Quality-Control Results for Ground-Water and Surface-Water Data, Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

By Cathy Munday *and* Joseph L. Domagalski

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FOREWORD

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

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

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

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

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

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

Robert M. Hirsch
Associate Director for Water

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CONVERSION FACTORS

Multiply	By	To obtain
centimeter (cm)	0.3937	inch
centimeter per year (cm/y)	0.3937	inch per year
cubic meter per day (m^3/d)	0.000811	cubic foot per day
meter (m)	3.281	foot
meter per day (m/d)	3.281	foot per day
square kilometer (km^2)	0.3861	square mile

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

$$°F = (1.8)°C + 32$$

VERTICAL DATUM

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviations and Acronyms

µg/L	microgram per liter
µS/cm	microsiemen per centimeter
mg/L	milligram per liter

DCP/AES	direct current plasma-atomic emission spectrometry
DOC	dissolved organic carbon
GC/MS	gas chromatography/mass spectrometry
HPLC	high performance liquid chromatography
ICP/AES	inductively coupled plasma/atomic emission spectrometry
ICP/MS	inductively coupled plasma/mass spectrometry
MTBE	methyl *tert*-butyl ether
NAWQA	National Water-Quality Assessment (Program)
NWQL	National Water Quality Laboratory
RPD	relative percentage difference
SOC	suspended organic carbon
USGS	U.S. Geological Survey
VOC	volatile organic compound

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ABSTRACT

Evaluating the extent that bias and variability affect the interpretation of ground- and surface-water data is necessary to meet the objectives of the National Water-Quality Assessment (NAWQA) Program. Quality-control samples used to evaluate the bias and variability include annual equipment blanks, field blanks, field matrix spikes, surrogates, and replicates. This report contains quality-control results for the constituents critical to the ground- and surface-water components of the Sacramento River Basin study unit of the NAWQA Program. A critical constituent is one that was detected frequently (more than 50 percent of the time in blank samples), was detected at amounts exceeding water-quality standards or goals, or was important for the interpretation of water-quality data. Quality-control samples were collected along with ground- and surface-water samples during the high intensity phase (cycle 1) of the Sacramento River Basin NAWQA beginning early in 1996 and ending in 1998.

Ground-water field blanks indicated contamination of varying levels of significance when compared with concentrations detected in environmental ground-water samples for ammonia, dissolved organic carbon, aluminum, and copper. Concentrations of aluminum in surface-water field blanks were significant when compared with environmental samples. Field blank samples collected for pesticide and volatile organic compound analyses revealed no contamination in either ground- or surface-water samples that would effect the interpretation of environmental data, with the possible exception of the volatile organic compound trichloromethane (chloroform) in ground water.

Replicate samples for ground water and surface water indicate that variability resulting from sample collection, processing, and analysis was generally low. Some of the larger maximum relative percentage differences calculated for replicate samples occurred between samples having lowest absolute concentration differences and(or) values near the reporting limit.

Surrogate recoveries for pesticides analyzed by gas chromatography/mass spectrometry (GC/MS), pesticides analyzed by high performance liquid chromatography (HPLC), and volatile organic compounds in ground- and surface-water samples were within the acceptable limits of 70 to 130 percent and median recovery values between 82 and 113 percent. The recovery percentages for surrogate compounds analyzed by HPLC had the highest standard deviation, 20 percent for ground-water samples and 16 percent for surface-water samples, and the lowest median values, 82 percent for ground-water samples and 91 percent for surface-water samples. Results were consistent with the recovery results described for the analytical methods.

Field matrix spike recoveries for pesticide compounds analyzed using GC/MS in ground- and surface-water samples were comparable with published recovery data. Recoveries of carbofuran, a critical constituent in ground- and surface-water studies, and desethyl atrazine, a critical constituent in the ground-water study,

could not be calculated because of problems with the analytical method. Recoveries of pesticides analyzed using HPLC in ground- and surface-water samples were generally low and comparable with published recovery data. Other methodological problems for HPLC analytes included nondetection of the spike compounds and estimated values of spike concentrations.

Recovery of field matrix spikes for volatile organic compounds generally were within the acceptable range, 70 and 130 percent for both ground- and surface-water samples, and median recoveries from 62 to 127 percent. High or low recoveries could be related to errors in the field, such as double spiking or using spike solution past its expiration date, rather than problems during analysis. The methodological changes in the field spike protocol during the course of the Sacramento River Basin study, which included decreasing the amount of spike solution added to volatile organic compound samples and changing the method of spike delivery, had no apparent effect on recovery results.

INTRODUCTION

The U.S. Geological Survey (USGS) began the National Water-Quality Assessment (NAWQA) Program in 1991. The goals of the NAWQA Program are to describe water-quality conditions and trends in a representative part of the nation's surface- and ground-water resources, and to identify the natural and human factors affecting the quality of these resources (Leahy and others, 1990).

In 1994, the Sacramento River Basin in northern California was among the NAWQA study units selected for implementation of the first cycle of the program. Three ground-water studies were undertaken between 1996 and 1998: a study of randomly selected wells in the southeast Sacramento Valley aquifer referred to as the Sacramento River Basin subunit survey (hereinafter referred to as subunit survey), an agricultural land-use study in rice growing areas, and an urban land-use study (fig. 1). The surface-water study began in February 1996 and ended in April 1998 (fig. 2). Design details for ground- and surface-water studies for the NAWQA Program, including the Sacramento River Basin, are presented in Gilliom and others (1995).

As part of the NAWQA Program, surface- and ground-water samples were collected and analyzed for selected chemical constituents according to published protocols [Koterba and others (1995) for ground water; Shelton (1994) and Mueller and others (1997) for surface water]. Dissolved organic carbon (DOC) samples of ground water and surface water were collected using NAWQA protocol and processed using methods described by Alpers and others (2000). A study of mercury in surface water was incorporated into the Sacramento River Basin study unit plan. Collection and analysis of mercury samples in surface water followed protocols of the USGS Mercury Research Laboratory in Middleton, Wis. (Olson and DeWild, 1999). The water-quality and quality-control data collected during the Sacramento River Basin study area are given in Domagalski and others (2000). Additional infomation regarding the surface water quality study in the Sacramento River Basin during 1996–1998 can be found in Domagalski and Dileanis (2000). Also available are interpretive analyses of pesticides in surface water (Domagalski, 2001) and analyses of ground-water data collected during the subuint survey (Dawson, 2001a) and the agricultural land-use study (Dawson, 2001b).

Data obtained from field quality-control samples are used to estimate the bias and variability that result from sample collection, processing, and analysis. Bias refers to a systematic, consistent positive or negative deviation from the known or true value. Variability is random error in independent measurements, the result of repeated application of the process under specified conditions. Estimates of bias and variability were based on quality-control sample analysis for constituents considered critical to this study (table 1).

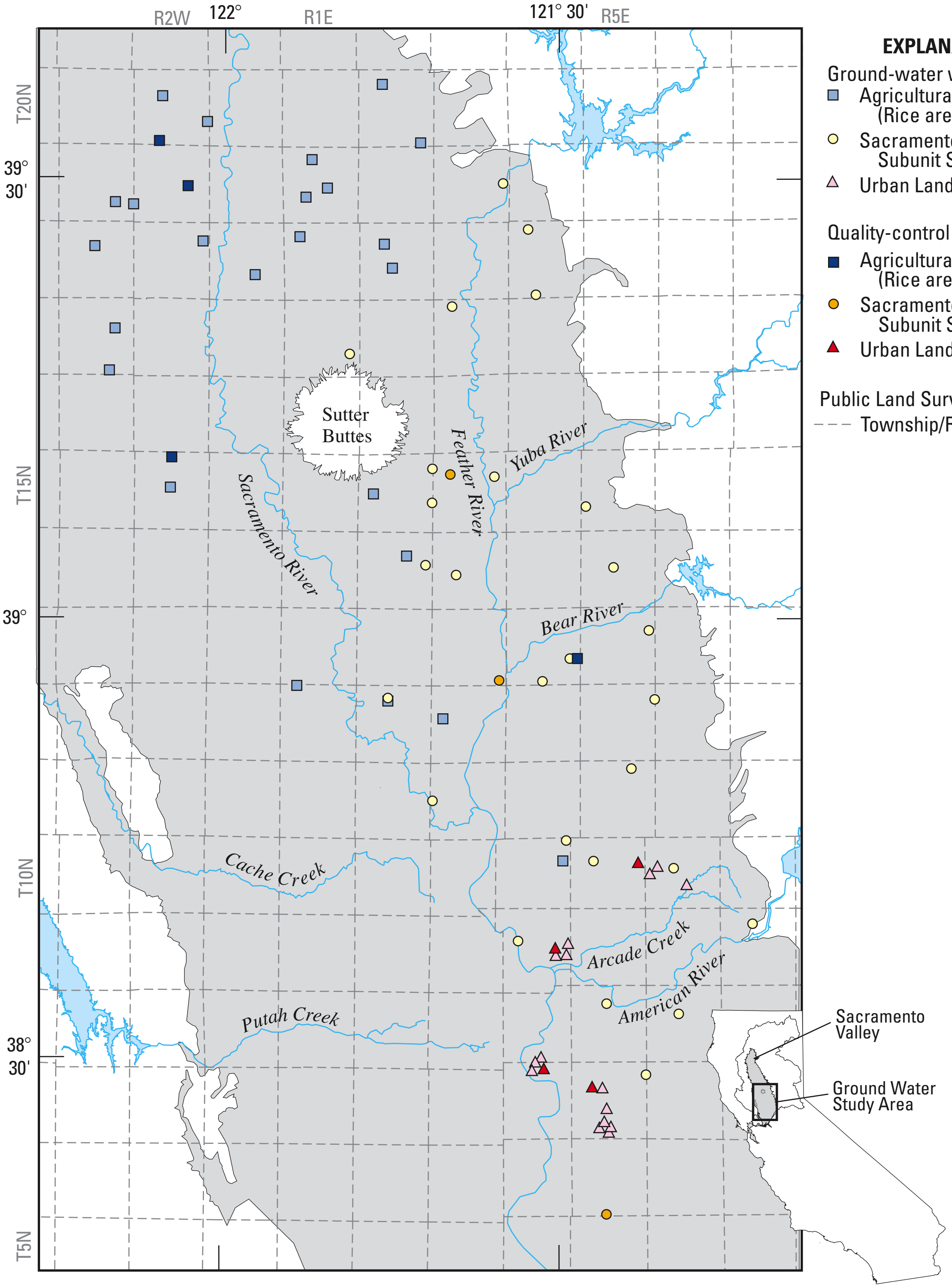

Figure 1. National Water-Quality Assessment ground-water sampling sites in the Sacramento River Basin, California.

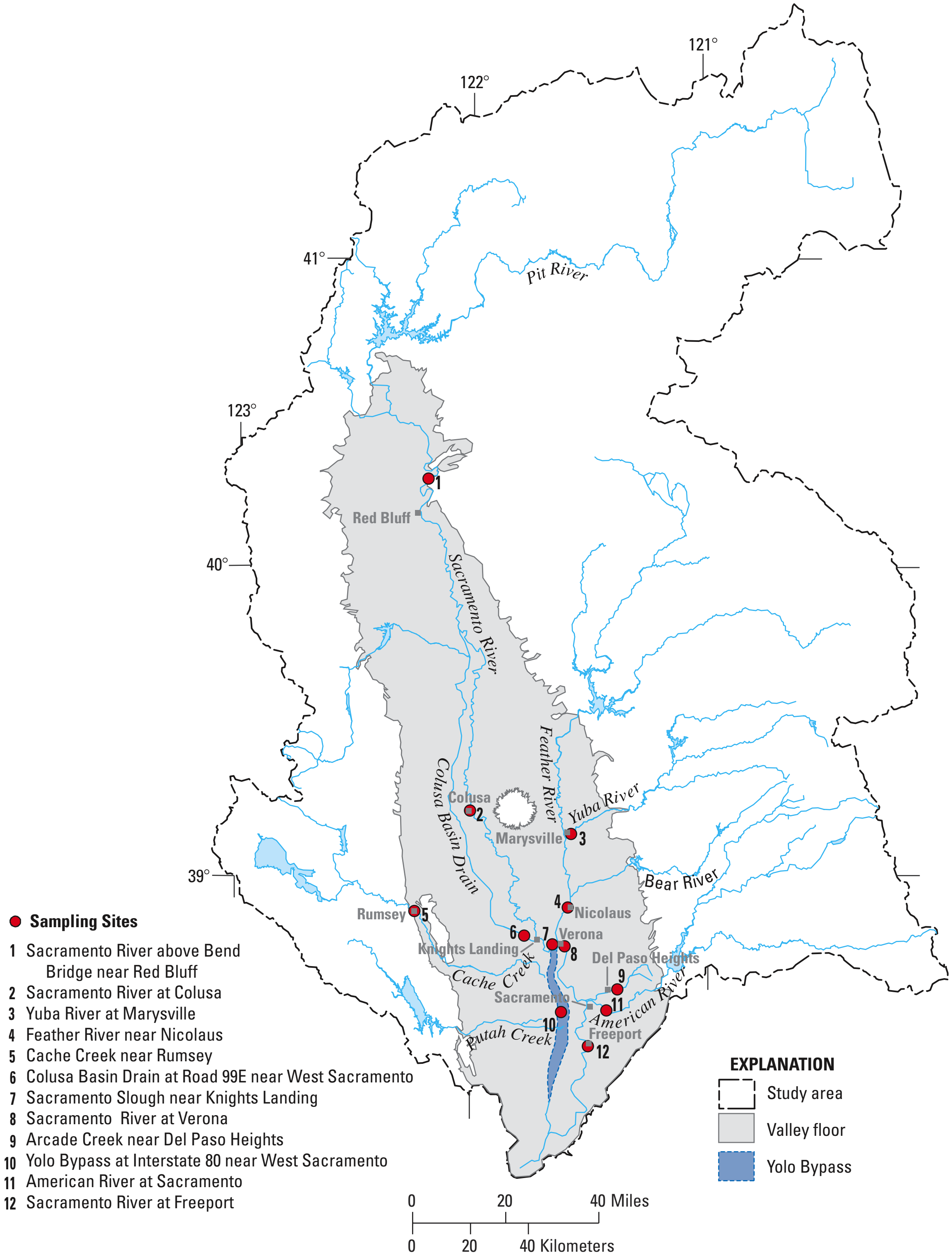

Figure 2. National Water-Quality Assessment surface-water sampling sites in the Sacramento River Basin, California.

