg/L (fig. 25; table A2). If the concentration of chloroform in tap water were 32 µg/L [the average concentration of trihalomethanes in Sacramento, California, tap water in 2010 (City of Sacramento, 2010)], then the median detected concentrations observed in the field blanks would correspond to a mixture of 0.12 percent tap water and 99.88 percent source-blank water. This is equivalent to approximately one drop of tap water in a 40-mL VOC vial.

SRL for Chloroform

The methods for determining SRLs yield SRLs that result in censoring of vastly different amounts of the groundwater data. The BD-90/90 and BD-95/90 methods do not yield SRLs and therefore would result in no censoring of the groundwater data. Use of the maximum LT-MDL method would yield an SRL of 0.02 µg/L and result in a slight decrease in detection frequency in groundwater from 27 percent to 23 percent (table 7). At the other extreme, application of the maximum concentration detected in the QCFBs (0.127 µg/L) as the SRL would result in reducing the detection frequency of chloroform in groundwater to 9.3 percent. The fact that the detection frequency in the QCFBs (1.8 percent) is so much lower than the detection frequency in groundwater samples suggests that contamination has a negligible effect on chloroform detections; therefore, an SRL that results in little or no censoring of the groundwater data is warranted. On this basis, either the BD-95/90 method (no SRL) or maximum LT-MDL method would yield appropriate values for the SRL for chloroform (table 7). The BD-95/90 method was selected for consistency with other VOCs.

The occurrence of chloroform in field blanks collected with monitoring-well equipment (17 percent) was significantly greater than the occurrence in field blanks collected with long (3.2 percent) or short sampling lines (1.0 percent) (table 6), suggesting that an SRL may be warranted for groundwater samples collected with monitoring-well equipment. There were 18 field blanks collected at monitoring wells that were not affected by methanol, which is an insufficient number to define a BD-95/90. The maximum LT-MDL for chloroform, 0.02 µg/L, was used as the SRL for groundwater samples collected with monitoring-well equipment. Application of this SRL decreases the detection frequency of chloroform in groundwater samples collected with monitoring-well equipment from 18 percent to 14 percent (table 8). Bender and others (2011) also reported that the detection frequency in field blanks collected at monitoring wells by the NAWQA Program (28 percent) was significantly greater than the frequency in field blanks collected at production wells (11 percent).

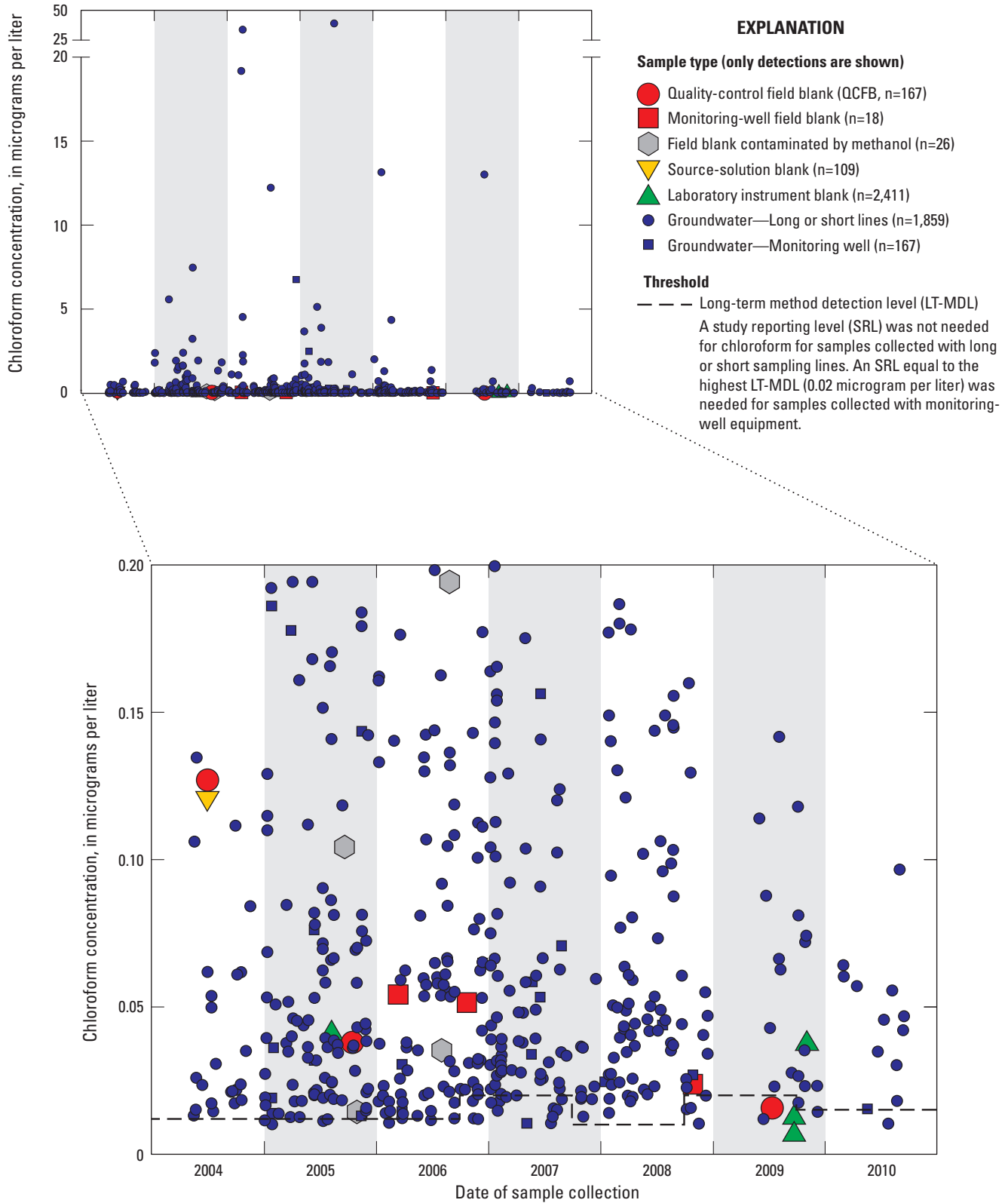


Figure 25. Concentrations of chloroform detected in field blanks, source-solution blanks, laboratory blanks, and groundwater samples, California GAMA Priority Basin Project, May 2004 through September 2010. Non-detections are not shown.

The detection frequency of chloroform in field blanks collected at production wells (11 percent) by the NAWQA Program (Bender and others, 2011) was significantly greater than the detection frequency observed in this study (fig. 3). Bender and others (2011) used the BD-90/90 method to calculate the SRL of 0.02 µg/L for data from production wells; the BD-90/90 method applied to the QCFBs in this study would have yielded no SRL because the detection frequency of chloroform in the QCFBs was only 1.8 percent.

Application of SRLs and Maximum LT-MDLS

The GAMA-PBP uses 10-percent detection frequency in a study unit as a threshold for identifying organic constituents that may be of concern (for example, Landon and others, 2010). There are three primary issues associated with comparing detection frequencies at low concentrations: (1) discerning between VOC detections that are the result of extrinsic contamination and those that are representative of aquifer conditions; (2) comparing data collected at different times if laboratory reporting levels have changed over time; and (3) defining an acceptable probability of false-positive detections. The first issue is addressed by censoring water-quality data by using SRLs, and the latter two issues require examining the reporting of detections with concentrations near the LT-MDLS.

Application of SRLs had a noticeable effect on the identification of organic constituents that may be of concern. Initially, 20 VOCs had raw detection frequencies greater than 10 percent in at least 1 of the 32 study units. Of these 20 VOCs, 5 have SRLs that were determined in this report: *m*- and *p*-xylenes, toluene, 1,2,4-trimethylbenzene, carbon disulfide, and chloroform. Application of the SRLs for the hydrocarbons resulted in large changes in detection frequencies: initial raw detection frequencies for *m*- and *p*-xylenes, toluene, and 1,2,4-trimethylbenzene were greater than or equal to 10 percent in 2, 5, and 11 of the 32 study units, respectively, and after application of the SRLs, there were no study units with raw detection frequencies greater than 10 percent (table 9). Initial raw detection frequency for carbon disulfide was greater than 10 percent in three GAMA study units; after application of the SRL it was greater than 10 percent in one study unit (study unit S3). Application of the SRL for chloroform caused no change in the number of study units with raw detection frequency greater than 10 percent (table 9).

There were a total of 2,580 detections of 60 different VOCs in the 2,026 groundwater samples. Of those 2,580 detections, 489 were censored by application

of the recommended SRLs (table 8). Toluene and 1,2,4-trimethylbenzene account for 74 percent of the detections censored. Of the remaining 2,091 detections in groundwater samples, 231 had concentrations below the highest LT-MDL used during the study period. Nearly half of the detections with concentrations below the highest LT-MDL were of three VOCs: tetrachloroethene (49 of 259 detections had concentrations below 0.03 µg/L, fig. 20), chloroform (35 of 539 detections had concentrations below 0.02 µg/L, fig. 25), and methyl *tert*-butyl ether (29 of the 113 detections had concentrations below 0.08 µg/L, not shown). All detections of four other VOCs had concentrations below the highest LT-MDL: 4-isopropyltoluene (3), bromomethane (1), methyl *tert*-pentyl ether (1), and *sec*-butylbenzene (1).