Table 1. Critical constituents in the analysis and interpretation of ground- and surface-water data, Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[A constituent was determined to be critical if it was detected in more than 50 percent of the blank samples, was detected in environmental samples at amounts exceeding water-quality standards or goals, or was otherwise important to the interpretation of water-quality data. GC/MS, gas chromatography/mass spectrometry; HPLC, high performance liquid chromatography]

GROUND WATER

Major ions
Calcium, magnesium, sodium, potassium, chloride, sulfate, boron, silica

Dissolved organic carbon

Nutrients
Nitrite plus nitrate, ammonia

Trace Elements
Arsenic, aluminum, copper, chromium, cadmium, barium

Pesticides analyzed by GC/MS
Atrazine, carbofuran, desethyl atrazine, molinate, simazine, thiobencarb

Pesticides analyzed by HPLC
Bentazon, carbofuran

Volatile organic compounds
Trichloromethane (chloroform), methyl *tert*-butyl ether, trichloroethene

SURFACE WATER

Major ions
Calcium, magnesium, sodium, potassium, chloride, sulfate, silica

Dissolved organic carbon/suspended organic carbon

Nutrients
Nitrite plus nitrate, phosphorus (total phosphorus, dissolved phosphorus, and orthophosphorus)

Trace elements
Aluminum, chromium, copper, manganese, nickel, zinc, iron

Mercury
Total mercury, methylmercury

Pesticides analyzed by GC/MS
Chlorpyrifos, carbofuran, diazinon, metolachlor, molinate, simazine, thiobencarb

Pesticides analyzed by HPLC
Carbofuran, diuron

Volatile organic compounds
Methyl *tert*-butyl ether

A critical constituent is one that was detected frequently (greater than 50 percent of blank samples), was detected in environmental samples at amounts exceeding water-quality standards or goals, or was important to the interpretation of water-quality data. For example, DOC is a critical constituent because it can react with chlorine to form disinfection byproducts, most commonly trihalomethanes, which are dominated by trichloromethane (chloroform) (Thurman, 1985). Trihalomethanes are of concern to human heath and are regulated under the U.S. Environmental Protection Agency's drinking water standards and health advisories (U.S. Environmental Protection Agency, 2000). Nitrate also is considered a critical constituent because of its potential affect on human health when standards are exceeded. Phosphorus is an important component in aquatic health, whereas mercury has a potential affect on human health and is of particular interest in the Sacramento Valley because of its wide occurrence and distribution both from natural sources and as a remnant of gold and mercury mining. Mercury and the pesticides diazinon and chlorpyrifos are critical constituents because they are being considered for future regulation. The pesticides molinate, thiobencarb, and carbofuran are critical constituents because of ongoing regulatory controls.

This report describes and interprets field level quality-control data collected in the Sacramento River Basin during water years 1996–1998. Analysis and interpretation of laboratory quality-control results and performance evaluation for the USGS National Water Quality Laboratory (NWQL) is available online (U.S. Geological Survey, accessed October 8, 2001). The quality assurance manual for the USGS Wisconsin District Office's Mercury Laboratory (U.S. Geological Survey, accessed October 15, 2001) provides information on laboratory quality-control results.

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QUALITY-CONTROL SAMPLE TYPES

Three types of field quality-control samples are routinely collected during NAWQA studies: blanks (field, source solution, ambient, and trip), field matrix spikes, and field replicates. Blanks and field matrix spikes estimate bias, and field replicates estimate variability. Equipment blanks, required annually, are collected in a laboratory setting rather than in the field to evaluate contamination introduced by sample-collection and sample-processing equipment. The number, type, and sites for quality-control sampling were chosen in accordance with published protocols (Koterba and others, 1995; Mueller and others, 1997). Information about the quality-control samples collected during the Sacramento River Basin study (appendix A-1 through A-7) include sample types, quantities, dates, and locations.

Surrogate compounds, which are added to all environmental, spike, and blank samples analyzed for pesticides and volatile organic compounds (VOC), help detect sample handling problems throughout the analytical processes. Surrogate compounds are similar in chemical properties to some of the target analytes, but are not expected in the environmental samples. Surrogates also can be used to evaluate matrix effects on analyte recovery when compared with recovery in reagent spike samples (Fitzgerald, 1997).

Blank Samples

A blank sample consists of water that has undetectable concentrations of measured constituents. Inorganic-grade deionized water used for the major ion, nutrient, and trace element blank samples was from the USGS Water Quality and Research Laboratory in Ocala, Fla. Pesticide-grade water for pesticide and DOC blank samples, and volatile-grade water for VOC blank samples, was from the NWQL in Denver, Colo., (Mueller and others, 1997). Blank water for mercury analysis was from the USGS Mercury Research Laboratory in Middleton, Wis. Blank samples were evaluated to determine any bias due to contamination introduced during sample collection, processing, shipping, or analysis. Once collected, the blank samples were processed and analyzed as a typical environmental water-quality sample.

Field Blanks

Field blanks, which were prepared at environmental sampling sites, help ensure that equipment had been adequately cleaned prior to sample collection. Field blanks also verify that onsite sample collection and processing, and sample handling and transport, had not introduced contamination (Mueller and others, 1997). For the surface-water study, blank water was passed through sampling and processing equipment at an environmental sampling site after the equipment had been used and field cleaned. The blank samples were collected in a manner similar to environmental water-quality sample collection procedures. For the ground-water study, the pump was placed in a clean 1,500-mL glass graduated cylinder. Blank water was then poured into the cylinder and pumped through the field-cleaned equipment. Field blank samples were collected onsite following ground-water sample collection and field cleaning.

Equipment Blanks

Equipment blanks evaluate contamination introduced during sample collection or by the processing equipment (Mueller and others, 1997) and confirm the effectiveness of cleaning procedures used prior to sampling. Blank water was poured through clean equipment routinely used for environmental sample collection and processing. The equipment blanks were collected and processed in the USGS California District laboratory, at the field office, or in the mobile laboratory and, therefore, were not subject to the ambient conditions associated with the environmental sampling sites.

Trip Blanks

Trip blanks identify contamination that might occur during sample transport, interim storage, and analysis rather than during sample collection and processing in the field (Mueller and others, 1997). The blanks were submitted for VOC analysis. The trip blanks were prepared by the NWQL using VOC grade water, shipped to Sacramento, and transported unopened to the field with other VOC bottles. They were then shipped back to NWQL with the environmental VOC samples for analysis.

Source Solution Blanks

Source solution blanks verify that blank water is contaminant-free prior to use as a field blank. The blanks were collected in a clean environment by placing the stock solution directly into the sample container.

Ambient Blanks

Ambient blanks identify any contaminants in the sampling and processing areas that might affect the environmental samples. One ambient blank sample was submitted for analysis of VOCs. The blank was collected by placing the stock solution directly into the VOC vials and exposing the open vials to the laboratory environment when the equipment blank was collected and processed.

Spiked Samples

Spiked samples measure bias caused by analyte degradation or sample matrix interference, or test the effects of sample matrix on the analyses of specific constituent groups. A spike is an environmental sample fortified with a known concentration of selected analytes. Pesticide and VOC samples were spiked and submitted for analysis. Ground-water pesticide samples, ground-water VOC samples, and surface-water VOC samples were collected as sequential replicate sample sets. One of the samples was fortified with analysis-specific spike solution from the NWQL, and the other was designated as the environmental sample. Routinely, a third ground-water VOC sample was collected, spiked, and submitted as a spike replicate. Surface-water samples submitted for pesticide analysis were prepared by dividing a single volume of water into two subsamples. One of those subsamples was fortified with a spike solution appropriate to either the gas chromatography/mass spectrometry (GC/MS) or the high performance liquid chromatography (HPLC) analytical method and submitted to the NWQL along with the unfortified environmental subsample. (Mueller and others, 1997; Domagalski and others, 2000).

Replicate Samples

Replicates measure the variability in water samples during sample collection, processing, and analysis. The samples are collected and processed so that the samples are virtually identical in composition. Split replicates were collected for surface-water pesticide samples and prepared by dividing a single volume of water into two subsamples. Sequential replicates, multiple samples collected at the same location, were collected for ground-water pesticide and VOC samples and for surface-water VOC samples.

Analysis

The NWQL analyzed all ground- and surface-water samples for the Sacramento River Basin study, with the exception of total mercury and methylmercury analyses (table 2). The comprehensive quality-control program in place at the NWQL is outlined in Pirkey and Glodt (1998). Analytical data from the NWQL are presented in the following ways:

1. A measured value.
2. A value preceded by a “<” (less than) annotation; this means the analyte was not detected at the laboratory at the method reporting limit.
3. A “U-delete” comment means that the value was determined to be invalid at the laboratory level and deleted from the database.
4. An “E” preceding a value for a pesticide or VOC compound is used to signify that a measured concentration is estimated by the NWQL (Connor and others, 1998; Childress and others, 1999).

When analyzing for VOCs, laboratory quality-control procedures may include the dilution of samples prior to analysis. To minimize instrument contamination, samples are diluted when a selected compound is present at a concentration greater than the highest calibration standard. Samples that foam when shaken also will be diluted to prevent instrument malfunction; all of the VOC samples collected at the Arcade Creek site were diluted at the laboratory because of foaming. Samples containing hydrogen sulfide also should be diluted to prevent damage to analytical instruments. Analytical results from diluted samples are reported with raised reporting limits (Connor and others, 1998).

The USGS Mercury Research Laboratory conducted total mercury and methylmercury analyses. However, at the time of testing during this study, the analytical methods for total and methylmercury had not yet received approval by the U.S. Environmental Protection Agency and, therefore, data must be considered provisional. Information about the laboratory's quality-assurance plan is available online (U.S. Geological Survey, accessed October 15, 2001).

Table 2. Analytical methods by constituent category used during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[N, nitrogen; P, phosphorus; CVAFS, cold vapor atomic fluorescence spectrometry]

Constituent category	Method of Analysis	Reference
Inorganic compounds		
Boron	Inductively coupled plasma-atomic emission spectrometry	Struzeski and others, 1996
Bromide	Colorimetry, automated-segmented flow, fluroscein	Fishman and Friedman, 1989
Chloride, sulfate	Ion chromatography	Fishman and Friedman, 1989
Fluoride	Colorimetry, automated-segmented flow, ion-selective electrode	Fishman and Friedman, 1989
Potassium	Atomic absorption, flame	Fishman and Friedman, 1989
Iron, magnesium, silica, sodium, calcium	Inductively coupled plasma	Fishman, 1993
Trace metals		
Arsenic and selenium	Graphite furnace-atomic absorption spectrometry	Jones and Garbarino, 1999
Cobalt, cadmium, nickel, beryllium, antimony, silver, barium, uranium (natural), zinc, molybdenum, lead, aluminum, chromium, copper, manganese	Inductively coupled plasma/mass spectrometry	Faires, 1993
Low level blank sample analysis		
Inorganic compounds: Major ions and trace metals		
Arsenic, selenium (added to analysis)	See Trace metals above - Arsenic and selenium were added as “lab codes” and analyzed under the “trace metals” methodology	Jones and Garbarino, 1999
Zinc, chromium, beryllium, barium, manganese, molybdenum, cadmium, cobalt, silver, antimony, copper, uranium (natural), lead	Inductively coupled plasma/mass spectrometry	Faires, 1993
Magnesium, silica, iron, sodium, boron, calcium	Inductively coupled plasma	Fishman, 1993
Aluminum, nickel	Inductively coupled plasma/mass spectrometry	Faires, 1993
Nutrient compounds		
Phosphorus (total)	Low level total phosphorus, filtered	U.S. Environmental Protection Agency, 1993
Phosphorus, phosphate, dissolved phosphorus, orthophosphorus	Colorimetry, automated-segmented flow, phosphomolybdate, P, orthophosphate as P	Fishman, 1993
Nitrogen, ammonia + organic nitrogen	Colorimetry, automated-segmented flow, Microkjeldahl digestion, N, ammonia + organic nitrogen as N	Fishman, 1993
Nitrogen, nitrite	Colorimetry, automated-segmented flow, N, nitrite as N,	Fishman, 1993
Nitrogen, ammonia	Colorimetry, automated-segmented flow, salicylate-hypochlorite, N, ammonia	Fishman, 1993

Table 2. Analytical methods by constituent category used during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998 —Continued

Constituent category	Method of Analysis	Reference
Nitrogen, nitrite + nitrate	Colorimetry, automated-segmented flow, cadmium reduction– diazotization, N, nitrite + nitrate, N	Fishman, 1993
Dissolved organic carbon		
Organic carbon	Unacidified uv-promoted persulfate oxidation and infrared spectrometry	Brenton and Arnett, 1993
Pesticides	Gas chromatography/mass spectrometry with selected ion monitoring	Zaugg and others, 1995
Pesticide (acetechlor only)	Automated solid-phase extraction and gas chromatography with mass-selective detection	Lindley and others, 1996
Pesticides	High-performance liquid chromatography	Werner and others, 1996
Volatile organic compounds	Gas chromatography/mass spectrometry	Connor and others, 1998
Total mercury and methylmercury		
Total mercury	U.S. Environmental Protection Agency Method 1631:Mercury in water by oxidation, purge and trap, and CVAFS with modifications	Olson and DeWild, 1999
Methylmercury	U.S. Environmental Protection Agency Method 1630: Methylmercury in water by distillation, aqueous ethylation, purge and trap, and CVAFS with minor modifications	Olson and DeWild, 1999

QUALITY-ASSURANCE AND QUALITY-CONTROL DESIGN

Ground Water

The ground water study had three components: a subunit survey, an agricultural land-use study, and an urban land-use study. For the subunit survey, 31 shallow, domestic wells were sampled from May through August 1996; most were privately owned. Wells were selected randomly in both agricultural and urban settings. Equipment blank samples were collected and processed at the field office prior to the initial environmental sampling. In addition, quality-control samples were collected at 3 of the 31 environmental sites.

For the agricultural land-use study, 30 shallow observation wells were drilled at randomly selected sites in the rice growing regions of the Sacramento Valley, of which 28 were sampled from July through October 1997. Prior to sampling the first environmental site, equipment blank samples were collected and processed at the field office. Quality-control samples also were collected at 4 of the 28 environmental sampling sites.

To assess the effects of recent urbanization on shallow ground water, 19 shallow observation wells were drilled in the Sacramento metropolitan area at sites randomly chosen in areas developed between 5 to 25 years ago. The wells were sampled from June through August 1998. Equipment blank samples were collected and processed at the field office prior to sampling the urban wells. Quality-control samples were collected from 4 of the 19 urban wells.

The collection and processing of all ground-water quality-control samples followed published protocols (Koterba and others, 1995). Corrective action was taken when quality-control samples indicated the introduction of systematic contamination during sample collection and(or) processing. Environmental and quality-control data for the Sacramento River Basin study are presented in Domagalski and others (2000).

Blank Samples

Results of field blank sample analyses for critical constituents in the ground-water study are given in table 3.

Major Ions

Two equipment blanks and 11 field blanks (table 3) were submitted for analysis of major ions and trace metals between May 23, 1996, and August 19, 1998. Sodium, potassium, chloride, and sulfate were undetectable in all equipment and field blank samples, but were detected in every environmental sample. Of the two equipment blanks, calcium was detected in both, magnesium was detected in neither, and silica was detected in one. Calcium, magnesium, and silica were detected in fewer than 50 percent of the field blank samples (table 3), but were detected in all 78 environmental samples (Domagalski and others, 2000). At least 2 orders of magnitude separate the highest concentration of calcium, magnesium, or silica in the blank samples from the lowest value reported in ground-water samples; therefore, there is no indication of bias in the analytical method that would affect data for these major ions.