Effect of LT-MDL Changes on VOC Detection Frequencies

After application of SRLs, chloroform and tetrachloroethene were the two most commonly detected VOCs in GAMA groundwater samples collected between May 2004 and September 2010 (table 7). Comparisons were made between the detection frequencies of chloroform and tetrachloroethene in the 32 study units sampled during that period. Therefore, it was important to evaluate whether changes in LT-MDLS affected reporting of detections with low concentrations. This was evaluated by comparing data from periods with different LT-MDLS.

Of the 2,026 groundwater samples, 1,357 were analyzed during periods when the LT-MDL for chloroform was 0.01 µg/L, and 699 were analyzed when the LT-MDL was 0.015 µg/L or 0.02 µg/L. Samples in the two groups were divided into seven categories by concentration (non-detections, detections with concentrations less than 0.02 µg/L, and detections with concentrations in five different ranges between 0.02 µg/L and 40 µg/L), and the frequencies in each category were compared (fig. 26A). There were no significant differences in frequencies in any category between samples analyzed during periods with the higher and lower LT-MDLS. During periods when the LT-MDL was 0.01 µg/L, 74 percent of samples had a non-detection of chloroform, and 3.8 percent had a detection with concentration less than 0.02 µg/L. During periods that the LT-MDL was 0.015 µg/L or 0.02 µg/L, 71 percent of samples had a non-detection of chloroform, and 3.6 percent had a detection with concentration less than 0.02 µg/L. These results suggest that changes in LT-MDL may not have affected reporting of detections with concentrations less than the maximum LT-MDL. Therefore, detection frequencies of chloroform in study units sampled during periods having different LT-MDLS should be able to be compared without re-censoring the data to the maximum LT-MDL.

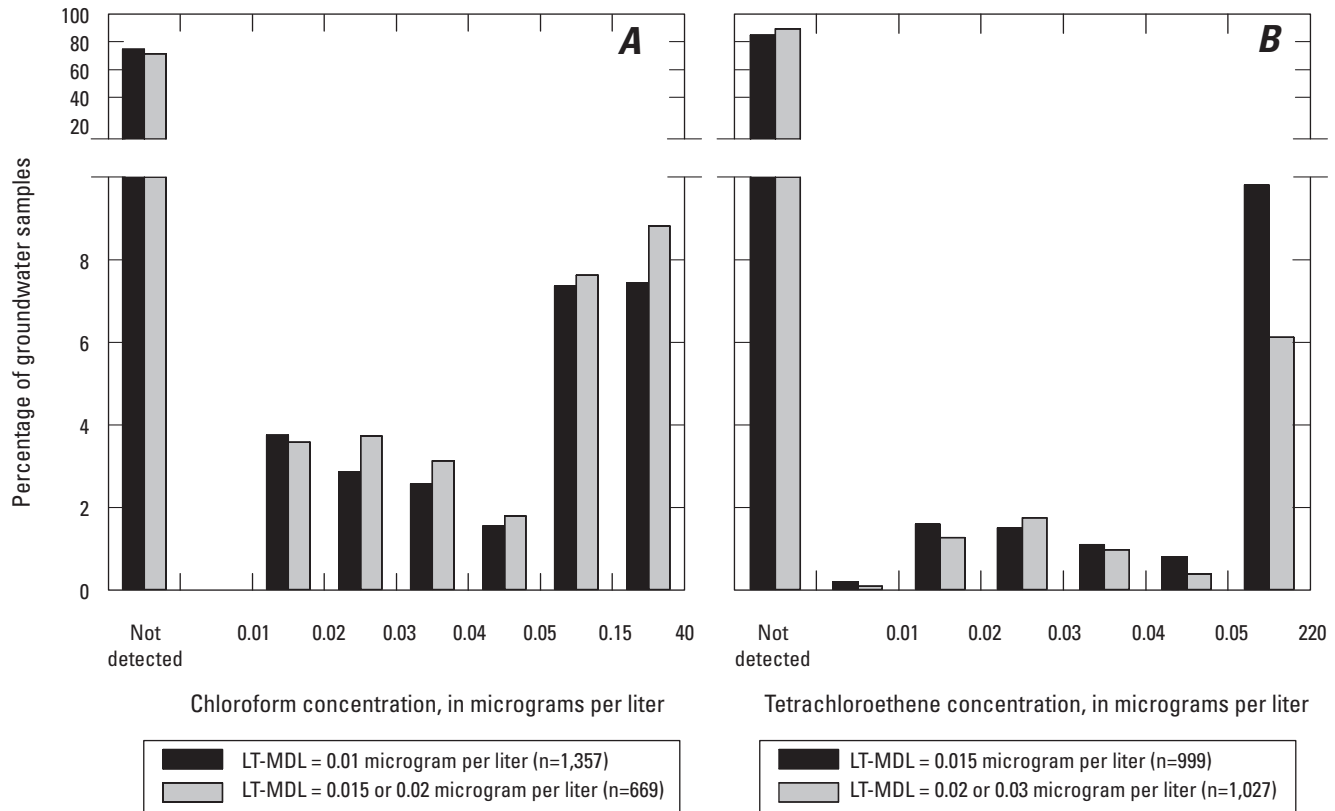


Figure 26. Percentages of groundwater samples in concentration range categories for different long-term method detection levels (LT-MDLs) for (A) chloroform and (B) tetrachloroethene.

A similar analysis for tetrachloroethene was also conducted, with statistically significant differences in two of the seven categories and no significant differences in five of the categories. Of the 2,026 groundwater samples, 999 were analyzed during periods when the LT-MDL was 0.015 µg/L, and 1,027 were analyzed during periods when the LT-MDL was 0.02 µg/L or 0.03 µg/L. The percentage of samples having a non-detection for tetrachloroethene was significantly greater during the period with higher LT-MDL (89 percent) than during the period with lower LT-MDL (85 percent) (contingency table test, $p=0.003$; [fig. 26B](#)). However, the types of study units sampled during the two periods were not the same. Periods with the higher LT-MDLs had a significantly higher percentage of samples from Desert or Mountain study units (28 percent) than did periods with the lower LT-MDL (20 percent) (contingency table test, $p<0.001$). These study units generally have lower population densities and therefore may have fewer sources of tetrachloroethene to groundwater. There were no significant differences in the percentages of samples having detections with concentrations in the four categories with concentrations between 0.01 and 0.05 µg/L. The percentage of samples having detections with

concentrations greater than 0.05 µg/L was significantly lower during periods with the higher LT-MDL than during periods with the lower LT-MDL (contingency table test, $p=0.002$) ([fig. 26B](#)); this difference is consistent with the difference in the population densities of study units sampled during the two periods. These observations—no significant difference in five of the seven categories and plausible explanation for significant differences in the other two categories—suggest that the lower detection frequency of tetrachloroethene in samples analyzed during periods when the LT-MDL was 0.02 µg/L or 0.03 µg/L compared to periods when the LT-MDL was 0.015 µg/L may reflect true differences in the samples rather than being an artifact of differences in reporting of detections with low concentrations between the periods.

These results suggest that changes in LT-MDLs between May 2004 and September 2010 did not significantly affect the reporting of detections with low concentrations. Therefore, differences in detection frequencies of VOCs in GAMA study units sampled at different times likely reflect differences between the aquifers and are not artifacts of the LT-MDL changes.

LT-MDLs and Probabilities of False-Positive Detections

Depending on project objectives and how the data will be used, it may be appropriate to include detections with greater than a 1-percent probability of being false-positive detections (concentrations below the LT-MDL) in the dataset. However, if concentrations below the LT-MDL are included, the level of confidence in these detections should be stated in the report. The probability (α) of false-positive detection for a detection with concentration less than the LT-MDL can be estimated from the equation for the LT-MDL:

$$t_{LTMDL} = t_{23,0.01} = \frac{LTMDL}{s} \quad (\text{revision of Equation 1) and} \quad (5)$$

$$t_{f \times LTMDL} = t_{23,1-\alpha} = \frac{f \times LTMDL}{s} \quad (6)$$

where

f is the fraction of the LT-MDL, and
 α is the probability.

The probabilities were calculated by assuming that the number of samples used to determine the LT-MDL ($n=24$) and the standard deviation of the values for those samples (s) remained the same as in the original determination of the LT-MDL. The probability of false-positive detection increases from 1 percent at the LT-MDL to 40 percent at one-tenth of the LT-MDL (table 10).

After application of the SRLs, a total of 231 detections of VOCs had concentrations less than the maximum LT-MDL. Most had concentrations between the LT-MDL and one-half of the LT-MDL. The difference between the minimum and maximum LT-MDL was less than a factor of 2 for most VOCs (table 2); therefore, many of these detections may have had concentrations greater than the LT-MDL in effect at the time the samples were analyzed. Thirty-five detections of VOCs had concentrations below one-half of the LT-MDL (table 10). The probability of false-positive detection at concentrations less than one-half of the LT-MDL is greater than 11 percent. Of these 35 detections, 12 were of tetrachloroethene.

Table 10. Probability of false-positive detections at fractions of the long-term method detection level (LT-MDL), and numbers of detections with concentrations below the threshold, California GAMA Priority Basin Project, May 2004 through September 2010.

[Probability calculated assuming that the standard deviation(s) and number of samples ($n=24$) used in the calculation of the original LT-MDL remain constant]

Threshold concentration	Probability of false-positive detection (percent)	Number of detections with concentrations less than threshold
LT-MDL	1.0	231
3/4 LT-MDL	3.7	169
1/2 LT-MDL	11	35
1/4 LT-MDL	27	3
1/10 LT-MDL	40	0

Assessment of Methods Used for Determining Study Reporting Levels

Three philosophical issues relevant to analysis of field-blank data were introduced earlier in this report: use of statistical or deterministic methods for analysis of field-blank data, use of methods based on contamination having a characteristic pattern of concentrations or a characteristic detection frequency, and use of different methods for different VOCs.

In this report we have followed a statistical approach in that blanks and environmental samples are treated as independent populations. In other words, a field blank collected at a particular site is considered representative of conditions under which environmental samples are collected at all sites, and field blanks are not directly compared to the “paired” environmental sample collected at the same site. Even in the evaluations of hypotheses about specific sources of contamination, a statistical approach was followed. Contamination, even from known sources, is a probabilistic process.

The case of 1,2,4-trimethylbenzene provides an example of the probabilistic nature of contamination. The detection frequencies of 1,2,4-trimethylbenzene at concentrations less than the SRL were 11 percent in field blanks collected with long sampling lines and 17 percent in groundwater samples collected with long sampling lines. The field blanks likely were contaminated by a mechanism that also would affect groundwater samples, namely airborne contact with 1,2,4-trimethylbenzene that had contaminated field vehicles from storage of radon sampling kits or materials that had come in contact with radon sampling vials. However, of the seven field blanks collected with long sampling lines that had detection of 1,2,4-trimethylbenzene, only one was paired with an environmental sample that also had a detection of 1,2,4-trimethylbenzene. The association between radon sampling and 1,2,4-trimethylbenzene likely would not have been apparent from only comparing the paired field blank and environmental sample data.

The reason for this apparent discrepancy is that not all of the field blanks or environmental samples were contaminated. There was an 11-percent probability that a field blank collected with long sampling lines would be contaminated with 1,2,4-trimethylbenzene and a 17-percent probability that an environmental sample collected with long sampling lines would be contaminated. Thus, if no other factors caused a greater or lesser tendency toward co-occurrence at the same site, there was a 1.8-percent probability that a field blank and environmental sample collected at the same site would both be contaminated, which is in agreement with the observed detection frequency in the data collected with long sampling lines (1 co-occurrence in 62 instances, which is a frequency of 1.6 percent).

After examining the different methods of determining SRLs for a range of VOCs, we reached the conclusion that selection of the most appropriate method for determining SRLs depended on the hypothesized or inferred mechanisms and frequencies of contamination of field blanks and environmental samples. We found that using different methods for different VOCs yielded SRLs that resulted in more rational censoring of groundwater data than attempting to apply a single approach for all compounds.

For most VOCs having significantly lower detection frequencies in field blanks than in groundwater samples, the method selected for determining SRLs was the binomial probability method, using the BD-95/90 concentration as the SRL. For dichloromethane, tetrachloroethene, trichloroethene, chloroform, and trichlorofluoromethane, application of this method resulted in no SRL because the BD-95/90 was a non-detection (detection frequency in QCFBs was less than 3 percent). Maximum LT-MDLs could also have been selected as SRLs for these VOCs; however, censoring was not considered necessary on the basis of detections in blanks because detection frequencies in the QCFBs (0.6 percent for

dichloromethane, trichloroethene, and trichlorofluoromethane; 1.8 percent for chloroform and tetrachloroethene) were so low. Selection of the maximum QCFBs as SRLs would have resulted in unwarranted, high degrees of censoring of the groundwater data. Comparison of detection frequencies in source-solution blanks, groundwater samples, and different types of field blanks did not result in well-defined hypotheses for the sources and mechanisms of contamination to field blanks or groundwater samples.

In contrast, for VOCs having higher detection frequencies in field blanks than in groundwater samples, application of the binomial probability method would have resulted in insufficient censoring. Ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene had higher detection frequencies in field blanks than in groundwater samples, and the concentrations detected in blanks were similar to most concentrations detected in groundwater samples. Hydrocarbon ratios indicated that the likely source of contamination to field blanks and most groundwater samples was fuel exhaust or fumes. Comparison among detection frequencies in different types of field blanks suggested that the primary mechanism of contamination was contact with field sampling equipment, and differences in the amount of rinsing of field equipment plausibly accounted for the higher detection frequencies in field blanks compared to groundwater samples. The hydrocarbon ratios also indicated that the ethylbenzene and *o*-xylene in the groundwater samples with the highest concentrations (which were much higher than all of the concentrations in blanks) were likely from a different source. Selection of the maximum concentrations detected in the QCFBs as SRLs resulted in censoring of nearly all detections in groundwater. If the BD-95/90 values had been selected as the SRLs, many detections in groundwater with hydrocarbon ratios and concentrations indistinguishable from those in field blanks would have been retained.

For VOCs with similar detection frequencies in field blanks and groundwater, the choice of the most appropriate method for determining an SRL was more complicated. In the case of 1,2,4-trimethylbenzene, the highest concentration detected in the QCFBs was deemed the most appropriate because it resulted in censoring of the most data; nearly all occurrences of 1,2,4-trimethylbenzene in groundwater samples could be accounted for by the same source and mechanism as were inferred for contamination of the field blanks. The likely source of the 1,2,4-trimethylbenzene was the scintillation fluid in the vials used for collection of radon samples, and the likely mechanism was pervasive contamination of field vehicles due to presence of materials (kits, used gloves, etc.) associated with sampling for radon. Selection of the SRL from the binomial probability method (BD-95/90 or BD-90/90) would have resulted in insufficient censoring of the groundwater data, although for different reasons than for the other hydrocarbons.

In the case of carbon disulfide, the BD-95/90 and maximum concentration in the QCFBs methods both would have resulted in over-censoring of the groundwater data. The inferred source and mechanism of contamination—contact with the gloves worn by field and laboratory personnel—does affect field blanks and groundwater samples. However, the occurrence pattern of carbon disulfide in groundwater samples was broadly consistent with geochemical predictions (higher frequency of detection in anoxic groundwater), suggesting that extrinsic contamination was not the dominant source of carbon disulfide to the samples; therefore, the data were largely representative of aquifer conditions. The highest LT-MDL was selected as the SRL because it resulted in censoring of fewer data than the BD-95/90 SRL would have caused.

Summary and Conclusions

Volatile organic compounds (VOCs) were analyzed in quality-control samples collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program Priority Basin Project (PBP). The project is being conducted by the U.S. Geological Survey (USGS) in cooperation with the California State Water Resources Control Board to assess and monitor the quality of groundwater resources used for drinking-water supply and to improve public knowledge of groundwater quality in California. From May 2004 through September 2010, a total of 2,026 groundwater samples, 211 field blanks, and 109 source-solution blanks were collected and analyzed for concentrations of 85 VOCs. Results from these field and source-solution blanks, and from 2,411 laboratory instrument blanks analyzed during the same time period were used to assess the quality of data for the 2,026 groundwater samples.

Of the 85 VOCs analyzed, 18 were detected in field blanks or source-solution blanks, and 67 were not detected. The VOCs detected in blanks can be divided into three groups:

Hydrocarbons	Solvents	Other VOCs
benzene	acetone	bromodichloromethane
ethylbenzene	2-butanone	carbon disulfide
styrene	1,1-dichloroethene	chloroform
toluene	dichloromethane	trichlorofluoromethane
1,2,4-trimethylbenzene	tetrachloroethene	
<i>m</i> - and <i>p</i> -xylenes	tetrahydrofuran	
<i>o</i> -xylene	trichloroethene	

The objective of the evaluation of the VOC-blank data was to determine if study reporting levels (SRLs) were needed for any of the VOCs detected in blanks to ensure the quality of the data from groundwater samples. An SRL is equivalent to a raised reporting limit that is used in place of the reporting limit used by the analyzing laboratory [laboratory reporting level (LRL) or long-term method detection level (LT-MDL)] to reduce the probability of reporting false positives.

Evaluation of VOC-blank data was done in three stages: (1) identification of a set of representative quality-control field blanks (QCFBs) to be used for calculation of SRLs and identification of VOCs amenable to the SRL approach, (2) evaluation of potential sources of contamination to blanks and groundwater samples by VOCs detected in field blanks, and (3) selection of appropriate SRLs from among the SRLs defined using different approaches for determining SRLs for VOCs detected in field blanks and application of those SRLs to the groundwater data.