Boron was detected in 5 of the 11 (45 percent) field blanks, but in neither of the 2 equipment blanks (table 3). The method reporting limit changed three times during the study. Until June 1, 1996, the direct current plasma/atomic emission spectrometry (DCP/AES) method was used, which has a reporting limit of less than 10 µg/L. After that date, the inductively coupled plasma/atomic emission spectrometry (ICP/AES) technique was used, which has a reporting limit of less than 4 µg/L (U.S. Geological Survey, 1996). Finally, the systematic evaluation of reporting levels for NWQL methods resulted in a change of the minimum reporting level for boron analysis by ICP/AES from 4 to 16 µg/L, effective December 22, 1997 (U.S. Geological Survey, 1997).

Boron was detected in all 78 of the environmental samples (Domagalski and others, 2000); concentrations ranged from 13 to 1,790 µg/L. Boxplot analysis (fig. 3) and the Mann–Whitney statistical test of the median values were used to compare blank and environmental sample results. Boxplots indicate no significant overlap between blank and environmental data. The Mann–Whitney statistical test also shows that the medians of the environmental and blank data are dissimilar (p=0.0001). Thus, the environmental data can be used without qualification.

Table 3. Detections of critical constituents in ground-water field blank samples, Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[All data are given in concentration units. Changes in the method reporting limit (MRL) occurred during the course of the data collecton for some of the analyses as indicated by multiple values. Number of significant figures do not reflect analytical MRLs. D, detections expressed as percentages; maximum, maximum observed value or concentration; median, median observed value or concentration; N, nitrogen. mg/L, milligram per liter; µg/L, microgram per liter; <, less than; E-value, laboratory estimated result; NA, not applicable]

Constituent or compound	Number of field blank samples	D	Concentration		
			MRL(s)	Maximum	Median
Major ions					
Calcium (mg/L)	11	36	0.011	0.062	<0.020
Magnesium (mg/L)	11	18	0.010, 0.004	0.016	<0.005
Sodium (mg/L)	11	0	0.20, 0.10		
Potassium (mg/L)	11	0	0.1		
Chloride (mg/L)	11	0	0.1		
Sulfate (mg/L)	11	0	0.1		
Silica (mg/L)	11	45	0.01, 0.1	0.045	0.04
Boron (µg/L)	11	45	4, 10, 16	11	7.80
Dissolved Organic Carbon (mg/L as carbon)	11	91	0.1	1.6	0.30
Nutrients					
Ammonia (mg/L as N)	11	64	0.015, 0.020	0.098	0.025
Nitrite (NO_2) + nitrate (NO_3) (mg/L as N)	11	36	0.05	0.085	<0.050
Trace Elements					
Arsenic (µg/L)	8	0	1		
Aluminum (µg/L)	8	100	0.3	4	3.55
Copper (µg/L)	8	62	0.2	0.65	0.28
Chromium (µg/L)	8	25	0.2	0.89	<0.20
Cadmium (µg/L)	8	12	0.3	0.42	<0.30
Barium (µg/L)	8	75	0.2	0.60	0.28
Pesticides					
Analyzed by gas chromatography/mass spectrometry					
Atrazine (µg/L)	11	NA	0.001	1 E-value only	
Carbofuran (µg/L)	11	0	0.003		
Desethyl atrazine (µg/L)	11	0	0.002		
Molinate (µg/L)	11	0	0.004		
Simazine (µg/L)	11	0	0.005		
Thiobencarb (µg/L)	11	0	0.002		
Analyzed by high performance liquid chromatography					
Bentazon (µg/L)	11	NA	0.014	1 E-value only	
Carbofuran (µg/L)	11	0	0.0280; 0.120		
Volatile Organic Compounds					
Trichloromethane (Chloroform) (µg/L)	7	NA	0.052	2 nondetects; 5 E-values	
Methyl *tert*-butyl ether (µg/L)	7	0	0.1, 0.112, 0.166		
Trichloroethene (µg/L)	7	0	0.050, 0.038		

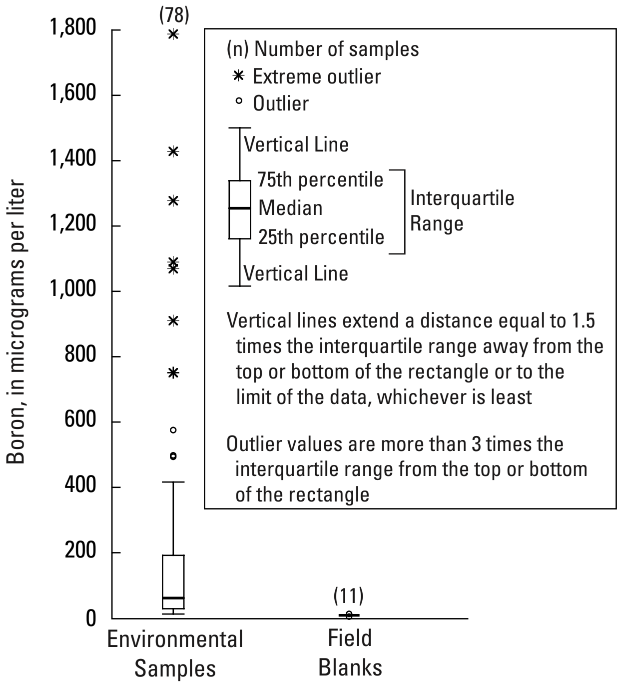

Figure 3. Boxplots of boron concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

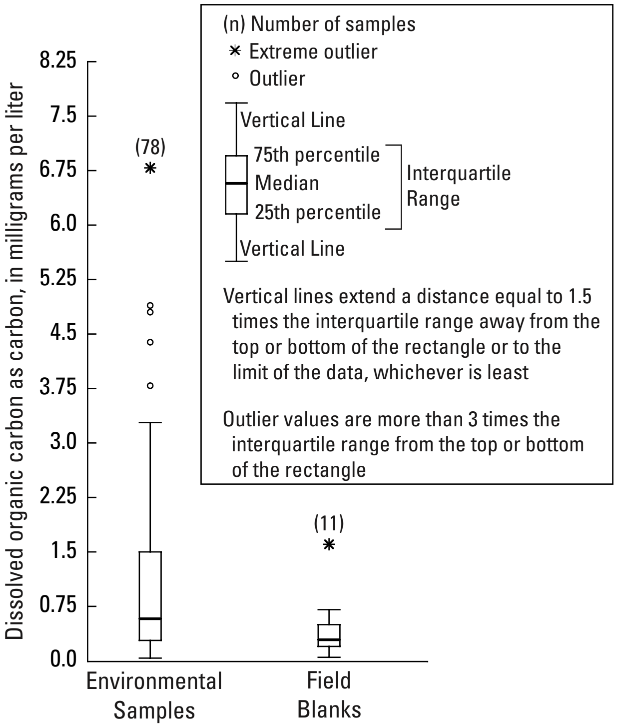

Figure 4. Boxplots of dissolved organic carbon concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

The boron in blank samples probably was solubilized from the borosilicate glass ampoules that contained the nitric acid used to preserve water samples. To alleviate this problem, beginning in September 1998, nitric acid has been dispensed in polypropylene vials (U.S. Geological Survey, 1998).

Dissolved Organic Carbon

Of the 28 blank samples submitted for DOC analysis, 3 were equipment blanks and 11 were field blanks. A source solution blank was submitted with each blank, for a total of 28 samples. DOC was not detected at the reporting limit of 0.1 mg/L (as carbon) in 10 of the 11 source solution blanks. One source solution blank had a reportable detection of 0.2 mg/L, just above the reporting limit. These results effectively eliminate organic-free water as the source of contamination and show the laboratory analytical method to be free of positive bias. However, DOC was detected in 10 of the 11 (91 percent) field blanks (table 3) at concentrations from 0.2 to 1.6 mg/L, and in 74 of the 78 environmental samples (Domagalski and others, 2000), with more than 50 percent of detections in the environmental samples at 0.6 mg/L or less. Boxplot analysis of the ground-water environmental samples and the field blanks (fig. 4) reveals overlap between the data sets (p=0.0411, Mann–Whitney statistical test).

Although the data make the majority of environmental DOC values suspect, qualifying the environmental data may not be necessary when taking field procedures into consideration. DOC contamination in the field blank samples is likely due to cleaning methods that used other organic constituents to prevent carryover contamination between sampling sites. The soap and methanol used to clean sampling equipment could have contributed DOC in detectable amounts. Sampling equipment, including about 61 m of tubing, was cleaned according to NAWQA protocol at each site following ground-water sampling. After field cleaning, if a field blank was to be collected, 4 liters of organic-free water was pumped through the lines to flush the tubing of any residual cleaning media. It is possible that more organic-free water is needed to effectively purge cleaning media residue. While other sources of contamination, including processing equipment, cannot be completely eliminated, review of these data suggests that blank sample collection procedures rather than processing is the source of contamination. Insufficient purging is not considered an issue with environmental samples because a minimum of three well casing volumes of water are pumped through the sampling lines and tubing prior to sample collection. Although the environmental data for DOC were not qualified or deleted from the database, and the source of contamination in blank samples has probably been identifed, environmental data should be used with caution in interpretive analyses; for example, Dawson (2001a, p. 9) did not use DOC data for analytical purposes and stated, “DOC in field blanks indicate that ground-water sample concentrations measured below 1.8 mg/L in this study may be partly or entirely due to sample contamination introduced during sample collection or analysis” (Dawson, 2001b, p. 17).

Nutrients

Fourteen blank samples—3 equipment blanks and 11 field blank samples—were analyzed for nutrients, including ammonia and nitrite plus nitrate. The frequency and magnitude of ammonia detections in blanks indicate contamination that would affect the interpretation of ground-water data. Ammonia was detected in 2 of the 3 equipment blanks and in 7 of the 11 (64 percent) field blanks. The median concentration of ammonia in field blank samples is greater than the concentration reported for 46 of the 78 (about 59 percent) ground-water samples (Domagalski and others, 2000). The boxplot comparison of the analytical results for ammonia in the ground-water environmental samples and field blanks is shown on figure 5. The Mann–Whitney statistical test results (p=0.9630) indicate that there is no significant difference between the environmental and blank data sets. There are temporal and land-use pattern variations (table 4) in the number of detections for ammonia in both the ground-water samples and field blanks, with the highest number of detections reported during the urban study of 1998. The source of ammonia contamination has not been determined. Environmental data for ammonia were not deleted from the database; however, the quality-control data indicate that ammonia in the environmental samples may be due wholly, or in part, to contamination as indicated by the ‘V’ code applied to those values in the database. Because of contamination in the blank samples, ground-water ammonia data were not used in either report published by Dawson (2001a,b).

Analysis of blank samples for nitrite plus nitrate ($NO_2 + NO_3$) indicates an absence of systematic contamination. Although nitrite plus nitrate was detected in 4 of the 11 (36 percent) field blanks at levels ranging from 0.05 to 0.085 mg/L (table 3), it was in 66 of the 78 (85 percent) environmental samples at concentrations ranging from 0.06 to 12 mg/L. The majority of those environmental detections (43 of 78) were at levels exceeding 0.86 mg/L (Domagalski and others, 2000). Because nitrite plus nitrate was detected in fewer than 50 percent of the blank samples, neither a boxplot nor statistical analyses were applied to the data. Environmental data may be used without qualification.

Trace Elements

Blank samples were submitted for arsenic analysis by graphite furnace-atomic absorption (Jones and Garbarino, 1999) at the same method reporting limit as the environmental samples (1.0 µg/L). Aluminum, cadmium, copper, chromium, and barium samples were analyzed by an inductively coupled plasma/mass spectrometry (ICP/MS) method used specifically to detect low levels of contamination in blank samples (Faires, 1993); low-level analysis was not available for arsenic. During the subunit survey of 1996, an equipment blank was submitted, but no environmental trace element samples were collected. During the rice land-use study of 1997 and the urban land-use study of 1998, equipment blanks and field blank samples were submitted. Ground-water samples were submitted for trace metal analysis during the 1997 and 1998 studies. The method reporting limits for low-level blank sample analysis were 3 to 5 times lower than those for environmental samples analyzed by ICP/MS (Faires, 1993). The method reporting limit comparison between ICP/MS environmental sample analysis and ICP/MS low-level blank sample analysis is given in table 5.

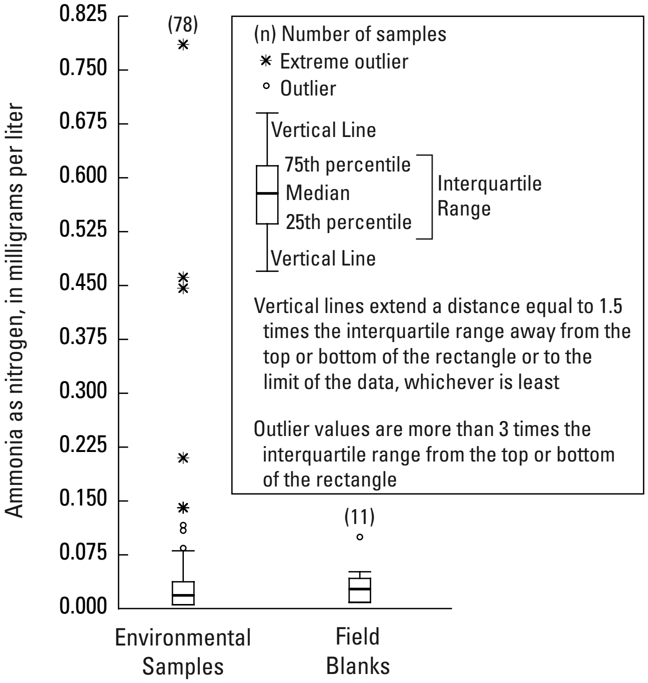

Figure 5. Boxplots of ammonia concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

Table 4. Comparison of ammonia detections in ground-water samples and field blanks by study type, Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[mg/L, milligram per liter]

Study (method reporting limit)	Ground-water samples			Field blanks		
	Number of samples	Number of detections	Detections in percent	Number of samples	Number of detections	Detections in percent
1996 Subunit Survey (0.015 mg/L)	31	24	74	5	3	60
1997 Agricultural Land-Use Study [rice areas (0.015 mg/L)]	28	10	36	5	1	20
1998 Urban Land-Use Study (0.02 mg/L)	19	17	89	5	5	100

Table 5. Method reporting limit comparison between inductively coupled plasma/mass spectrometry analysis of ground-water environmental samples and low-level analysis of blank samples for selected constituents, Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[All reporting limits are in microgram per liter (µg/L). Blank samples were analyzed for arsenic at 1.0 µg/L. NA, low-level analysis not available for arsenic blanks]

	Environmental samples	Blank samples
Arsenic	1.0	NA
Aluminum	1.0	0.3
Copper	1.0	0.2
Chromium	1.0	0.2
Cadmium	1.0	0.3
Barium	1.0	0.2

Arsenic

Arsenic (1 µg/L detection limit) was not detected in the blank samples (table 3), but was detected in 75 of 78 ground water samples at concentrations ranging from 1 to 62 µg/L (Domagalski and others, 2000). Environmental data may be used without qualification.

Aluminum

Ground-water samples may have been affected by aluminum contamination, which was detected in the field blank samples. All eight of the field blank samples (table 3) had aluminum at concentrations ranging from 2.5 to 4 µg/L. Ground-water samples were not analyzed for aluminum in 1996 during the subunit survey, but were tested for aluminum and other trace elements during the rice land-use and urban land-use studies undertaken in 1997 and 1998, respectively. All ground-water samples contained aluminum ranging from 2.2 to 10.37 µg/L, with 17 of 47 (36 percent) of the detections below 4 µg/L and within the range of the blank sample results (Domagalski and others, 2000).