An important conclusion from this study is that to ensure the quality of the data from groundwater samples, it was necessary to apply different approaches of determining SRLs from field-blank data to different VOCs, rather than use the same approach for all VOCs. There are multiple potential sources and mechanisms of extrinsic contamination of blanks and groundwater samples; these mechanisms do not have equal probabilities of affecting blanks and groundwater samples. The differences in detection frequencies and concentrations among different types of blanks (laboratory instrument blanks, source-solution blanks, and field blanks collected with three different sampling equipment configurations) and groundwater samples were used to infer the sources and mechanisms of contamination for each VOC detection in field blanks. Other chemical data for the groundwater samples (oxidation-reduction state, co-occurrence of VOCs, groundwater age) and ancillary information about the well sites (land use, presence of known sources of contamination) were used to evaluate whether the patterns of detections of VOCs in groundwater samples, before and after application of potential SRLs, were plausible.

The SRL approach assumes that extrinsic contamination adds relatively low concentrations of VOCs to samples, and that there is a threshold concentration above which detections in groundwater samples have an acceptably small probability of being false positives. Contamination with acetone, 2-butanone, and tetrahydrofuran did not follow this pattern; therefore, these three VOCs were not amenable to the SRL approach. An inadvertent field test indicated that contamination with methanol can introduce 2-butanone, acetone, and tetrahydrofuran into field blanks, and observations from field sites indicated that the presence of fresh PVC-cement can also contaminate groundwater samples and field blanks with these VOCs. In both cases, there was no threshold concentration above which detections in groundwater samples could be assumed to represent aquifer conditions rather than extrinsic contamination. Reported detections of 2-butanone, acetone, and tetrahydrofuran in groundwater samples were coded as “reviewed and rejected” in NWIS, which is interpreted to be the same as if the groundwater sample was not analyzed for those VOCs. Detection frequencies for acetone, 2-butanone, and tetrahydrofuran in groundwater samples therefore cannot be defined.

Of the 211 field blanks, 167 constituted the set of QCFBs that was used to assess the quality of the groundwater data for VOCs. The 26 field blanks containing evidence of contamination with methanol [presence of acetone and (or) 2-butanone] were not included in the QCFBs. Contamination with methanol primarily was related to steps in the sample collection process at which there are small differences in sample collection procedures between field blanks and groundwater samples; thus, field blanks contaminated with methanol were not considered representative of conditions under which groundwater samples were collected. The 18 field blanks collected with monitoring-well equipment and not contaminated with methanol also were not included in the QCFBs because they had significantly higher concentrations and detection frequencies of chloroform than field blanks collected with other sampling equipment configurations. There were no significant differences between field blanks collected with long sampling lines (62 field blanks) and short sampling lines (105 field blanks); these were grouped together as the QCFBs. Because the small number of field blanks collected with monitoring-well equipment precluded robust calculation of separate SRLs for groundwater samples collected with monitoring-well equipment, the SRLs determined from the QCFBs were applied to groundwater samples collected with all three sampling equipment configurations.

Four potential SRL values were defined for each VOC using three approaches: two potential SRL values were defined using a binomial probability method based on one-sided, nonparametric upper confidence limits, one was defined as equal to the maximum concentration detected in the field blanks, and one was defined as the maximum LT-MDL used during the period samples were collected for the project. These four SRL values were compared, and one value was selected for each VOC as the SRL for use with GAMA groundwater data.

Ethylbenzene, *m*- and *p*-xylenes, and *o*-xylene had higher detection frequencies in QCFBs than in groundwater. All blanks and most groundwater samples had the same ratios of ethylbenzene and *o*-xylene to *m*- and *p*-xylenes, and concentrations in groundwater samples and field blanks were similar, implying a common source of contamination. Hydrocarbon ratios and comparisons between detection frequencies in different types of blanks suggest that the likely source is fuel or exhaust components sorbed onto sampling lines. The highest concentrations detected in the QCFBs [ethylbenzene, 0.06 microgram per liter ($\mu\text{g/L}$); *m*- and *p*-xylenes, 0.33 $\mu\text{g/L}$; and *o*-xylene, 0.12 $\mu\text{g/L}$] were selected as the SRLs because they resulted in the most censoring of groundwater data. Application of these SRLs resulted in censoring of 14 of 18 ethylbenzene detections, all 49 *m*- and *p*-xylenes detections, and 13 of 14 *o*-xylene detections in the 2,026 groundwater samples.

Toluene was the most frequently detected VOC in QCFBs, source-solution blanks, and laboratory instrument blanks, and detection frequencies in blanks were greater than in groundwater. Comparisons between detection frequencies in different types of blanks suggest two sources

of toluene contamination: the source of contamination with low concentrations may be the vials used for VOC samples and (or) contamination of the source-blank water during transit to field sites or storage in bottles, and the source of contamination with high concentrations may be fuel or exhaust components sorbed onto sampling lines. The highest concentration detected in the QCFBs, 0.69 $\mu\text{g/L}$, was selected as the SRL because it resulted in the most censoring of groundwater data. Application of this SRL resulted in censoring of 152 of the 156 detections of toluene in groundwater samples.

1,2,4-Trimethylbenzene detections in blanks and groundwater samples were not correlated with detections of other hydrocarbons. Three of the five field mobile labs used during the GAMA-PBP were used at sites where samples for radon were collected (approximately 30 percent of the 2,026 groundwater sampling sites), and detections of 1,2,4-trimethylbenzene in groundwater and blanks were confined to samples collected at sites visited by those mobile labs. Radon samples are collected in vials containing a scintillation cocktail composed of 1,2,4-trimethylbenzene and mineral oil. Although radon samples are collected at the wellhead, not in the mobile lab, the mobile labs apparently are subject to contamination from 1,2,4-trimethylbenzene, likely from storage of the kits used for radon sample collection and (or) disposal of gloves and other materials that may have come in contact with the radon sample vials. The highest concentration detected in the QCFBs, 0.56 $\mu\text{g/L}$, was selected as the SRL because it resulted in the most censoring of groundwater data. Application of this SRL resulted in censoring of 212 of the 216 detections of 1,2,4-trimethylbenzene in groundwater samples.

Carbon disulfide was detected at similar concentrations and detection frequencies in QCFBs and source-solution blanks and at slightly lower frequency in laboratory instrument blanks. Most carbon disulfide detections in groundwater samples occurred in anoxic samples, which is consistent with predicted occurrence of carbon disulfide formed naturally under sulfate-reducing conditions. The most probable source of carbon disulfide contamination is the gloves worn by field and laboratory personnel. The recommended SRL for carbon disulfide is the maximum LT-MDL, 0.03 $\mu\text{g/L}$. Application of this SRL resulted in censoring of 20 of the 87 detections of carbon disulfide.

Chloroform was the most frequently detected VOC in groundwater samples. The detection frequency of chloroform in field blanks collected at monitoring wells was significantly greater than in QCFBs; chloroform was the only VOC for which different SRLs were recommended for groundwater samples collected at production wells and at monitoring wells. The SRL recommended for groundwater samples collected at monitoring wells was the highest LT-MDL, 0.02 $\mu\text{g/L}$. Application of this SRL resulted in censoring of 6 of the 30 detections of chloroform in samples collected at monitoring wells. No SRL was recommended for groundwater samples collected with long or short sampling lines.

No SRLs were established for the remaining eight VOCs detected in field blanks. Benzene, styrene, 1,1-dichloroethene, and bromodichloromethane were not detected in QCFBs, and the detection frequencies of dichloromethane, tetrachloroethene, trichloroethene, and trichlorofluoromethane in QCFBs were less than 3 percent; thus the BD-95/90s of the QCFBs were non-detections.

The 2,026 groundwater samples had a total of 2,580 detections of 60 different VOCs. Of those 2,580 detections, 489 were censored by application of the SRLs determined in this report. Of the remaining detections, 231 had concentrations below the highest LT-MDL used during the study period. LT-MDLs changed by less than a factor of 2 between May 2004 and September 2010 for most VOCs, and the changes did not significantly alter reporting of detections with low concentrations. Therefore, censoring at the highest LT-MDLs for VOCs that do not have SRLs does not appear to be necessary to ensure comparability between study units sampled at different times during that period.

Acknowledgments

We thank the members of the U.S. Geological Survey (USGS) Groundwater Ambient Monitoring Assessment (GAMA) Program Team who did all the field work, tracked all of the data, and wrote the data-series reports for individual study units. We especially thank the many well owners and water purveyors who allowed the USGS to collect samples from their wells. The GAMA Priority Basin Project is funded by State of California bonds authorized by Proposition 50 and administered by the California State Water Resources Control Board.

References Cited

- Agency for Toxic Substances and Disease Registry, 1996, Toxicological profile for carbon disulfide: U.S. Government Printing Office 1996-739-324, 219 p., accessed August 3, 2012, at <http://www.atsdr.cdc.gov/ToxProfiles/tp82.pdf>.
- Agresti, A., and Coull, B.A., 1998, Approximate is better than “exact” for interval estimation of binomial proportions: *The American Statistician*, v. 52, no. 2, p. 119–126.
- Belitz, Kenneth, Dubrovsky, N.M., Burow, K.R., Jurgens, B.C., and Johnson, T., 2003, Framework for a ground-water quality monitoring and assessment program for California: U.S. Geological Survey Water-Resources Investigations Report 03-4166, 78 p. (Also available at <http://pubs.usgs.gov/wri/wri034166/>.)
- Belitz, Kenneth, Jurgens, B.C., Landon, M.K., Fram, M.S., and Johnson, T., 2010, Estimation of aquifer scale proportion using equal area grids—Assessment of regional scale groundwater quality: *Water Resources Research*, v. 46, W11550, doi:10.1029/2010WR009321.
- Bender, D.A., Zogorski, J.S., Mueller, D.K., Rose, D.L., Martin, J.D., and Brenner, C.K., 2011, Quality of volatile organic compound data from groundwater and surface water for the National Water-Quality Assessment Program, October 1996–December 2008: U.S. Geological Survey Scientific Investigations Report 2011-5204, 128 p. (Also available at <http://pubs.usgs.gov/sir/2011/5204/>.)
- Brown, L.D., Cai, T.T., and DasGupta, A., 2001, Interval estimation for a binomial proportion: *Statistical Science*, v. 16, v. 2, p. 101–133.
- Burton, C.A., and Belitz, Kenneth, 2008, Ground-water quality data in the southeast San Joaquin Valley, 2005–2006—Results from the California GAMA Program: U.S. Geological Survey Data Series Report 351, 103 p. (Also available at <http://pubs.usgs.gov/ds/351/>.)
- California Department of Public Health, 2006, California Code of Regulation. Title 22. Division 4. Environmental Health. Chapter 15. Domestic water quality and monitoring regulations. Article 16. Secondary water standards, accessed January 2011 at <http://www.cdph.ca.gov/certlic/drinkingwater/Documents/Recentlyadoptedregulations/R-21-03-finalregtext.pdf>.
- California Department of Public Health, 2008, Maximum contaminant levels and regulatory dates for drinking water, U.S. EPA VS California, November 2008, accessed January 2011 at <http://www.cdph.ca.gov/certlic/drinkingwater/Documents/DWdocuments/EPAandCDPH-11-28-2008.pdf>.
- California Department of Public Health, 2010, Drinking water notification levels and response levels—An overview: California Department of Public Health Drinking Water Program, accessed January 2011 at <http://www.cdph.ca.gov/certlic/drinkingwater/Documents/Notificationlevels/notificationlevels.pdf>.
- California Department of Public Health, 2011, California Code of Regulations. Title 22. Division 4. Environmental Health. Chapter 15. Domestic water quality and monitoring regulations. Article 5.5. Primary Standards—Organic Chemicals. Section §64445.1. Monitoring and Compliance—Organic Chemicals.
- California State Water Resources Control Board, 2003, A comprehensive groundwater quality monitoring program for California: Assembly Bill 99 Report to the Governor and Legislature, March 2003, 100 p., available at http://www.waterboards.ca.gov/water_issues/programs/gama/docs/final_ab_599_rpt_to_legis_7_31_03.pdf.

- Childress, C.J.O., Foreman, W.T., Connor, B.F., and Maloney, T.J., 1999, New reporting procedures based on long-term method detection levels and some considerations for interpretations of water-quality data provided by the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 99-193, 19 p. (Also available at http://water.usgs.gov/owq/OFR_99-193/index.html.)
- Chin, M., and Davis, D.D., 1993, Global sources and sinks of OCS and CS₂ and their distributions: *Global Biogeochemical Cycles*, v. 7, p. 321–337.
- City of Sacramento, 2010, 2010 Water quality report—A consumer confidence report for the citizens of Sacramento: City of Sacramento Department of Utilities, accessed December 2, 2011, at http://www.cityofsacramento.org/utilities/water/documents/CCR_LINO_web.pdf.
- Connor, B.F., Rose, D.L., Noriega, M.C., Murtaugh, L.K., and Abney, S.R., 1998, Methods of analysis by the U.S. Geological Survey National Water Quality Laboratory—Determination of 86 volatile organic compounds in water by gas chromatography/mass spectrometry, including detections less than reporting limits: U.S. Geological Survey Open-File Report 97-829, 78 p. (Also available at <http://nwql.usgs.gov/Public/pubs/OFR97-829/OFR97-829.html>.)
- Daisey, J.M., Hodgson, A.T., Fisk, W.J., Mendell, M.J., and Ten Brinke, J., 1994, Volatile organic compounds in twelve California office buildings—Classes, concentrations and sources: *Atmospheric Environment*, v. 28, no. 22, p. 3557–3562.
- Devai, I., and DeLaune, R.D., 1995, Formation of volatile sulfur compounds in salt marsh sediment as influenced by soil redox condition: *Organic Geochemistry*, v. 23, no. 4, p. 283–287.
- Ferrari, M.J., Fram, M.S., and Belitz, Kenneth, 2008, Groundwater quality in the Central Sierra study unit, California, 2006—Results from the California GAMA Program: U.S. Geological Survey Data Series 335, 60 p. (Also available at <http://pubs.usgs.gov/ds/335/>.)
- Fram, M.S., Munday, C.M., and Belitz, Kenneth, 2009, Groundwater quality data for the Tahoe-Martis study unit, 2007—Results from the California GAMA Program: U.S. Geological Survey Data Series 432, 88 p. (Also available at <http://pubs.usgs.gov/ds/432/>.)
- Hahn, G.J., and Meeker, W.Q., 1991, *Statistical intervals—A guide to practitioners*: New York, John Wiley and Sons, 392 p.
- Helsel, D.R., 2005, *Nondetects and data analysis—Statistics for censored environmental data*: New York, John Wiley and Sons, 268 p.
- Helsel, D.R., and Hirsch, R.M., 2002, *Statistical methods in water resources*: U.S. Geological Survey Techniques of Water-Resources Investigations, book 4, chap. A3, 510 p. (Also available at <http://pubs.usgs.gov/twri/twri4a3/>.)
- Horton, T.R., 1983, *Methods and results of EPA's study of radon in drinking water*: U.S. Environmental Protection Agency Office of Radiation Programs, Eastern Environmental Radiation Facility, Montgomery, Ala., EPA-520/5-83-027, 25 p.
- J&W Scientific, 1998, *Catalog, technical reference, and cookbook*: Folsom, California, J&W Scientific Incorporated, 420 p.
- Landon, M.K., and Belitz, Kenneth, 2012, *Geogenic sources of benzene in aquifers used for public supply, California: Environmental Science and Technology*, v. 46, p. 8689–8697.
- Landon, M.K., Belitz, Kenneth, Jurgens, B.C., Kulongoski, J.T., and Johnson, T.D., 2010, *Status and understanding of groundwater quality in the Central–Eastside San Joaquin Basin, 2006—California GAMA Priority Basin Project*: U.S. Geological Survey Scientific Investigations Report 2009-5266, 97 p. (Also available at <http://pubs.usgs.gov/sir/2009/5266/>.)
- Maloney, T.J., ed., 2005, *Quality management system*, U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Open-File Report 2005-1263. (Also available at <http://pubs.usgs.gov/of/2005/1263/>.)
- Martin, J.D., Gilliom, R.J., and Schertz, T.L., 1999, *Summary and evaluation of pesticides in field blanks collected for the National Water-Quality Assessment Program, 1992–95*: U.S. Geological Survey Open-File Report 98-412, 102 p. (Also available at <http://pubs.usgs.gov/of/1998/0412/report.pdf>.)
- Monod, Anne, Sive, B.C., Avino, Pasquale, Chen, Tai, Blake, D.R., and Rowland, F.S., 2001, *Monoaromatic compounds in ambient air of various cities—A focus on correlations between the xylenes and ethylbenzene*: *Atmospheric Environment*, v. 35, p. 135–149.
- Moran, M.J., Zogorski, J.S., and Rowe, B.L., 2006, *Approach to an assessment of volatile organic compounds in the nation's ground water and drinking-water supply wells*: U.S. Geological Survey Open-File Report 2005-1452, 36 p. (Also available at <http://pubs.usgs.gov/of/2005/1452/>.)