A comparison of aluminum data for field blanks and environmental samples is shown in figure 6. Although the boxplot shows some overlap between the environmental and blank data sets, the Mann–Whitney statistical test (*p*=0.0269) shows the medians of the data sets to be dissimilar. The aluminum detected in field blank and ground-water samples may have been solubilized from glass ampoules containing the nitric acid preservative used in sample processing (U.S. Geological Survey, 1998); nitric acid preservative has been dispensed from polypropylene vials since September 1998 to eliminate the solubilization problem. Environmental data for aluminum were not deleted from the database; however, the quality-control data indicate that some concentrations of aluminum may be due wholly, or in part, to contamination as indicated by the ‘V’ code applied to those values in the database. Because of contamination in the blank samples, ground-water aluminum data were not used by Dawson (2001a) for interpretive analysis.

Copper

Low-level analysis detected copper (0.2 µg/L detection level) in 5 of the 8 (62 percent) field blank samples at concentrations ranging from 0.28 to 0.65 µg/L (table 3). Environmental samples contained copper concentrations (1.0 µg/L detection level) ranging from 1.0 to 8.6 µg/L for 16 wells, and nondetections for the remaining 31 (Domagalski and others, 2000). Although the source of copper contamination in the blank samples is unknown, detections of copper in blank samples do not appear to affect the validity of the environmental data. Results of the Mann–Whitney statistical test show that the medians of the environmental and blank data are dissimilar (*p*=0.0090). A boxplot comparison of field blanks and environmental samples data for copper is shown in figure 7. Environmental data for copper were not qualified or deleted from the database, and environmental data can be considered without qualification.

Chromium

Blank sample analysis does not provide evidence of systematic chromium contamination that affected ground-water samples. Chromium was detected in 2 of the 8 (25 percent) field blank samples (table 3) at 0.72 and 0.89 µg/L, but was in 46 of the 47 environmental samples at levels ranging from 1.8 to 16 µg/L (Domagalski and others, 2000). Environmental data for chromium can be considered without qualification.

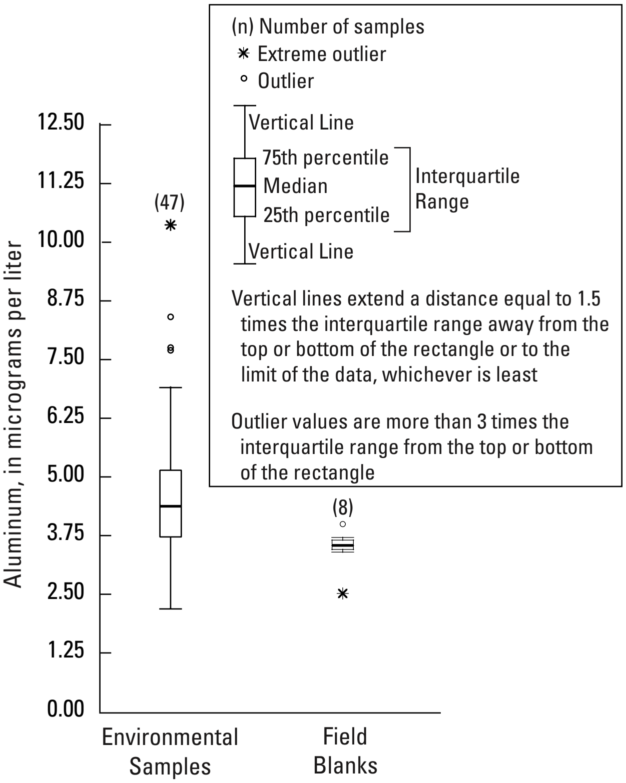

Figure 6. Boxplots of aluminum concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

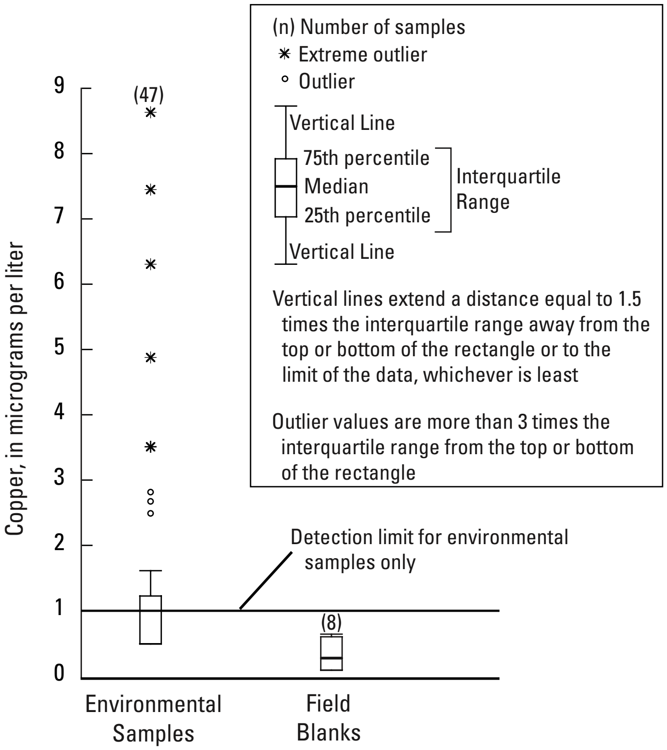

Figure 7. Boxplots of copper concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

Cadmium

Blank samples do not provide evidence of cadmium contamination affecting ground-water samples. Cadmium was detected in only 1 of the 8 (12 percent) blank samples at 0.42 µg/L and in 3 of the 47 environmental samples at concentrations ranging from 6.1 to 7.4 µg/L (Domagalski and others, 2000). Environmental data for cadmium can be considered without qualification.

Barium

Barium was reported in 1 of the 3 equipment blanks and in 6 of the 8 (75 percent) field blanks (table 3) at concentrations ranging from 0.22 to 0.6 µg/L. Barium was detected in all ground-water samples at concentrations ranging from 10 to 5,050 µg/L (Domagalski and others, 2000). Because there is more than an order of magnitude between the highest barium concentration in a field blank and the lowest barium concentration in an environmental sample, ground-water barium data can be considered unaffected by contamination and useful without qualification.

Pesticides in Filtered Water Analyzed by Gas Chromatography/Mass Spectrometry

Three equipment blanks and 11 field blanks were submitted to the NWQL for analysis. Blank sample analysis provided no evidence of contamination for any of the 47 analytes, including the critical constituents atrazine, carbofuran, desethyl atrazine, molinate, simazine, and thiobencarb. Data can be used without qualification.

Pesticides in Filtered Water Analyzed by High Performance Liquid Chromatography

Three equipment blanks and 11 field blanks were analyzed for 39 pesticide compounds by the NWQL. Blank sample analysis provided no evidence of contamination for any of the compounds, including the critical constituents bentazon and carbofuran. Data can be used without qualification.

Volatile Organic Compounds

Ground-water samples were analyzed for 85 VOCs during the subunit survey of 1996 and the urban study of 1998. The 12 blank samples included 2 equipment blanks, 2 trip blanks, 1 ambient blank, and 7 field blanks. Critical constituents include trichloromethane (chloroform), methyl *tert*-butyl ether (MTBE), and trichloroethene.

Trichloromethane was reported as a low-level estimated value (E0.030 to E0.050 µg/L) in the equipment blank, ambient blank, and the three field blank samples submitted in 1996 during the subunit survey. Only the trip blank from 1996 had a nondetection result for trichloromethane. The equipment blank collected prior to the urban land-use study of 1998 had the highest trichloromethane concentration (0.334 µg/L) (Domagalski and others, 2000) and the only nonestimated detection reported among any of the blank samples. Two of the four subsequent field blanks submitted during the 1998 study had estimated low-level concentrations of 0.064 and 0.006 µg/L. Trichloromethane was not detected in the other two field blanks or in the trip blank sample during the 1998 study.

The most likely source of trichloromethane in blank samples is the blank water itself or residual contamination from chlorinated tap water used during the initial rinse of the sampling lines. Blank water is suspected because, although it was not labeled at the time, nitrogen-purged VOC blank water has a recommended shelf life of only 2 weeks from the nitrogen purge date. The water used in the equipment blank submitted on June 5, 1998, which had the highest reported trichloromethane concentration in a blank sample at 0.334 µg/L, was laboratory certified as nitrogen purged on March 27, 1998.

Contamination from tap water also is suspected because, following the review of the June 5, 1998, equipment blank results and subsequent elimination of tap water from the cleaning protocol, trichloromethane was not detected in field blank samples submitted on July 22 or August 19, 1998. An estimated trichloromethane value was reported for the blank sample submitted on August 6, 1998, but at an estimated concentration of 0.006 µg/L it was the lowest value reported for any blank or environmental sample collected during the subunit survey of 1996 or urban land-use study of 1998.

Boxplot comparison (fig. 8) of the field blanks and environmental samples show an overlap in concentration between the two data sets, and the Mann–Whitney statistical test shows similarity between their median values (p=0.4852). The effect of this contamination on trichloromethane concentrations in environmental samples is unclear, however, because the compound was estimated or detected in only 3 of the 31 subunit survey wells at concentrations ranging from 0.03 (estimated) to 1.1µg/L (Domagalski and others, 2000). In addition, of the 19 urban land-use wells sampled, five trichloromethane detections ranged from 0.119 to 5.05 µg/L and estimated values for 11 wells ranged from 0.010 to 0.14 µg/L. Although environmental data was not qualified, the data should be used with caution.

There were no detections of MTBE or trichloroethene in any of the blank samples. Reporting limits changed for both of these compounds and for trichloromethane during the course of the study, as indicated by different "less-than" values in the ground-water blank sample data (Domagalski and others, 2000). Environmental data for both trichlorethene and MTBE can be used without qualification.

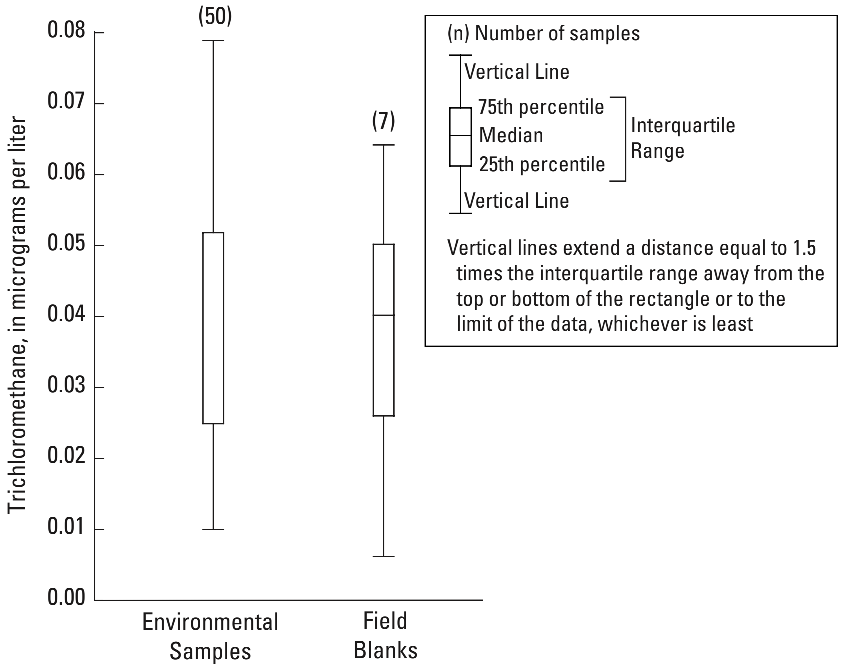

Figure 8. Boxplots of trichloromethane (chloroform) concentration in ground-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998. Outliers are not shown.

Replicate Samples

The variability of ground-water replicate samples in the Sacramento River Basin NAWQA, represented as the relative percentage difference (RPD) and as the absolute difference in concentration units, is given in table 6. The RPD is calculated as the absolute difference between values of the replicate pair divided by their average value and multiplied by 100. For calculation purposes, if a less-than value result was paired with a detection, 50 percent of the method reporting limit value was used in place of the less-than value. The number of detections varied among the critical constituents; for example, arsenic was detected in all 8 replicate sets (16 samples), whereas cadmium replicate results included only 3 detections (16 samples).

The median RPD for critical constituents in ground water ranged from 0 percent for calcium, magnesium, sodium, sulfate, silica, ammonia, arsenic, and cadmium to 17 percent for aluminum. The maximum RPD ranged from 3.4 percent for silica (detections in all samples) to 170 percent for cadmium. Other constituents that have maximum RPDs greater than 100 include boron (detections in all samples), nitrite plus nitrate (1 set of nondetects and 1 set with only one detection out of 11 sets), copper (4 sets of nondetects and 1 split set out of 8 sample sets), and chromium (detections in all samples) (table 6).

The maximum RPD of 170 percent for cadmium (table 6) was based on only three detections out of 16 samples: One replicate pair had cadmium concentrations of 7.1 and 1.3 µg/L, and another pair had 6.1 µg/L of cadmium detected in the environmental sample, but no detectable concentration in the replicate (Domagalski and others, 2000). The reason for the variability of the ground-water cadmium data is unknown because so few detections of the compound were in both the replicate sample sets and in the environmental ground-water samples. Cadmium samples were not submitted during the subunit survey of 1996. Cadmium was detected in only 3 of the 28 samples submitted during the rice land-use study of 1997, but was not in any of the 19 samples submitted during the urban land-use study of 1998 (Domagalski and others, 2000).