- Nowell, L.H., Ludtke, A.S., Mueller, D.K., and Scott, J.C., 2011, Organic contaminants, trace and major elements, and nutrients in water and sediment sampled in response to the Deepwater Horizon oil spill: U.S. Geological Survey Open-File Report 2011-1271, 126 p. (Also available at <http://pubs.usgs.gov/of/2011/1271/>.)
- Olsen, L.D., Fram, M.S., and Belitz, Kenneth, 2010, Review of trace-element field-blank data collected for the California Groundwater Ambient Monitoring and Assessment (GAMA) Program, May 2004–January 2008: U.S. Geological Survey Scientific Investigations Report 2009-5220, 47 p. (Also available at <http://pubs.usgs.gov/sir/2009/5220/>.)
- Pirkey, K.D., and Glodt, S.R., 1998, Quality control at the U.S. Geological Survey National Water Quality Laboratory: U.S. Geological Survey Fact Sheet 026-98, 4 p.
- Thiros, S.A., Bender, D.A., Mueller, D.K., Rose, D.L., Olsen, L.D., Martin, J.D., Bernard, B., and Zogorski, J.S., 2011, Design and evaluation of a field study on the contamination of selected volatile organic compounds and wastewater-indicator compounds in blanks and groundwater samples: U.S. Geological Survey Scientific Investigations Report 2011-5027, 85 p. (Also available at <http://pubs.usgs.gov/sir/2011/5027/>.)
- Toccalino, P.L., Norman, J.E., and Hitt, K.J., 2010, Quality of source water from public-supply wells in the United States, 1993–2007: U.S. Geological Survey Scientific Investigations Report 2010-5024, 126 p. (Also available at <http://pubs.usgs.gov/sir/2010/5024/>.)
- U.S. Environmental Protection Agency, 1985, Intent to cancel registrations of pesticide products containing carbon tetrachloride, carbon disulfide, and ethylene dichloride (effective November 22, 1985): Federal Register, v. 50, p. 42997–42999.
- U.S. Environmental Protection Agency, 1997, Definition and procedure for the determination of the method detection limit—Revision 1.11: U.S. Code of Federal Regulations, Title 40, chap. 1, subchap. D, part 136, appendix B.
- U.S. Environmental Protection Agency, 2009a, 2009 Edition of the drinking water standards and health advisories, accessed January 2011 at <http://water.epa.gov/action/advisories/drinking/upload/dwstandards2009.pdf>.
- U.S. Environmental Protection Agency, 2009b, National primary drinking water regulations, accessed January 2011 at <http://water.epa.gov/drink/contaminants/upload/mcl-2.pdf>.
- U.S. Geological Survey, 2012, NAWQA Data Warehouse Home, Groundwater, accessed August 3, 2012, at http://infotrek.er.usgs.gov/nawqa_queries/jsp/gwmaster.jsp.
- U.S. Geological Survey, variously dated, National field manual for the collection of water-quality data: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A1–A9. (Also available at <http://water.usgs.gov/owq/FieldManual/>.)
- Vitz, Ed, and Martin, R.D., 1991, Toward a standard method for determining waterborne radon: American Association of Radon Scientists and Technologists 1991 Radon Symposium Research Papers, p. 317–339, accessed August 3, 2012, at http://www.aarst.org/proceedings/1991/1991_22_Toward_a_Standard_Method_for_Determining_Waterborne.pdf.
- Whittaker, E.L., Akridge, J.D., and Giovino, J., 1989, Two test procedures for radon in drinking water—Interlaboratory collaborative study: Las Vegas, Nev., U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Office of Research and Development, EPA-600/2-87/082, 45 p.
- Wilde, F.D., ed., 2004, Cleaning of equipment for water sampling (ver. 2.0): U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chap. A3.
- Worthington, C.E., Sebastian, J.E., Gilmore, D.F., and Benfield, R.C., 2007, Investigative report of carbon disulfide contamination in powder-free latex exam gloves, in Tennessee Department of Environment & Conservation, Department of Energy Oversight Division, Environmental Monitoring Report, January through December 2006, p. 233–236.
- Zogorski, J.S., Carter, J.M., Ivahnenko, T., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalino, P.L., 2006, Volatile organic compounds in the Nation's ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p. (Also available at <http://pubs.usgs.gov/circ/circ1292/>.)

Appendix

References for the Data Series Reports for GAMA study units sampled between May 2004 and September 2010 are listed in [table A1](#). Concentrations of the 17 VOCs detected in field or source-solution blanks are listed in [table A2](#) for the 211 field blanks, and in [table A3](#) for the 109 source-solution blanks.

Table A1. Study unit names and Data Series Reports, California GAMA Priority Basin Project, May 2004 through September 2010.

[USGS, U.S. Geological Survey; DS, Data Series]

Study unit	Map code	Data Series Report	Online
Desert study units			
Antelope Valley	D1	Schmitt, S.J., Dawson, B.J., Belitz, K., 2009, Groundwater-quality data in the Antelope Valley study unit, 2008: Results from the California GAMA Program: USGS DS 479, 79 p.	http://pubs.usgs.gov/ds/479/
Mojave	D2	Mathany, T.M., Belitz, K., 2009, Ground-water quality data in the Mojave study unit, 2008: Results from the California GAMA Program: USGS DS 440, 80 p.	http://pubs.usgs.gov/ds/440/
Coachella Valley	D3	Goldrath, D.A., Wright, M.T., Belitz, K., 2009, Ground-water quality data in the Coachella Valley study unit, 2007: Results from the California GAMA Program: USGS DS 373, 70 p.	http://pubs.usgs.gov/ds/373/
Colorado River	D4	Goldrath, D.A., Wright, M.T., Belitz, K., 2010, Groundwater-quality data in the Colorado River study unit, 2007: Results from the California GAMA Program: USGS DS 474, 66 p.	http://pubs.usgs.gov/ds/474/
Central Desert-Borrego	D5	Mathany, T.M., Wright, M.T., Beutzel, B.S., Belitz, K., 2012, Groundwater-quality data in the Borrego Valley, Central Desert, and Low-Use Basins of the Mojave and Sonoran Deserts, 2008–2010: USGS DS 659, 100 p.	http://pubs.usgs.gov/ds/659/
Mountain study units			
Sierra Nevada Regional	M1	Shelton, J.L., Fram, M.S., Munday, C.M., Belitz, K., 2010, Groundwater-quality data for the Sierra Nevada study unit, 2008: Results from the California GAMA Program: USGS DS 534, 106 p.	http://pubs.usgs.gov/ds/534/
Owens-Indian Wells	M2	Densmore, J.N., Fram, M.S., Belitz, K., 2009, Ground-water quality data in the Owens and Indian Wells Valleys study unit, 2006: Results from the California GAMA Program: USGS DS 427, 86 p.	http://pubs.usgs.gov/ds/427/
Southern Sierra Nevada	M3	Fram, M.S., Belitz, K., 2007, Ground-water quality data in the Southern Sierra study unit, 2006—Results from the California GAMA Program: USGS DS 301, 78 p.	http://pubs.usgs.gov/ds/301/
Central Sierra Nevada	M4	Ferrari, M.J., Fram, M.S., Belitz, K., 2008, Ground-water quality in the Central Sierra study unit, California, 2006: Results from the California GAMA Program: USGS DS 335, 60 p.	http://pubs.usgs.gov/ds/335/
Tahoe–Martis	M5	Fram, M.S., Munday, C.M., Belitz, K., 2009, Groundwater quality data for the Tahoe–Martis study unit, 2007: Results from the California GAMA Program: USGS DS 432, 88 p.	http://pubs.usgs.gov/ds/432/
Cascades–Modoc Plateau	M6	Shelton, J.L., Fram, M.S., Belitz, K., 2012, Groundwater-quality data for the Cascades–Modoc Plateau study unit, 2010: Results from the California GAMA Program: USGS DS 688, 126 p.	http://pubs.usgs.gov/ds/688/

Table A1. Study unit names and Data Series Reports, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[USGS, U.S. Geological Survey; DS, Data Series]

Study unit	Map code	Data Series Report	Online
North and Central Coast study units			
Eureka-Crescent City	N1	Mathany, T.M., Dawson, B.J., Shelton, J.L., Belitz, K., 2011, Groundwater quality data in the Northern Coast Ranges study unit, 2009: Results from the California GAMA Program: USGS DS 609, 92 p.	http://pubs.usgs.gov/ds/609/
Ukiah-Clear Lake	N2		
North San Francisco Bay	N3	Kulongoski, J.T., Belitz, K., Dawson, B.J., 2006, Ground-water quality data in the North San Francisco Bay hydrologic provinces, California, 2004: Results from the California Ground-Water Ambient Monitoring Assessment (GAMA) Program: USGS DS 167, 100 p.	http://pubs.usgs.gov/ds/ds167/
San Francisco Bay	N4	Ray, M.C., Kulongoski, J.T., Belitz, K., 2009, Ground-water quality data in the San Francisco Bay study unit, 2007: Results from the California GAMA Program: USGS DS 396, 92 p.	http://pubs.usgs.gov/ds/396/
Livermore-Gilroy-Cuyama	N5	Mathany, T.M., Kulongoski, J.T., Ray, M.C., Belitz, K., 2009, Groundwater quality data in the South Coast Interior Basins study unit, 2008: Results from the California GAMA Program: USGS DS 463, 82 p.	http://pubs.usgs.gov/ds/463/
Monterey-Salinas	N6	Kulongoski, J. T., Belitz, K., 2007, Ground-water quality data in the Monterey Bay and Salinas Valley Basins, California, 2005—Results from the California GAMA Program: USGS DS 258, 84 p.	http://pubs.usgs.gov/ds/2007/258/
Santa Maria-Lompoc	N7	Mathany, T.M., Burton, C.A., Land, M.T., Belitz, K., 2010, Groundwater-quality data in the South Coast Range-Coastal study unit, 2008: Results from the California GAMA Program: USGS DS 504, 106 p.	http://pubs.usgs.gov/ds/504/
South Coast study units			
Santa Clarita-Ventura	S1	Montrella, J., Belitz, K., 2009, Ground-water quality data in the Santa Clara River Valley study unit, 2007: Results from the California GAMA Program: USGS DS 408, 84 p.	http://pubs.usgs.gov/ds/408/
Southern California Coastal Plain	S2	Mathany, T.M., Land, M.T., Belitz, K., 2008, Ground-water quality data in the coastal Los Angeles Basin Study Unit, 2006: Results from the California GAMA Program: USGS DS 387, 98 p.	http://pubs.usgs.gov/ds/387/
San Gabriel-San Fernando	S3	Land, M.T., Belitz, K., 2008, Ground-water quality data in the San Fernando-San Gabriel study unit, 2005—Results from the California GAMA Program: USGS DS 356, 84 p.	http://pubs.usgs.gov/ds/356/
Santa Ana-San Jacinto	S4	Kent, R.H., Belitz, K., 2009, Ground-water quality data in the Upper Santa Ana Watershed Study Unit, November 2006 to March 2007: Results from the California GAMA Program: USGS DS 404, 116 p.	http://pubs.usgs.gov/ds/404/
San Diego area	S5	Wright, M.T., Belitz, K., Burton, C.A., 2005, California GAMA Program—Ground-water quality in the San Diego Drainages hydrogeologic province, California, 2004: USGS DS 129, 91 p.	http://pubs.usgs.gov/ds/2005/129/