Table 6. Variability of ground-water replicate samples collected during the Sacramento River Basin National Water-Quality Assessment, 1996–1998

[If one of the 2 results for a replicate pair was reported as a "<" (less than the reporting limit) value, a value equal to 1/2 the reporting limit was used to complete the calculations used for this table. Number of significant figures do not reflect analytical method reporting levels. NWQL, National Water Quality Laboratory. mg/L, milligram per liter; µg/L, microgram per liter]

Analyte (number of detections)	Number of sets	Relative difference, in percent			Difference, in concentration units		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Major ions							
Calcium (mg/L) (detections in all samples)	11	0	6.5	0	0	10	0
Magnesium (mg/L) (detections in all samples)	11	0	6.9	0	0	2	0
Sodium (mg/L) (detections in all samples)	11	0	6.9	0	0	3	0
Potassium (mg/L) (detections in all samples)	11	0	18	3.1	0	0.2	0.02
Chloride (mg/L) (detections in all samples)	11	0	30	1.7	0	31	1
Sulfate (mg/L) (detections in all samples)	11	0	18	0	0	300	0
Silica (mg/L) (detections in all samples)	11	0	3.4	0	0	2	0
Boron (µg/L) (detections in all samples)	11	0	109	4.7	0	65	3
Dissolved organic carbon (mg/L as carbon) (detections in all samples)	11	0	67	10.7	0	0.2	0.07
Nutrients							
Ammonia (mg/L as nitrogen) (4 sets of nondetects out of 11 sample sets)	11	0	30	0	0	0.07	0.01
Nitrite (NO_2) + nitrate (NO_3) (detections in mg/L as nitrogen) [1 set of nondetects; 1 split set (1 of the 2 samples has a nondetect result)]	11	0	117	0.5	0	1	0.02
Trace elements							
Arsenic (µg/L) (detections in all samples)	8	0	5.7	0	0	2	0
Aluminum (µg/L) (detections in all samples)	8	2.5	88	17	0.1	4.9	0.95
Copper (detections in µg/L) [4 sets of nondetects; 1 split set (1 of the 2 samples has a nondetect result)]	8	0	150	3.6	0	3	0.05
Chromium (µg/L) (detections in all samples)	8	0	114	7.5	0	8.7	0.5
Cadmium (detections in µg/L) [6 sets of nondetects; 1 split set (1 of the 2 samples has a nondetect result)]	8	0	170	0	0	5.8	0
Barium (detections in all samples in µg/L)	8	0	8	2.7	0	13	1.5
Pesticides analyzed by gas chromatography/mass spectrometry	No replicates collected						

Table 6. Variability of ground-water replicate samples collected during the Sacramento River Basin National Water-Quality Assessment, 1996–1998—Continued

Analyte (number of detections)	Number of sets	Relative difference, in percent			Difference, in concentration units		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Pesticides analyzed by high performance liquid chromatography	No replicates collected						
Volatile Organic Compounds	No replicates collected						
Alkalinity as $CaCO_3$ (calcium carbonate): Comparison of field alkalinity values (mg/L)							
Sacramento River Basin Subunit Survey 1996	29	0	10	1	0	9	2
Rice Land-Use Study 1997	20	0	19	1	0	87	3.5
Urban Land-Use Study 1998	19	0	15	1	0	17	3
Specific conductance: NWQL values versus field values (microsiemens per centimeter at 25 degrees Celsius)							
Sacramento River Basin Subunit Survey 1996	31	0	17	1	0	57	6
Rice Land-Use Study 1997	28	0	10	3	0	1200	34
Urban Land-Use Study 1998	19	0	10	2	1	320	10

The maximum RPD of 109 percent for boron (table 6) is the result of one anomalous sample set in which boron was reported at 27 µg/L in the environmental sample and 92 µg/L in the replicate (Domagalski and others, 2000). While the reason for the anomalous result is unknown, the majority of the boron replicate samples indicate that environmental data for boron are not affected by variability in the analytical method. The median RPD calculated for boron in the 11 replicate sample sets was 4.7 percent.

Similarly, the maximum RPD of 117 percent for nitrite plus nitrate (table 6) is not indicative of variability in the analytical method that would affect the interpretation of environmental data. The replicate set resulting in this RPD had a nondetection result for nitrite plus nitrate in the environmental sample and a detection of 0.095 mg/L in the replicate sample (Domagalski and others, 2000). To apply the relative percentage difference calculation, 50 percent of the method reporting limit (0.025 mg/L) was used as the environmental sample value. The result was the largest RPD value for nitrite plus nitrate between samples whose difference in concentration units was only 0.07 mg/L and where one of the two values assigned was based on a nondetection result. The median RPD calculated for nitrate plus nitrite in the 11 replicate sample sets was 0.5 percent.

Like nitrite plus nitrate, the maximum RPD of 150 percent for copper (table 6) is the result of a detectable concentration in the environmental sample paired with a nondetection result for the replicate sample. With a median RPD value of 3.6 percent, there is not enough evidence of variability to indicate that the environmental data interpretation would be affected.

The maximum RPD of 114 percent for chromium (table 6) was between an environmental and replicate sample set with detection results of 12 and 3.3 µg/L, respectively (Domagalski and others, 2000). The cause of the variation between these two values is unknown. It is uncertain whether this level of variability in the analytical method would affect interpretation of the chromium environmental data.

The median difference in concentrations of critical constituents ranged from 0 for calcium, magnesium, sodium, sulfate, silica, arsenic and cadmium to 3 µg/L for boron. Arsenic had the lowest maximum difference (2 µg/L) in concentration. The highest maximum difference in concentration, sulfate at 300 mg/L, was between an environmental and replicate sample that also had the highest sulfate concentrations detected during the ground-water study (1,500 and 1,800 mg/L, respectively). The corresponding RPD of the samples was 18 percent. The other 10 replicate pairs show no difference in sulfate concentration for 6 of the sets, differences of between 0.1 and 1 mg/L for 3 sets, and a difference of 10 mg/L for one replicate set (220 and 230 mg/L) (Domagalski and others, 2000).

Although not listed on the critical constituents table, replicate data also are included on table 6 for alkalinity and specific conductance. These data may facilitate the interpretation of other analytical data collected during this study.

Surrogate Recovery

Three surrogate compounds were added to each of the 103 ground-water samples analyzed for pesticides by GC/MS. Median recoveries were 100, 113, and 96 percent for diazinon-d_{10}, terbuthylazine, and alpha HCH-d_6 (hexachlorocyclohexane), respectively (table 7). The surrogate 4-bromo-3,5-dimethylphenyl-*n*-methylcarbamate (BDMC) was added to 103 ground-water samples submitted for pesticide analysis by the HPLC method. For the 103 samples analyzed by HPLC, 83 had reportable results with a median recovery of 82 percent. The laboratory deleted 3 of the surrogate recoveries from the database and reported 17 others as estimates. In addition, the surrogate toluic acid was deleted from the HPLC procedure because of variability in performance (Werner and others, 1996). Three surrogates added to VOC samples analyzed by GC/MS—1,2,-dichloroethane-d_4, *p*-bromofluorobenzene, and toluene-d_8—had median recoveries of 104, 84, and 98 percent, respectively.

Table 7. Recovery of surrogate compounds in Sacramento River Basin, California, ground-water samples, 1996–1998

[The minimum, maximum, and median values are in percentage recovered. HPLC, high performance liquid chromatography]

	Samples	Minimum	Maximum	Median	Standard deviation
GROUND-WATER PESTICIDES					
Pesticides analyzed by gas chromatography/mass spectrometry					
Diazinon-d_{10}	103	66	132	100	14
Terbuthylazine	103	69	141	113	15
alpha HCH-d_6 (hexachlorocyclohexane)	103	59	117	96	12
Pesticides analyzed by HPLC					
4-Bromo-3,5-dimethylphenyl-*n*-methylcarbamate (BDMC)	[1]83	33	148	82	20
GROUND-WATER VOLATILE ORGANIC COMPOUNDS					
1,2,-Dichloroethane-d_4	74	80	153	104	12
p-Bromofluorobenzene	74	72	104	84	8
Toluene-d_8	74	93	107	98	2

[1] 103 samples were analyzed by HPLC; however, 17 estimated (E) values and 3 laboratory deleted resultes were omitted from these calculations.

Although all three of the analyses returned median recovery results between 80 and 120 percent, within the recovery limits considered acceptable for this report (70 to 130 percent), the variable recoveries of surrogates analyzed using HPLC illustrate the tendency toward negatively biased and inconsistent results. However, the affect on the interpretation of data for environmental ground-water samples analyzed by HPLC probably is negligible. Of the 78 ground-water samples submitted for analysis of 39 compounds, only 4 compounds were detected. The majority of ground-water samples analyzed for 48 pesticides by GC/MS also resulted in nondetections (Domagalski and others, 2000). Although environmental pesticide data are not being qualified on the basis of the surrogate recovery results, the data should be used with caution; the lack of detection of some compounds may be due to poor analytical performance.

Field Spiked Samples

Pesticide and VOC samples were spiked and submitted for analysis; percentage of spike recovered was calculated according to instructions provided by the NWQL (Mueller and others, 1997). The corresponding environmental sample submitted with each spiked sample was used to determine detectable background concentrations of the spiked analytes. If an analyte was detected in the environmental sample, the concentration was subtracted from the concentration result of the spiked sample to provide the adjusted values for calculating the spike recovery percentages (tables 8 through 12).

Pesticides in Filtered Water Analyzed by Gas Chromatography/Mass Spectrometry

Ten environmental samples spiked with 47 compounds were analyzed for selected pesticides by GC/MS (table 8). Mean recoveries for all compounds with reported detection values (not estimates) were within the acceptable limits of 70 to 130 percent, except for permethrin and *p,p′*-DDE, which had the lowest mean recoveries at 57 and 64 percent, respectively. Similar results for permethrin and *p,p′*-DDE were obtained during the method of analysis study done at the laboratory (Zaugg and others, 1995).

Table 8. Recovery of field matrix spikes for pesticides from Sacramento River Basin, California, ground-water samples analyzed by gas chromatography/mass spectrometry, 1996–1998

[Recovery data are given in percentages. Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated values. Critical constituents are in **bold**. No. samples, number of samples where recovery values could be calculated]

Compound	No. samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
2,6-Diethylaniline	9	80	105	86	90
Acetochlor	9	73	132	113	106
Alachlor	10	73	133	109	107
Atrazine	**10**	**66**	**120**	**96**	**97**
Methyl azinphos	0	Estimated values			
Benfluralin	9	44	104	73	70
Butylate	9	85	121	94	98
Carbaryl	0	Estimated values			
Carbofuran	**0**	**Estimated values**			
Chlorpyrifos	10	66	103	89	87
Cyanazine	10	46	146	111	107
DCPA	10	87	122	99	101
Desethyl atrazine	**0**	**Estimated values**			
Diazinon	10	62	113	103	97
Dieldrin	10	72	142	94	101
Disulfoton	10	56	100	85	85
EPTC	9	83	110	92	94
Ethalfluralin	9	56	122	91	85
Ethoprop	10	82	130	94	98
Fonofos	10	69	136	93	98
Lindane	10	72	135	92	95
Linuron	9	94	166	128	130
Malathion	10	43	140	99	96
Metolachlor	10	73	143	113	112
Metribuzin	10	53	122	85	86
Molinate	**9**	**85**	**106**	**92**	**94**
Napropamide	10	61	121	103	95
Parathion	10	56	135	96	98
Methyl parathion	9	43	120	87	86
Pebulate	9	83	105	92	93
Pendimethalin	10	45	141	67	74
Phorate	10	54	105	88	85
Prometon	10	73	122	95	99
Propachlor	9	74	112	103	98
Propanil	10	83	136	104	107
Propargite	10	62	128	101	96
Pronamide	10	70	117	98	98
Simazine	**10**	**60**	**121**	**95**	**95**
Tebuthiuron	8	64	159	108	111
Terbacil	0	Estimated values			
Terbufos	10	53	113	75	78
Thiobencarb	**10**	**79**	**128**	**106**	**105**
Triallate	10	81	109	99	97
Trifluralin	9	50	116	77	75
Alpha-BHC	10	72	115	94	94
Permethrin	9	33	97	46	57
p,p'-DDE	10	47	84	63	64

Of the compounds considered critical for this study (table 1), recovery of carbofuran and desethyl atrazine could not be evaluated because all results were estimated (table 8). These compounds performed poorly during the methods of analysis study (Zaugg and others, 1995), and results were reported as estimates for the reagent, environmental ground-water, and environmental surface-water samples tested. Table 9 gives the recovery data for the critical constituents atrazine, molinate, simazine, and thiobencarb. During this study, all four of these compounds performed better (mean recoveries from 94 to 105 percent for ground-water samples) than during the methods of analysis study (Zaugg and others, 1995), which reported mean spike recoveries from 73 to 82 percent for ground-water samples and from 76 to 89 percent for reagent (blank) water samples. Although environmental data are not being qualified owing to spike recovery results, the data should be used with caution; the lack of detection of some compounds may be due to poor analytical performance. [See interpretive analyses of spike recovery data for the subunit survey (Dawson, 2001a) and the agricultural land-use study (Dawson, 2001b).]

Pesticides in Filtered Water Analyzed by High Performance Liquid Chromatography

Seven ground-water samples were spiked with 39 compounds and analyzed for pesticides by HPLC (table 10). Mean recoveries for compounds that had reported detections (not estimated) ranged from 3 percent for chloramben (1 recovery value) to 87 percent recovery for fluometuron (7 recovery values) and propham (4 recovery values). The pesticides DNOC and dichlobenil had only estimated values and could not be included in the spike recovery calculations. Chlorothalonil also was omitted from the summary because of estimated or undetectable concentrations in the spiked samples.

The HPLC methods of analysis study (Werner and others, 1996) indicates a tendency toward negatively biased results. The mean recovery for 30 field matrix spike compounds in 81 samples “spiked at 1.0 µg/L” ranged from 9 percent for chlorothalonil to 101 percent for propham. Twenty-five of the 30 compounds in the field matrix spike solution had mean recoveries of 65 percent or less, and 10 of the 30 compounds had mean recoveries less than 50 percent. Bentazon and carbofuran, two critical constituents, had comparable low recovery results in both the HPLC methods study and in the Sacramento River Basin study (table 11).

Table 9. Spike recovery data for selected pesticides from Sacramento River Basin, California, ground-water samples, 1996–1998, and recovery and precision data published in the methods of analysis report

[Recovery and precision data are in Zaugg and others (1995). Spike recovery data are in percentages. Pesticides added to water samples at 0.1 microgram per liter]

Compound	Sacramento River Basin				Methods of analysis report			
	Ground water (10 samples)				Ground water (7 samples)		Reagent (blank) water (6 samples)	
	Minimum	Maximum	Median	Mean	Mean	Relative standard deviation (percent)	Mean	Relative standard deviation (percent)
Atrazine	66	120	96	97	79	3	89	6
Molinate	85	106	92	94	82	4	82	3
Simazine	60	121	95	95	73	4	76	3
Thiobencarb	79	128	106	105	74	4	85	3

Table 10. Recovery of field matrix spikes for pesticides from Sacramento River Basin, California, ground-water samples analyzed by high performance liquid chromatography, 1996–1998

[Recovery data are in percentages. Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated values. Critical constituents are in **bold**. Some spike solutions did not contain all compounds. No. samples, number of samples where recovery values could be calculated]

Compound	No. samples	Spike recovery in percent			
		Minimum	Maximun	Median	Mean
2,4,5-T	7	14	98	76	69
2,4-D	6	60	71	68	67
2,4-DB	7	44	78	64	64
Silvex	7	63	87	72	72
3-Hydroxycarbofuran	5	52	77	62	64
DNOC	0	Estimated values			
Acifluorfen	6	41	75	70	66
Aldicarb	2	51	53	52	52
Aldicarb sulfone	3	8	41	22	24
Aldicarb sulfoxide	4	27	82	51	53
Bentazon	**7**	**55**	**71**	**63**	**63**
Bromacil	7	62	93	72	75
Bromoxynil	7	63	77	71	70
Carbaryl	6	63	82	68	70
Carbofuran	**6**	**66**	**99**	**76**	**78**
Chloramben	1	3	3	3	3
Chlorothalonil	0	Estimated values			
Clopyralid	5	8	57	41	38
Dacthal	6	49	78	72	69
Dicamba	7	5	89	67	52
Dichlobenil	0	Estimated values			
Dichlorprop	7	57	74	68	66
Dinoseb	7	49	76	67	65
Diuron	6	49	94	73	74
Fenuron	7	56	136	70	80
Fluometuron	7	70	120	77	87
Linuron	7	69	127	72	83
MCPA	7	51	80	62	61
MCPB	6	48	67	64	60
Methiocarb	6	62	85	68	71
Methomyl	6	61	93	77	76
Neburon	7	54	132	71	78
Norfluorazon	6	69	91	73	76
Oryzalin	5	45	84	72	69
Oxamyl	6	37	72	54	55
Picloram	6	60	75	65	67
Propham	4	55	133	80	87
Propoxur	6	53	84	67	68
Triclopyr	6	46	79	69	65

Table 11. Spike recovery data for selected pesticides from Sacramento River Basin, California, ground-water samples, 1996–1998, and recovery and precision data published in the methods of analysis report

[Recovery and precision data are in Werner and others (1996). Spike recovery data are in percentages]

Compound	Sacramento River Basin (10 samples)				Methods of analyses report (81 samples)
	Minimum	Maximum	Median	Mean	Mean recovery
Bentazon	55	71	63	63	60 (relative standard deviation ± 23)
Carbofuran	66	99	76	78	62 (relative standard deviation ± 32)

Although ground-water data were not qualified because of spike recovery results, only 14 of the 39 compounds analyzed by the HPLC method returned acceptable recoveries of 70 percent or greater. While there were few detections of pesticides in ground-water samples analyzed by HPLC, the analytical data should be used with caution; the lack of detection of some compounds in the environmental samples may be due to poor analytical performance. [See interpretive analyses of spike recovery data for the subunit survey (Dawson, 2001a) and the agricultural land-use study (Dawson, 2001b).]