Table A1. Study unit names, and Data Series Reports, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[USGS, U.S. Geological Survey; DS, Data Series]

Study unit	Map code	Data Series Report	Online
Central Valley study units			
Northern Sacramento Valley	V1	Bennett, P.A., Bennett, G.L., V. Belitz, K., 2009, Groundwater quality data in the northern Sacramento Valley, 2007: Results from the California GAMA Program: USGS DS 452, 90 p.	http://pubs.usgs.gov/ds/452/
Middle Sacramento Valley	V2	Schmitt, S.J., Fram, M.S., Dawson, B.J., Belitz, K., 2008, Ground-water quality data in the middle Sacramento Valley study unit, 2006—Results from the California GAMA Program: USGS DS 385, 100 p.	http://pubs.usgs.gov/ds/385/
Southern Sacramento Valley	V3	Dawson, B.J., Bennett, G.L., V. Belitz, K., 2008, Ground-water quality data in the Southern Sacramento Valley, California, 2005—Results from the California GAMA Program: USGS DS 285, 93 p.	http://pubs.usgs.gov/ds/285/
Northern San Joaquin	V4	Bennett, G.L., V. Belitz, K., Dawson, B.J., 2006, California GAMA Program—Ground-water quality data in the northern San Joaquin basin study unit, 2005: USGS DS 196, 122 p.	http://pubs.usgs.gov/ds/2006/196/
Central Eastside	V5	Landon, M.K., Belitz, K., 2008, Ground-water quality data in the Central Eastside San Joaquin Basin 2006: Results from the California GAMA Program: USGS DS 325, 88 p.	http://pubs.usgs.gov/ds/325/
Madera-Chowchilla	V6	Shelton, J.L., Fram, M.S., Belitz, K., 2009, Groundwater-quality data for the Madera–Chowchilla study unit, 2008: Results from the California GAMA Program: USGS DS 455, 80 p.	http://pubs.usgs.gov/ds/455/
Southeast San Joaquin	V7	Burton, C.A., Belitz, K., 2008, Ground-water quality data in the southeast San Joaquin Valley, 2005–2006—Results from the California GAMA Program: USGS DS 351, 103 p.	http://pubs.usgs.gov/ds/351/
Kern Basin	V8	Shelton, J.L., Pimentel, I., Fram, M.S., Belitz, K., 2008, Ground-water quality data in the Kern County subbasin study unit, 2006—Results from the California GAMA Program: USGS DS 337, 75 p.	http://pubs.usgs.gov/ds/337/
Western San Joaquin Valley	V9	Mathany, T.M., Landon, M.L., Belitz, K., 2012, Ground-water quality data in the Western San Joaquin Valley Study Unit, 2010: Results from the California GAMA Program: USGS DS 706 (in press)	

Table A2. Volatile organic compounds (VOCs) detected in field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[See [table 1](#) for study unit names. Concentrations are reported here as unrounded values; data for these samples are reported as rounded values in the Data Series reports. **Abbreviations:** SSB, source-solution blank; µg/L, micrograms per liter; —, not detected]

Collection date	Collection time	Paired SSB analyzed	Study unit	Sampling line configuration	Inferred contamination with methanol	Hydrocarbons						
						Benzene (µg/L)	Ethylbenzene (µg/L)	Styrene (µg/L)	1,2,4-Trimethylbenzene (µg/L)	Toluene (µg/L)	<i>m</i> - and <i>p</i> -Xylenes (µg/L)	<i>o</i> -Xylene (µg/L)
06/22/2005	0948	Yes	S3	Long	No	—	0.060	—	—	0.077	0.328	0.120
07/11/2005	1438	Yes	S3	Short	No	—	—	—	—	0.009	—	—
07/19/2005	0908	Yes	N6	Long	No	—	0.028	—	—	0.051	0.118	0.047
07/25/2005	1128	Yes	N6	Short	No	—	—	—	—	—	—	—
08/02/2005	1218	Yes	N6	Long	No	—	—	—	—	0.012	—	—
08/03/2005	0908	Yes	N6	Long	No	—	—	—	0.556	0.036	0.065	—
08/09/2005	1008	Yes	N6	Long	No	—	0.011	—	—	0.048	0.057	0.020
08/10/2005	1208	Yes	N6	Short	No	—	—	—	—	0.194	—	—
08/30/2005	1138	Yes	N6	Short	No	—	—	—	—	0.049	—	—
09/01/2005	1008	Yes	N6	Long	Yes	—	—	—	—	0.022	—	—
09/15/2005	0848	No	N6	Short	No	—	—	—	—	—	—	—
09/19/2005	1148	No	N6	Short	No	—	—	—	—	—	—	—
09/21/2005	1108	Yes	N6	Monitor	Yes	—	—	—	—	0.020	—	—
10/17/2005	1338	Yes	V7	Short	No	—	—	—	—	0.065	—	—
10/18/2005	0808	Yes	V7	Long	No	—	0.022	—	—	0.047	0.126	—
10/25/2005	0928	No	V7	Short	No	—	—	—	—	—	—	—
10/26/2005	1308	Yes	V7	Short	No	—	—	—	—	0.017	—	—
10/31/2005	1038	Yes	V7	Monitor	Yes	—	0.055	—	—	0.232	0.372	0.118
11/15/2005	1108	No	V7	Monitor	No	—	—	—	—	—	—	—
11/16/2005	1038	Yes	V7	Short	No	—	—	—	—	0.016	—	—
11/30/2005	0928	No	V7	Long	No	—	—	—	—	—	—	—
11/30/2005	1208	No	V7	Short	No	—	—	—	—	—	—	—
12/07/2005	1128	No	V7	Short	No	—	—	—	—	—	—	—
12/13/2006	0908	Yes	V7	Short	Yes	—	0.015	—	—	0.053	0.066	0.029
01/10/2006	1008	Yes	V8	Long	Yes	—	0.046	—	—	0.121	0.236	0.104
01/11/2006	1408	Yes	V8	Short	Yes	—	—	—	—	0.015	—	—
01/24/2006	1248	Yes	V8	Short	No	—	—	—	—	0.012	—	—
02/08/2006	1208	Yes	V8	Long	No	—	—	—	—	0.026	—	—
02/09/2006	0908	Yes	V8	Short	No	—	—	—	—	0.015	—	—
03/14/2006	0908	Yes	V5	Monitor	No	—	—	—	—	—	—	—
03/14/2006	9038	Yes	V5	Long	Yes	—	0.016	—	—	—	0.068	0.043
03/29/2006	0938	Yes	V5	Long	Yes	—	—	—	—	—	—	—
04/04/2006	1028	Yes	V5	Short	No	—	—	—	—	0.011	—	—
04/20/2006	0938	No	V5	Short	No	—	—	—	—	—	—	—

Table A2. Volatile organic compounds (VOCs) detected in field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[See [table 1](#) for study unit names. Concentrations are reported here as unrounded values; data for these samples are reported as rounded values in the Data Series reports. **Abbreviations:** SSB, source-solution blank; µg/L, micrograms per liter; —, not detected]

Collection date	Collection time	Paired SSB analyzed	Study unit	Sampling line configuration	Inferred contamination with methanol	Hydrocarbons						
						Benzene (µg/L)	Ethylbenzene (µg/L)	Styrene (µg/L)	1,2,4-Trimethylbenzene (µg/L)	Toluene (µg/L)	<i>m</i> - and <i>p</i> -Xylenes (µg/L)	<i>o</i> -Xylene (µg/L)
11/28/2006	1428	Yes	S4	Short	No	—	—	—	—	0.008	—	—
11/29/2006	0908	Yes	S4	Long	No	—	—	—	0.035	0.010	—	—
12/05/2006	0938	Yes	S4	Long	Yes	—	—	—	—	—	0.021	—
01/23/2007	1218	No	S4	Short	No	—	—	—	—	—	—	—
01/30/2007	1328	Yes	S4	Short	No	—	—	—	—	0.016	—	—
02/07/2007	0848	Yes	S4	Long	No	—	—	—	—	—	—	—
02/08/2007	1208	No	S4	Short	No	—	—	—	—	—	—	—
02/14/2007	1218	No	S4	Short	No	—	—	—	—	—	—	—
02/28/2007	0938	Yes	D3	Long	No	—	—	—	—	0.019	0.033	0.010
03/05/2007	1208	Yes	D3	Short	No	—	0.009	—	—	0.011	0.020	—
03/22/2007	1008	Yes	D3	Short	No	—	—	—	—	0.126	—	—
04/02/2007	0938	No	S1	Short	No	—	—	—	—	—	—	—
04/02/2007	0948	Yes	S1	Long	Yes	—	—	—	—	—	—	—
04/16/2007	0938	Yes	S1	Short	No	—	—	—	—	—	—	—
04/17/2007	0858	Yes	S1	Short	No	—	—	—	—	—	—	—
04/23/2007	0938	No	N4	Short	No	—	—	—	—	—	—	—
04/23/2007	1038	Yes	N4	Long	No	—	—	—	—	0.017	0.053	—
04/30/2007	1258	No	N4	Short	No	—	—	—	—	—	—	—
05/07/2007	1458	Yes	S1	Monitor	No	—	—	—	—	0.040	—	—
05/08/2007	0928	Yes	N4	Monitor	No	—	—	—	—	0.017	—	—
05/21/2007	0908	No	N4	Short	No	—	—	—	—	—	—	—
05/21/2007	1058	Yes	N4	Monitor	No	—	—	—	—	0.012	0.032	—
06/13/2007	0918	Yes	N4	Long	Yes	—	—	—	—	—	—	—
06/19/2007	0908	Yes	N4	Monitor	No	—	—	—	—	0.012	—	—
06/20/2007	1338	No	N4	Short	No	—	—	—	—	—	—	—
06/25/2007	1018	Yes	M5	Long	Yes	—	—	—	—	0.018	—	—
07/12/2007	0958	No	M5	Long	No	—	—	—	—	—	—	—
07/25/2007	0838	No	M5	Long	No	—	—	—	—	—	—	—
08/01/2007	0858	Yes	M5	Long	No	—	—	—	0.121	0.015	—	—
08/01/2007	0908	No	M5	Long	No	—	—	—	—	—	—	—
08/27/2007	1008	Yes	M5	Monitor	No	—	—	—	0.048	—	—	—
08/27/2007	1038	No	N3	Long	No	—	—	—	—	—	—	—
09/13/2007	0738	Yes	M5	Long	No	—	—	—	0.050	—	—	—
10/02/2007	0848	No	V1	Long	No	—	—	—	—	—	—	—
10/03/2007	1038	No	D4	Long	No	—	—	—	—	—	—	—

Table A2. Volatile organic compounds (VOCs) detected in field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[See [table 1](#) for study unit names. Concentrations are reported here as unrounded values; data for these samples are reported as rounded values in the Data Series reports. **Abbreviations:** SSB, source-solution blank; µg/L, micrograms per liter; —, not detected]

Collection date	Collection time	Paired SSB analyzed	Study unit	Sampling line configuration	Inferred contamination with methanol	Hydrocarbons						
						Benzene (µg/L)	Ethylbenzene (µg/L)	Styrene (µg/L)	1,2,4-Trimethylbenzene (µg/L)	Toluene (µg/L)	<i>m</i> - and <i>p</i> -Xylenes (µg/L)	<i>o</i> -Xylene (µg/L)
06/22/2010	1538	Yes	V9	Short	No	—	—	—	—	0.043	—	—
07/14/2010	0908	Yes	M6	Short	No	—	—	—	—	—	—	—
07/21/2010	0908	No	M6	Short	No	—	—	—	—	—	—	—
07/28/2010	0908	No	M6	Short	No	—	—	—	—	—	—	—
08/05/2010	1548	No	M6	Short	No	—	—	—	0.069	—	—	—
08/10/2010	1028	No	M6	Short	No	—	—	—	—	—	—	—
08/24/2010	0918	No	M6	Short	No	—	—	—	—	—	—	—
08/31/2010	0928	No	M6	Short	No	—	—	—	0.079	—	—	—

Table A2. Volatile organic compounds (VOCs) detected in field blanks, California GAMMA Priority Basin Project, May 2004 through September 2010.—Continued

[See [table 1](#) for study unit names. Concentrations are reported here as unrounded values; data for these samples are reported as rounded values in the Data Series reports. **Abbreviations:** SSB, source-solution blank; µg/L, micrograms per liter; —, not detected]

Collection date	Collection time	Solvents							Other VOCs			
		Acetone (µg/L)	2-Butanone (µg/L)	1,1-Dichloroethene (µg/L)	Dichloromethane (µg/L)	Tetrachloroethene (µg/L)	Tetrahydrofuran (µg/L)	Trichloroethene (µg/L)	Bromochloromethane (µg/L)	Carbon disulfide (µg/L)	Chloroform (µg/L)	Trichlorofluoromethane (µg/L)
07/29/2008	1038	—	—	—	—	—	—	—	—	—	—	—
08/06/2008	0928	—	—	—	—	—	—	—	—	—	—	—
08/07/2008	0848	—	—	—	—	—	—	—	—	—	—	—
08/11/2008	0838	—	—	—	—	—	—	—	—	—	—	—
08/18/2008	0848	—	—	—	—	—	—	—	—	—	—	—
08/25/2008	0918	—	—	—	—	—	—	—	—	—	—	—
08/26/2008	1128	—	—	—	—	—	—	—	—	—	—	—
09/15/2008	1048	—	—	—	—	—	—	—	—	—	—	—
09/17/2008	1008	—	—	—	—	—	—	—	—	—	—	—
09/22/2008	0948	—	—	—	—	—	—	—	—	—	—	—
10/09/2008	1048	—	—	—	—	—	—	—	—	—	—	—
10/22/2008	1448	—	—	—	—	—	—	—	—	—	—	—
10/29/2008	1108	—	—	—	—	—	—	—	—	—	0.024	—
12/02/2008	0908	—	—	—	—	—	—	—	—	—	—	—
12/11/2008	1018	—	—	—	—	—	—	—	—	—	—	—
12/16/2008	0908	—	—	—	—	—	—	—	—	—	—	—
06/01/2009	1048	—	—	—	—	—	—	—	—	—	—	—
06/24/2009	0938	—	—	—	—	—	—	—	—	—	—	—
07/14/2009	0948	—	—	—	—	—	—	—	—	—	0.016	—
07/29/2009	1108	—	—	—	—	—	—	—	—	—	—	—
08/17/2009	1008	—	—	—	—	—	—	—	—	0.056	—	—
10/05/2009	1058	—	—	—	—	—	—	—	—	—	—	—
10/20/2009	1218	—	—	—	—	0.021	—	—	—	—	—	—
12/08/2009	1418	—	—	—	—	—	—	—	—	—	—	—
03/03/2010	1028	—	—	—	—	—	—	—	—	—	—	—
03/17/2010	1208	—	—	—	—	—	—	—	—	—	—	—
04/06/2010	1048	—	—	—	—	—	—	—	—	—	—	—
04/14/2010	0808	—	—	—	—	—	—	—	—	—	—	—
05/18/2010	1208	0.327	—	—	—	—	—	—	—	—	—	—
06/07/2010	0908	—	—	—	—	—	—	—	—	—	—	—
06/15/2010	1008	—	—	—	—	—	—	—	—	0.056	—	—

Table A2. Volatile organic compounds (VOCs) detected in field blanks, California GAMA Priority Basin Project, May 2004 through September 2010.—Continued

[See [table 1](#) for study unit names. Concentrations are reported here as unrounded values; data for these samples are reported as rounded values in the Data Series reports. **Abbreviations:** SSB, source-solution blank; µg/L, micrograms per liter; —, not detected]

Collection date	Collection time	Solvents							Other VOCs			
		Acetone (µg/L)	2-Butanone (µg/L)	1,1-Dichloroethene (µg/L)	Dichloromethane (µg/L)	Tetrachloroethene (µg/L)	Tetrahydrofuran (µg/L)	Trichloroethene (µg/L)	Bromochloromethane (µg/L)	Carbon disulfide (µg/L)	Chloroform (µg/L)	Trichlorofluoromethane (µg/L)
06/22/2010	1538	—	—	—	—	—	—	—	—	—	—	—
07/14/2010	0908	—	—	—	—	—	—	—	—	—	—	—
07/21/2010	0908	—	—	—	—	—	—	—	—	—	—	—
07/28/2010	0908	—	—	—	—	—	—	—	—	—	—	—
08/05/2010	1548	—	—	—	—	—	—	—	—	0.092	—	—
08/10/2010	1028	—	—	—	—	—	—	—	—	—	—	—
08/24/2010	0918	—	—	—	—	—	—	—	—	—	—	—
08/31/2010	0928	—	—	—	—	—	—	—	—	0.060	—	—

This page intentionally left blank.

Publishing support provided by the U.S. Geological Survey Science
Publishing Network, Sacramento, Tacoma, and Raleigh Publishing Service Centers

For more information concerning the research in this report, contact the

Director, California Water Science Center

U.S. Geological Survey

6000 J Street, Placer Hall

Sacramento, California 95819

<http://ca.water.usgs.gov>



Printed on recycled paper