Volatile Organic Compounds

A total of 12 ground-water samples, each spiked with a solution containing 13 VOCs, were submitted for analysis during the subunit survey of 1996 and the urban study of 1998; VOC samples were not collected during the rice land-use study of 1997. Each spiked sample was submitted with a spike replicate. The relative percentage difference between the recovery results for each of the replicate spike pairs and the minimum, maximum, median, and mean percentage of spike recovered by compound for each sample are given in table 12. Two sets of data also are given, with and without the inclusion of an anomalous set of data collected on June 22, 1998, during the urban land-use study. The most likely explanation for those anomalous recoveries is that one of the samples was spiked twice, and the other sample was improperly spiked.

The median relative percentage difference between spike replicate pairs ranged from 3 percent for 1,2-dichloroethane to 22 percent (19 percent without anomalous recoveries) for chloroethene. The median recovery percentages spanned from 72 for chloroethene to 113 percent for 1,2-dichloroethane (table 12).

Of the three constituents listed as critical for the ground-water studies—trichloromethane, MTBE, and trichloroethene—only MTBE and trichloroethene were in the spike solutions. Data in the methods of analysis study (Connor and others, 1998) show the percentage of recovery as the mean recovery of seven replicates, each spiked at “1 and 10 µg/L”. Recovery results for the ground-water and blank water samples analyzed for MTBE ranged from 98 to 122 percent; tricholoethene ranged from 98 to 102 percent (Connor and others, 1998). The mean recovery results for 10 ground-water samples spiked with MTBE and trichloroethene during the Sacramento River Basin NAWQA were 93 and 97 percent, respectively (table 12 data without anomalous sample set), well within acceptable recovery limits (70 to 130 percent).

The samples submitted for the Sacramento River Basin study were spiked with 100 µL of spike solution during the subunit survey of 1996; because of an adjustment in protocol, the samples collected during the urban study of 1998 were spiked with 20 µL of spike solution using a 25-µL syringe (Connor and others, 1998). The changes had no apparent effect on recovery results. [See interpretive analyses of spike recovery data for the subunit survey (Dawson, 2001a) and the agricultural land-use study (Dawson, 2001b).]

Surface Water

Surface-water samples were collected from 12 sites throughout the Sacramento River Basin from February 1996 to April 1998 (fig. 2). Three of these sites—Colusa Basin Drain at Road 99E near Knights Landing, Arcade Creek near Del Paso Heights, and Sacramento River at Freeport—had increased sampling frequency for pesticides and(or) VOCs during selected seasonal periods (Domagalski and others, 2000).

Table 12. Relative percentage difference and recovery of field matrix spikes for volatile organic compounds in ground-water samples collected during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[Difference and recovery data are given in percentages. Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). In 1996 spike volume was 100 microliters according to protocol; by 1998, spike volume had been adjusted to 20 microliters (Connor and others, 1998). Percentage recovery calculations were based on values adjusted relative to concentrations detected in corresponding environmental samples, if applicable. Spike recovery results were not calculated when concentrations were reported by the laboratory as estimated values. VOC, volatile organic compound].Critical constituents are in **bold**]

Compound VOCs	Number of spike replicate pairs	Relative percentage difference in recovery results for spike replicate pairs				Number of samples	Spike recovery			
		Minimum	Maximum	Median	Mean		Minimum	Maximum	Median	Mean
Results calculated with the anomalous sample set:										
1,1,1-Trichloroethane	5	4	20	5	10	10	83	124	108	106
1,1-Dichloroethene	5	1	20	8	10	10	64	117	89	92
1,2-Dichloroethane	4	0	5	3	3	8	88	128	113	109
1,4-Dichlorobenzene	5	5	25	6	11	10	59	98	76	81
Bromodichloromethane	5	4	19	6	9	10	92	117	103	103
Tribromomethane	6	0	79	8	19	12	80	185	94	100
Chlorodibromomethane	6	0	74	6	18	12	80	175	94	100
Ethylbenzene	6	0	99	8	25	12	45	134	95	93
Tetrachloroethene	6	0	90	10	23	12	45	123	81	88
Tetrachloromethane	5	0	22	4	8	10	75	128	98	102
Trichloroethene	**6**	**0**	**81**	**7**	**20**	**12**	**70**	**165**	**100**	**100**
Chloroethene	6	6	77	22	28	12	47	154	72	82
Methyl *tert*-butyl ether	**6**	**0**	**80**	**7**	**18**	**12**	**67**	**156**	**95**	**96**
Results calculated without the anomalous sample set:										
1,1,1-Trichloroethane	5	4	20	5	10	10	83	124	108	106
1,1-Dichloroethene	5	1	20	8	10	10	64	117	89	92
1,2-Dichloroethane	4	0	5	3	3	8	88	128	113	109
1,4-Dichlorobenzene	5	5	25	6	11	10	59	98	76	81
Bromodichloromethane	5	4	19	6	9	10	92	117	103	103
Tribromomethane	5	0	13	6	7	10	88	105	94	94
Chlorodibromomethane	5	0	20	4	7	10	84	103	94	94
Ethylbenzene	5	0	29	6	10	10	72	108	95	94
Tetrachloroethene	5	0	24	9	10	10	59	123	81	89
Tetrachloromethane	5	0	22	4	8	10	75	128	98	102
Trichloroethene	**5**	**0**	**26**	**4**	**8**	**10**	**81**	**108**	**100**	**97**
Chloroethene	5	6	26	19	18	10	47	106	72	76
Methyl *tert*-butyl ether	**5**	**0**	**13**	**5**	**6**	**10**	**68**	**108**	**95**	**93**

Equipment blanks were collected under controlled conditions and submitted annually. Field blanks, spikes, and replicate samples were scheduled in conjunction with the monthly environmental sampling schedules. Quality-control data were reviewed to determine whether systematic contamination was being introduced that might require corrective action.

Blank Samples

Results of field blank sample analyses for critical constituents in the surface water study are given in table 13. These include analytical results for major ions, DOC, nutrients, trace elements, pesticides in filtered water, and VOCs.

Major Ions

Two equipment blanks and six field blank samples (table 13) were submitted for major ion analysis. Magnesium, sodium, and potassium were not detected in the equipment or field blank samples. Calcium was not detected in either of the equipment blanks, but was in one of the six field blanks at about 0.05 mg/L and in all surface-water samples at concentrations from 4 to 47 mg/L (Domagalski and others, 2000). Chloride and sulfate were not detected in either of the equipment blanks, but were in the same field blank. The detections of sulfate and chloride, along with a relatively high specific conductance of 73 μS/cm for the blank sample from Sacramento River at Verona on February 24, 1998 (Domagalski and others, 2000), are probably due to soap residue in the sampling equipment. Because the corresponding environmental sample data for these constituents are similar to data at that site throughout the study, contamination appears to be limited to the field blank sample.

Silica was detected in one of the two equipment blanks and in three of the six field blank samples at concentrations ranging from 0.01 to 0.022 mg/L. Of the 320 environmental samples analyzed for major ions, 319 had silica detections ranging from 3 to 45 mg/L, and one sample had a concentration of 1.1 mg/L (Domagalski and others, 2000). More than 2 orders of magnitude separate over 99 percent of the environmental data from the blank data. Silica found in blank samples was most likely solubilized from the glass ampoules containing the nitric acid used as a sample preservative (U.S. Geological Survey, 1998); polypropylene vials are now being used for nitric acid.

Detections of major ions in blank samples submitted during the surface-water study were few and at relatively low levels, reflecting random rather than systematic contamination. Therefore, environmental data can be used without qualification.

Dissolved Organic Carbon

Twenty-four DOC quality-control samples—13 field blanks (table 13) and 11 source solution blanks—were submitted for analysis. DOC was detected in all field blank samples at concentrations ranging from the reporting limit of 0.1 to 2.5 mg/L. DOC was in six of the source solution blanks, five at the detection limit of 0.1 mg/L, and one at 0.2 mg/L. The boxplot (fig. 9) shows no overlap between the field blank and environmental sample results, and the median values of the two data sets are not similar (p=0.0001, Mann–Whitney statistical test). With the environmental samples having concentrations ranging from 0.3 to 18 mg/L, however, some of the environmental data values near the reporting limit could have a positive bias. The source of the DOC contamination in blank samples collected in conjunction with surface-water sampling is unknown. Certificates of analysis that accompanied the five lots of blank water used during the course of the study did not provide conclusive evidence that blank water was the source of contamination. Although evidence of positive bias is insufficient to substantiate a qualification of the environmental data, environmental data near the reporting limit should be used with caution.

Table 13. Detections of critical constituents in surface-water field blank samples collected during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[All data are given in concentration units. Number of significant figures do not reflect analytical method reporting levels. Detections are in percentages. Changes in the method reporting limit (MRL) occurred during the course of the data collection for some of the analyses as indicated by multiple values. Maximum, maximum observed value or concentration; median, median observed value or concentration. mg/L, milligram per liter; µg/L, microgram per liter; <, less than; E-value, laboratory estimated result. NA, not applicable]

Constituent or compound	Number of field blank samples	Detections	MRL(s)	Concentration	
				Maximum	Median
Major ions					
Calcium (detections in mg/L)	6	17	0.02	0.049	<0.020
Magnesium (detections in mg/L)	6	0	0.01	NA	NA
Sodium (detections in mg/L)	6	0	0.20; 0.10	NA	NA
Potassium (detections in mg/L)	6	0	0.1	NA	NA
Chloride (detections in mg/L)	6	17	0.1	1.8	<0.10
Sulfate(detections in mg/L)	6	17	0.1	0.13	<0.10
Silica (detections in mg/L)	6	50	0.01; 0.10	0.022	0.01
Dissolved organic carbon (detections in mg/L as carbon)	13	100	0.1	2.5	0.2
Suspended organic carbon (detections in mg/L as carbon)	7	57	0.1; 0.2	0.2	0.1
Nutrients					
Nitrite (NO_2) + Nitrate (NO_3) (detections in mg/L as nitrogen)	7	29	0.05	0.125	<0.050
Whole-water phosphorus (detections in mg/L as phosphorus)	7	14	0.01	0.02	<0.010
Dissolved phosphorus (detections in mg/L as phosphorus)	7	0	0.01	NA	NA
Orthophosphorus (detections in mg/L as phosphorus)	7	43	0.01	0.022	<0.010
Trace elements					
Aluminum (detections in µg/L)	13	92	1.0	7	4
Chromium (detections in µg/L)	13	0	1.0	NA	NA
Copper (detections in µg/L)	13	8	1.0	1	<1.0
Manganese (detections in µg/L)	13	0	1.0	NA	NA
Nickel (detections in µg/L)	13	15	1.0	2	<1.0
Zinc (detections in µg/L)	13	23	1.0	3	<1.0
Iron (detections in µg/L)	6	33	3; 10	4.3	2.75
Mercury					
Total mercury (ng/L)	4	100	0.03	0.31	0.06
Methylmercury (ng/L)	1	0	0.02	NA	NA
Pesticides analyzed by gas chromatography/mass spectrometry					
Carbofuran (detections in µg/L)	6	0	0.003	NA	NA
Chlorpyrifos (detections in µg/L)	6	0	0.004	NA	NA
Diazinon (detections in µg/L)	6	0	0.002	NA	NA
Metolachlor (detections in µg/L)	6	0	0.002	NA	NA
Molinate (detections in µg/L)	6	NA	0.004	1 E-value only	
Simazine (detections in µg/L)	6	0	0.005	NA	NA
Thiobencarb (detections in µg/L)	6	0	0.002	NA	NA
Pesticides analyzed by high performace liquid chromatography					
Carbofuran (detections in µg/L)	6	0	0.280; 0.120	NA	NA
Diuron (detections in µg/L)	6	0	0.02	NA	NA
Volatile organic compounds					
Methyl *tert*-butyl ether (MTBE) (detections in µg/L)	7	NA	0.200; 0.100; 0.112	2 E-values only	NA

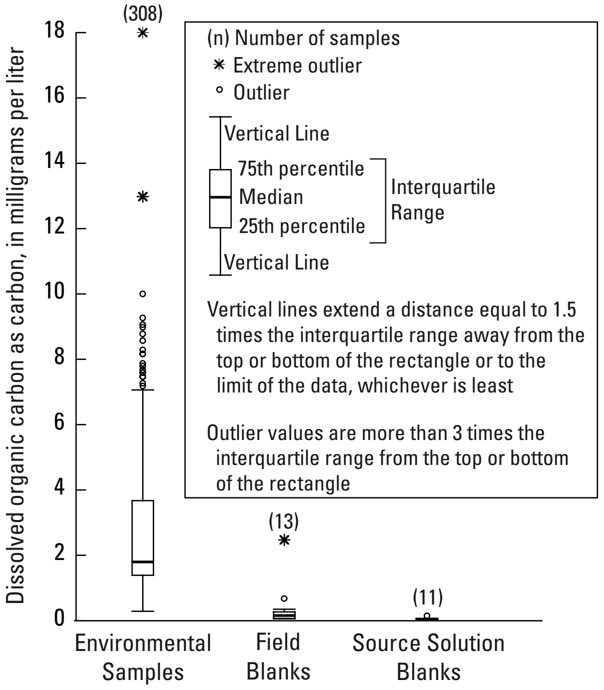

Figure 9. Boxplots of dissolved organic carbon concentration in surface-water environmental samples, field blanks, and source solution blanks in the Sacramento River Basin, California, 1996–1998.

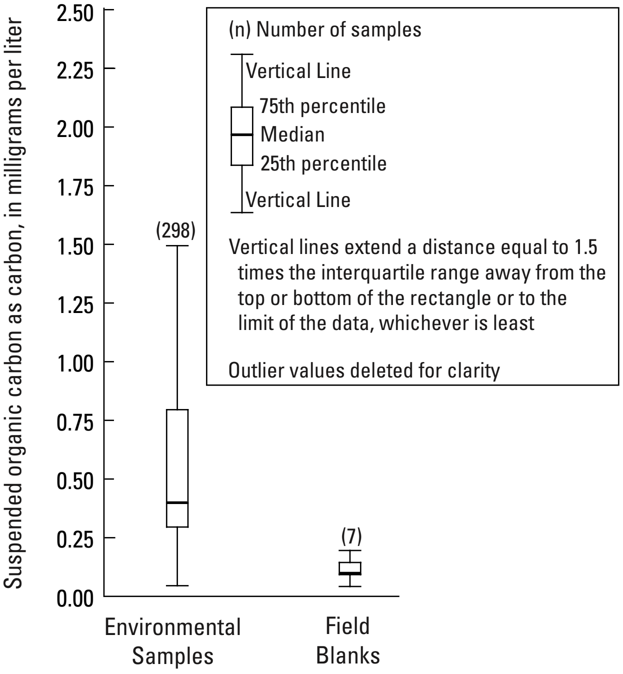

Figure 10. Boxplots of suspended organic carbon concentration in surface-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998.

Suspended Organic Carbon

Of the seven field blank samples submitted for suspended organic carbon analysis, low-level detections (0.1 and 0.2 mg/L) were reported for four of the samples. Although boxplot comparison (fig. 10) of environmental samples and field blanks reveals no overlap, and the median values of the two data sets are significantly different (p=0.0001, Mann–Whitney statistical test), a positive bias probably exists at concentrations near the reporting limit. This may affect 72 of the 298 environmental samples that had suspended organic carbon (SOC) concentrations of 0.2 mg/L or less.

Nutrients

Nine blank samples—seven field blanks and two equipment blanks—were collected and analyzed for eight nutrient compounds. Field blanks include two detections (29 percent) of nitrite plus nitrate (0.053 and 0.125 mg/L), a single detection (14 percent) of whole-water phosphorus (0.02 mg/L), and three detections (43 percent) of orthophosphorus (0.01–0.022 mg/L) (table 13). Dissolved phosphorus was not detected in field blanks, but was detected at 0.01 mg/L in one equipment blank. Orthophosphorus also was detected at 0.01 mg/L in one equipment blank. The maximum concentrations (table) for nitrite plus nitrate (0.125 mg/L as nitrogen) and orthophosphorus (0.022 mg/L as phosphorus), both of which are from the same field blank, are greater than twice the reporting limit. Although the source of the contamination is unknown, the three maximum concentrations appear to be anomalies and do not affect the environmental data.

Trace Elements

The trace elements analyzed by the NWQL considered critical to the surface-water component of the Sacramento River Basin NAWQA study include aluminum, chromium, copper, manganese, nickel, zinc, and iron (table 13). Sixteen blank samples were collected and analyzed for trace elements, excluding iron—13 field blanks and 3 equipment blanks. Six field blank samples and two equipment blanks were submitted for iron analysis using the analytical method [inductively coupled plasma (Fishman, 1993)] used for major ions.

Aluminum

Aluminum was detected in 12 of the 13 field blanks (92 percent) (table 13) and in all three equipment blanks at levels ranging from 3 to 7 µg/L. Aluminum in the 294 environmental samples ranged from 3 to 325 µg/L, and about 51percent had detections of 7 µg/L or less. Boxplot analysis (fig. 11) of these data shows minor overlap between the two data sets. Although the Mann–Whitney statistical test shows the medians of the environmental and blank data sets to be dissimilar (p=0.0001), environmental data have a positive bias, especially for low–end detection values. Some contamination in the blank samples could be attributed to the solubilization of aluminum from glass ampoules containing the nitric acid used as a sample preservative (U.S. Geological Survey, 1998); polypropylene vials are currently being used for nitric acid preservative. Because the boxplot provides justification for qualifying the aluminum values in the database, environmental samples that have low aluminum concentrations of 12 µg/L or less will be qualified with a V code in the database to indicate that the value may be due wholly, or in part, to contamination.

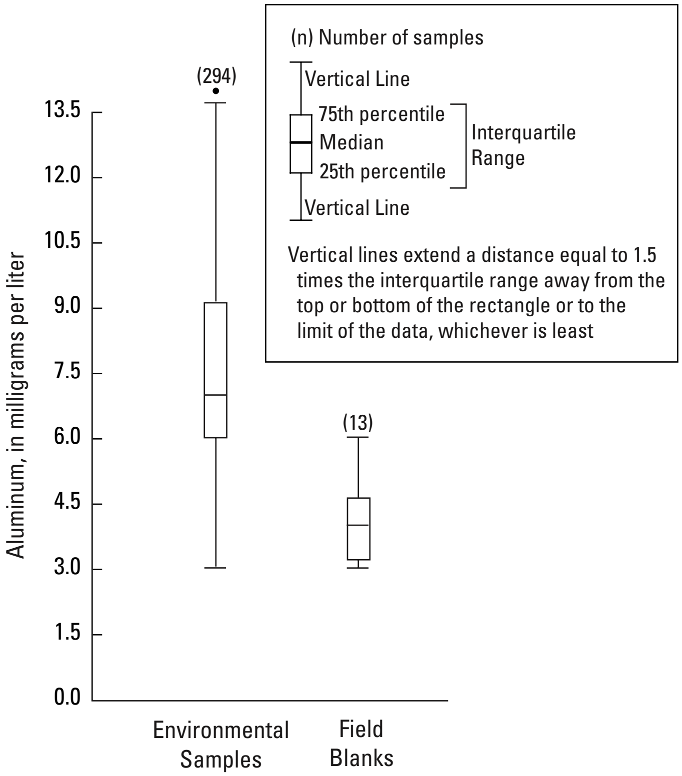

Figure 11. Boxplots of aluminum concentration in surface-water environmental samples and field blanks in the Sacramento River Basin, California, 1996–1998. Outliers are not shown.

Chromium, Copper, Manganese, Nickel, Zinc, and Iron

Blank samples were submitted to the NWQL and analyzed by ICP/MS for the trace elements chromium, copper, manganese, nickel, and zinc (Faires, 1993). Neither chromium nor manganese were detected in the blank samples (table 13). Of the 13 field samples, copper was detected in 1 sample (8 percent) at 1 µg/L, nickel was detected in 2 field blanks (15 percent) at values of 2 and 1µg/L, and zinc was detected in 1 equipment blank and in 3 field blanks (23 percent) at concentrations ranging from 1 to 3 µg/L. Iron was not detected in either equipment blank, but was detected in two of the six field blank samples (33 percent) at 4.0 and 4.3 µg/L. The infrequent detections of these analytes at low levels indicate no systematic contamination and, therefore, environmental data may be used without qualification.

Total Mercury

Six blank samples were analyzed for total mercury—four field blanks and two trip blanks. Mercury was detected in all six samples at concentrations ranging from the reporting limit of 0.03 to 0.31 ng/L; all of the 296 environmental samples contained concentrations of mercury ranging from 0.75 to 2,248 ng/L (Domagalski and others, 2000). The Mann–Whitney statistical test results (p=0.0001) provide no evidence of contamination that would effect the interpretation of environmental data.

Methylmercury

Only one blank sample was submitted for methylmercury analysis (table 13). Methylmercury was not detected in that sample; however, one sample provides insufficient data to make a determination about bias or any inference about the environmental data.

Pesticides in Filtered Water Analyzed by Gas Chromatography/Mass Spectrometry

Six blank samples were collected and analyzed for 47 pesticide compounds by GC/MS (table 13). Except for two estimated values—one for EPTC at 0.0011 µg/L (method reporting limit 0.0020 µg/L) and one for the critical constituent molinate at 0.0014 µg/L (method reporting limit 0.0040 µg/L)— no pesticides were detected in the blank samples. The blank data provide no evidence of contamination that would affect the interpretation of environmental data.

Pesticides in Filtered Water Analyzed by High Performance Liquid Chromatography

Six blank samples were collected and analyzed for 39 compounds by HPLC; no pesticides were detected in any of the samples (table 13). The blank data provide no evidence of contamination that would affect the interpretation of environmental data.

Volatile Organic Compounds

Thirteen blank samples were analyzed for VOCs—7 field blanks, 3 trip blanks, 2 source solution blanks, and 1 equipment blank. The blank samples provide no evidence of systematic contamination that would affect environmental data analysis. There were detections of acetone, dichloromethane, and methylbenzene—all noncritical constituents—in one trip blank sample set (sample date January 13, 1997). All of the vials in that set contained air bubbles when they arrived from the laboratory, suggesting the introduction of contamination at the point of origin or during transport. The environmental sample from the same date showed no anomalous detections.

Methyl *tert*-butyl ether (MTBE), a critical constituent, was not detected in 11 of the 13 blanks. Estimated values were reported for MTBE in two field blanks, but those estimated concentrations were less than 50 percent of the method reporting limit. The environmental data can be used without qualification.

Replicate Samples

Variability based on analysis of replicate samples is presented for critical constituents in surface-water samples (table 14). The variability between replicates is presented as the RPD and as the absolute difference in concentration units. For calculation purposes, if a less-than result was paired with a detection, 50 percent of the reporting limit was used in place of the less-than value.

Table 14. Variability of surface-water replicate samples collected during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

[If one of the two results for a replicate pair was reported as a "<" (less than the reporting limit) value, a value equal to 50 percent the reporting limit was used to complete the calculations used in this table. If reported as such, "E" (estimated) values were used in calculations for pesticides and the volatile organic compound methyl *tert*-butyl ether (MTBE). NWQL, National Water Quality Laboratory. Number of significant figures do not reflect analytical method reporting levels. µg/L, microgram per liter; mg/L, milligram per liter; ng/L, nanogram per liter]

Analyte (number of detections)	Total number of sets	Relative difference, in percentage			Difference, in concentration units		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Major ions							
Calcium (detections in all samples in mg/L)	6	0	1.9	0	0	0.1	0
Magnesium (detections in all samples in mg/L)	6	0	1.1	0	0	0.1	0
Sodium (detections in all samples in mg/L)	6	0	6.1	0	0	1	0
Potassium (detections in all samples in mg/L)	6	0	7.8	1.8	0	0.1	0
Chloride (detections in all samples in mg/L)	6	0	7.4	0	0	0.1	0
Sulfate (detections in all samples in mg/L)	6	0	4.7	1.3	0	0.2	0.1
Silica (detections in all samples in mg/L)	6	0	3.8	0	0	1	0
Dissolved organic carbon (detections in all samples in mg/L as carbon)	7	0	8.7	3.4	0	0.3	0.1
Suspended organic carbon [detections in mg/L as carbon; 1 split set (1 of the 2 samples has a nondetect result)]	7	0	67	0	0	0.3	0
Nutrients							
Nitrite (NO_2) + nitrate (NO_3) [detections in mg/L as nitrogen (1 set of nondetects)]	10	0	10	3.6	0	0.1	0.003
Whole-water phosphorus [detections in mg/L as phosphorus (2 sets of nondetects)]	10	0	40	8.2	0	0.031	0.008
Dissolved phosphorus [detections in mg/L as phosphorus (2 sets of nondetects; 2 split sets (1 of the 2 samples has a nondetect result)]	10	0	120	4	0	0.015	0.001
Orthophosphorus [detections in mg/L as phosphorus (2 sets of nondetects)]	10	0	32	0	0	0.006	0
Trace elements							
Aluminum (detections in all samples in µg/L)	4	0	32	5	0	11	0.35
Copper [detections in µg/L (1 set of nondetects)]	4	0	40	14	0	1	0.2
Manganese (detections in all samples in µg/L)	4	0	9.5	0.9	0	1	0.05
Nickel [detections in µg/L (2 sets of nondetects)]	4	0	0	0	0	0	0
Zinc [detections in µg/L (1 set of nondetects; 1 split set (1 of the two samples has a nondetect result)]	4	0	67	42	0	0.6	0.5
Iron (detections in all samples in µg/L)	6	17	93	37	2	26	8.6
Total mercury (detections in all samples in ng/L)	72	0	171	6	0.01	13.231	0.305

Table 14. Variability of surface-water replicate samples collected during the Sacramento River Basin, California, National Water-Quality Assessment, 1996–1998

Analyte (number of detections)	Total number of sets	Relative difference, in percentage			Difference, in concentration units		
		Minimum	Maximum	Median	Minimum	Maximum	Median
Methylmercury (detections in all samples in ng/L)	24	1	148	17	0.002	0.553	0.0165
Pesticides analyzed by gas chromatography/mass spectrometry							
Carbofuran [detections in µg/L (6 nondetect sets; 6 sets with E values)]	12	0	15	0	0	0.0056	0
Chlorpyrifos [detections in µg/L (6 nondetect sets; 2 split sets (1 of the 2 samples has a nondetect result)]	12	0	100	1.2	0	0.01	0.0002
Diazinon [detections in µg/L (1 nondetect set; 1 set with a nondetect and an E value)]	12	0	67	4.7	0	0.017	0.0015
Metolachlor [detections in µg/L (1 nondetect set; 2 sets with E values)]	12	0	18	3.9	0	0.025	0.001
Molinate [detections in µg/L (5 nondetect sets)]	12	0	3	0	0	0.016	0
Simazine [detections in µg/L (2 nondetect sets; 1 set with a nondetect and a detection; 1 set with a nondetect and an E value)]	12	0	186	3.5	0	0.0644	0.0006
Thiobencarb [detections in µg/L (6 nondetect sets)]	12	0	15	1.1	0	0.03	0.0002
Pesticides analyzed by high performace liquid chromatography							
Carbofuran [detections in µg/L (9 nondetect sets)]	10	0	22	0	0	0.05	0
Diuron [detections in µg/L (2 nondetect sets; 1 set with E values)]	10	0	25	4.5	0	0.9	0.01
Volatile organic compounds							
Methyl *tert*-butyl ether (MTBE) [detections in µg/L (1 nondetect set; 3 sets with E values)]	6	0	2.4	0	0	0.006	0
Alkalinity as $CaCO_3$ [calcium carbonate (comparison of field alkalinity values)]	215	0	33	2	0	33	1
Specific conductance: NWQL values versus field values (in microsiemen per centimeter at 25 degrees Celsius)	318	0	16	3	0	37	4

The median RPD is 0 percent for calcium, magnesium, sodium, chloride, silica, suspended organic carbon, orthophosphorus, nickel, the pesticides carbofuran (GC/MS and HPLC analyses) and molinate (GC/MS analysis), and the VOC MTBE. The highest median RPD is 42 percent for zinc followed by 37 percent for iron. Five analytes have maximum RPD values at or exceeding 100 percent, including dissolved phosphorus (120 percent), total mercury, (171 percent), methylmercury (148 percent), and the pesticides chlorpyrifos and simazine (100 and 186 percent, respectively). Although dissolved phosphorus has a maximum RPD value of 120 percent, the maximum difference in concentration was small (0.015 mg/L) and near the reporting limit (0.010 mg/L). Replicate data for alkalinity and specific conductance are also in table 14. Although not listed as critical constituents in table 1, these data may facilitate the interpretation of other analytical data collected during this study.

Surrogate Recovery

The three surrogate compounds—diazinon-d_{10}, terbuthylazine, and alpha HCH-d_6 (hexachlorocyclohexane)—added to the 104 samples analyzed for pesticides by GC/MS had median recoveries of 102, 109, and 99 percent, respectively (table 15); median recovery figures include anomalous results for one sample that probably had surrogate added improperly. The surrogate compound 4-bromo-3,5-dimethylphenyl-*n*-methylcarbamate (BDMC), which was added to 100 samples analyzed by HPLC, had a median recovery of 91 percent based on recovery results for 86 of the 100 samples. The laboratory deleted surrogate recovery results for 11 of the samples with the notation “unable to determine due to interference” (Wayne Nitta, U.S. Geological Survey, National Water Quality Laboratory, written commun., 1999). Three samples with estimated values were not included in the surrogate recovery summary. A second surrogate, toluic acid, was deleted from the HPLC procedure because of variable performance (Werner and others, 1996). The three surrogate compounds—1,2,-dichloroethane-d_4, *p*-bromofluorobenzene, and toluene-d_8—added to 64 surface-water samples analyzed for VOCs, had median recoveries of 105, 99, and 99 percent, respectively.

Table 15. Recovery of surrogate compounds in Sacramento River Basin, California, surface-water samples, 1996–1998

[The minimum, maximum, and median values are in percentage recovered. Minimum values (in **bold**) were verified as correct by National Water Quality Laboratory and are all from one sample, indicating that surrogate was improperly added to that sample. Except for the median value (in ***bold italics***), the median values were unaffected. Standard deviation values (in **bold**) were calculated using both sets of minimum values. HPLC, high performance liquid chromatography]

Surface water pesticides	Samples	Minimum	Maximum	Median	Standard deviation
SURFACE WATER PESTICIDES					
Pesticides analyzed by gas chromatography/mass spectrometry					
Diazinon-d_{10}	**104**/103	**8.8**/102	126	102	**13**/9
Terbuthylazine	**104**/103	**11.4**/88	148	***109***/110	**15**/12
alpha HCH-d_6 (hexachlorocyclohexane)	**104**/103	**10.5**/78	133	99	**14**/11
Pesticides analyzed by HPLC					
4-Bromo-3,5-dimethylphenyl-*n*-methylcarbamate (BDMC)	[1]86	47	138	91	16
SURFACE WATER VOLATILE ORGANIC COMPOUNDS					
1,2-Dichloroethane-d_4	64	89	133	105	9
p-Bromofluorobenzene	64	65	111	99	9
Toluene-d_8	64	87	105	99	3

[1] 100 samples were analyzed by HPLC; however, 3 estimated (E) values and 11 laboratory deleted results were omitted from these calculations.

Median recovery results for all surrogates are between 91 and 110 percent, which are within acceptable limits (70 to 130 percent). The performance of the HPLC method, however, provides further evidence that the procedure tends to be problematic. Although environmental pesticide data is not being qualified on the basis of the surrogate recovery results, lack of detection of some compounds analyzed by HPLC may be due to poor analytical performance, and environmental data should be used with caution.

Field Spiked Samples

Pesticide and VOC samples were spiked, submitted for analysis, and the percentage of spike recovered was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). The corresponding environmental sample submitted with each spiked sample was used to estimate detectable background concentrations of the spiked analytes. If an analyte was detected in the environmental sample, that concentration was subtracted from the concentration of the spiked sample and the adjusted value was used to calculate spike recovery percentages (tables 16 through 20).

Pesticides in Filtered Water Analyzed by Gas Chromatography/Mass Spectrometry

Surface-water samples were spiked with 47 pesticide compounds and submitted for analysis by GC/MS during the Sacramento River Basin study (table 16). Median recoveries for all compounds that had detection values (not estimates) ranged from 48 percent for *p,p′*-DDE to 118 percent for tebuthiuron, except for permethrin, which had the lowest median recovery (29 percent) of all the compounds. Permethrin also had the lowest median spike recovery result for ground-water samples submitted during the Sacramento River Basin NAWQA (table 8). Similar results for permethrin were obtained during a methods of analysis study (Zaugg and others, 1995) done at the laboratory in which six reagent water samples spiked at 0.1 μg/L yielded low mean recovery results (37 percent); seven surface-water samples spiked at 0.1 μg/L also had low mean recovery results (39 percent) for permethrin. The only compound having a lower mean recovery in the surface water sample set during method analysis was linuron (37 percent) (Zaugg and others, 1995; Lindley and others, 1996).

Of the pesticide compounds considered critical to the surface water component of the Sacramento River Basin NAWQA, carbofuran recovery could not be evaluated because all results were estimated (Domagalski, 2000, p. 15). Carbofuran also performed poorly during the method analysis study (Zaugg and others, 1995). Recovery data for the other critical constituents are given in table 17. Comparison of mean recovery data shows that spike recoveries for surface-water samples submitted by the Sacramento River Basin study were higher and nearer to 100 percent than recoveries for those compounds obtained by Zaugg and others (1995), which were spiked at similar concentrations.

Table 16. Recovery of field matrix spikes for pesticides from Sacramento River Basin, California, surface-water samples, 1996–1998, analyzed by gas chromatography/mass spectrometry

[Recovery data are given in percentages. Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated values. Critical constituents are in **bold**. No. samples, number of samples where recovery values could be calculated]

Compound	No. samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
2,6-Diethylaniline	6	77	91	86	85
Acetochlor	6	92	106	97	97
Alachlor	6	88	118	100	101
Atrazine	6	79	111	94	95
Methyl azinphos	0	Estimated values			
Benfluralin	6	79	97	89	88
Butylate	6	90	118	98	100
Carbaryl	0	Estimated values			
Carbofuran	**0**	**Estimated values**			
Chlorpyrifos	**6**	**63**	**104**	**85**	**87**
Cyanazine	6	88	131	110	110
DCPA	6	76	122	98	99
Desethyl atrazine	0	Estimated values			
Diazinon	**6**	**40**	**101**	**90**	**81**
Dieldrin	6	86	107	94	95
Disulfoton	6	42	84	59	60
EPTC	6	85	106	97	96
Ethalfluralin	6	96	129	103	109
Ethoprop	6	81	106	98	96
Fonofos	6	80	99	86	89
Lindane	6	79	105	92	91
Linuron	6	40	104	79	76
Malathion	6	71	112	99	93
Metolachlor	**6**	**90**	**124**	**105**	**106**
Metribuzin	6	82	127	100	102
Molinate	**6**	**90**	**109**	**101**	**100**
Napropamide	6	78	112	96	93
Parathion	6	96	139	116	116
Methyl parathion	6	91	178	104	122
Pebulate	6	89	107	99	99
Pendimethalin	6	66	103	94	91
Phorate	6	40	81	65	64
Prometon	6	22	119	94	86
Propachlor	6	93	129	109	109
Propanil	6	90	113	106	104
Propargite	6	60	92	82	81
Pronamide	6	93	113	101	102
Simazine	**6**	**62**	**114**	**91**	**90**
Tebuthiuron	6	36	158	118	108
Terbacil	0	Estimated values			
Terbufos	6	45	110	83	82
Thiobencarb	**6**	**84**	**101**	**95**	**94**
Triallate	6	80	102	92	91
Trifluralin	6	82	123	97	99
Alpha-BHC	6	84	102	96	95
Permethrin	6	16	59	29	31
p,p'-DDE	6	37	82	48	52

Table 17. Spike recovery data for selected critical constituents from Sacramento River Basin, California, surface-water samples, 1996–1997, with recovery and precision data published in the methods of analysis report

[Recovery and precision data are in Zaugg and others (1995). Spike recovery data are in percentages]

Compound	Sacramento River Basin				Methods of analysis report mean recoveries	
	Minimum	Maximum	Median	Mean	Surface water	Reagent water
Chlorpyrifos	63	104	85	87	80	83
Diazinon	40	101	90	81	[1]68	77
Metolachlor	90	124	105	106	87	92
Molinate	90	109	101	100	81	82
Simazine	62	114	91	90	[1]58	76
Thiobencarb	84	101	95	94	76	85

[1] Corrected for background concentrations of compound in surface water.

Of the 47 compounds analyzed by GC/MS, spike recoveries could not be calculated for five compounds because detection values were estimated (table 16). Spike recovery results for four other compounds were below the acceptable limit (70 percent). Although environmental data was not qualified because of spike recovery results, lack of detection of some compounds may be due to poor analytical performance, and data should be used with caution.

Pesticides in Filtered Water Analyzed by High Performance Liquid Chromatography

Five surface-water samples were spiked and submitted for pesticide analysis using the HPLC method (table 18). Median recovery values for compounds that had detections (not estimates) ranged from a minimum of 3 percent for dicamba, which had only one reportable recovery, to a maximum recovery of 89 percent for silvex, which had five recoveries. Recovery values were not calculated for aldicarb, aldicarb sulfone, or aldicarb sulfoxide because spike compounds were not detected in some of the samples or were reported only as estimated values. Recovery values also could not be calculated for DNOC, chlorothalonil, and dichlobenil because all detection results for these compounds were estimated; or for chloramben because some of the values were deleted from the database by the laboratory (U-delete), and the compound was not detected in the remaining samples. Altogether there were 22 incidents where spiked compounds were not detected in surface water samples. Of the 32 compounds where the spike recovery percentages were calculated, recovery values for all five samples were determined for only 16 (Domagalski and others, 2000).

The HPLC method tends to yield results that have a negative bias. The mean recovery range for 30 field matrix spike compounds in 81 samples spiked at “1.0 µg/L” during the laboratory evaluation of the HPLC method (Werner and others, 1996) was from 9 percent for chlorothalonil to 101 percent for propham. Twenty-five of the 30 compounds in the field matrix spike solution had mean recoveries of 65 percent or less, and 10 of those 30 compounds had mean recoveries under 50 percent. Recoveries of carbofuran and diuron, the constituents targeted as critical in surface water, are given in table 19, along with comparable mean accuracy results from the methods study (Werner and others, 1996).

Table 18. Recovery of field matrix spikes for pesticides from Sacramento River Basin, California, surface-water samples, 1996–1998, analyzed by high performance liquid chromatography

[Recovery data are given in percentages. Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated values. Results deleted by the laboratory are designated "U-delete." Several spiked compounds returned nondetect results. Critical constituents are in **bold**. No. samples, number of samples where recovery values could be calculated]

Compound	No. samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
2,4,5-T	5	43	92	73	70
2,4-D	3	41	84	54	60
2,4-DB	4	41	83	62	62
Silvex	5	51	100	89	81
3-Hydroxycarbofuran	5	28	100	71	62
DNOC	0	Estimated values			
Acifluorfen	3	23	94	75	64
Aldicarb	0	Spike nondetects and estimated values			
Aldicarb sulfone	0	Spike nondetects and estimated values			
Aldicarb sulfoxide	0	Spike nondetects and estimated values			
Bentazon	2	47	79	63	63
Bromacil	4	58	83	74	72
Bromoxynil	5	39	86	84	69
Carbaryl	4	66	88	73	75
Carbofuran	**5**	**47**	**92**	**69**	**68**
Chloramben	0	U-delete and spike nondetect values—cannot be calculated			
Chlorothalonil	0	Estimated values			
Clopyralid	1	25	25	25	25
Dacthal	3	43	79	54	59
Dicamba	1	3	3	3	3
Dichlobenil	0	Estimated values			
Dichlorprop	5	25	87	73	62
Dinoseb	5	51	103	84	77
Diuron	**4**	**38**	**91**	**84**	**74**
Fenuron	5	47	97	83	74
Fluometuron	5	64	93	80	78
Linuron	5	65	86	81	76
MCPA	4	27	78	76	64
MCPB	3	46	77	65	62
Methiocarb	5	69	92	82	80
Methomyl	5	51	133	88	85
Neburon	5	67	82	78	75
Norfluorazon	5	63	97	87	82
Oryzalin	5	0	68	64	51
Oxamyl	4	26	80	63	58
Picloram	1	60	60	60	60
Propham	1	67	67	67	67
Propoxur	3	38	86	41	55
Triclopyr	5	35	87	80	72

Table 19. Spike recovery data for selected pesticides from Sacramento River Basin, California, surface-water samples, 1996–1998, and field matrix spike recovery and precision data published in the methods of analysis report

[Field matrix spike recovery and precision data are in Werner and others (1996). Spike recovery data are in percentages]

Compound	Sacramento River Basin				Methods of analysis report: field matrix spike
	Minimum	Maximum	Median	Mean[1]	Mean recovery—81 samples
Carbofuran	47	92	69	68	62 (standard deviation +/- 32)
Diuron	38	91	84	74	43 (standard deviation +/- 18)

[1] Mean recoveries for the carbofuran and diuron spikes collected during the Sacramento surface-water study were compiled from data contained in Domagalski and others (2000).

Only 14 of the 39 analytes had mean spike recovery results within the acceptable limits of 70 to 130 percent (table 18). Although the data are not qualified based on spike recovery results, the lack of detection of some compounds may be due to poor analytical performance, and the data should be used with caution.

Volatile Organic Compounds

All surface-water VOC samples were collected at Arcade Creek near Del Paso Heights (table 20). Three of the samples collected in 1997 were spiked with 13 VOC analytes and submitted to the NWQL for analysis. In 1998, one replicate VOC sample set was spiked with a solution containing 84 of the 85 VOC analytes and submitted for analysis.

The VOC samples collected during 1997 were spiked with 13 analytes in 100 µL of spike solution delivered using a 100 µL syringe. By 1998, protocol had changed and samples were spiked with 85 analytes delivered in 20 µL of spike solution using a gas-tight 25-µL syringe. The VOC samples collected on March 9, 1998, however, were spiked with a solution that had an expiration date of May 22, 1997. Therefore, the relative percentage differences are not reported.

A maximum of five VOC spike recovery values could be calculated. Median recoveries ranged from a minimum of about 62 percent for methyl methacrylate, which had two reportable results, to a maximum of about 127 percent for methylbenzene, also having two reportable results. For those compounds where five recovery values were calculated, the median recovery results ranged from 70 percent for ethylbenzene to 100 percent for 1,2-dichloroethane and tetrachloroethene (table 20). Performance of VOCs spiked into seven surface water replicate samples tested during the methods of analysis evaluation (Connor and others, 1998) shows recovery percentages ranging from 89.2 percent for 1,1,2-trichloro-1,2,2-trifluoroethane (spiked at "1 µg/L") to 119.4 percent for *trans*-1,4-dichloro-2-butene (spiked at "10 µg/L").

MTBE was the only VOC listed as critical for the surface-water component of the Sacramento River Basin NAWQA (table 1). There were three spiked samples submitted during 1997 and two submitted in 1998. These five samples returned a median recovery of 85 percent and a mean recovery of 82 percent (table 20). During laboratory evaluation of the GC/MS method of VOC analysis (Connor and others, 1998), the mean recovery ranged from 100 to 121 percent for seven surface water and seven volatile blank water replicate samples spiked using "1 and 10 µg/L" MTBE solutions. Although the spike recovery results for the Sacramento River Basin surface-water samples appear to have a slightly negative bias, they are within acceptable limits. The relatively low spike recovery results are more likely attributable to problems with the spike procedures in the field rather than problems at the laboratory. Environmental data should be usable without qualification.

Table 20. Recovery of field matrix spikes for volatile organic compounds from Sacramento River Basin, California, surface-water samples, 1996–1998

[Recovery data are given in percentage. In 1997 spike volume was 100 microliters according to protocol; by 1998, spike volume had been adjusted to 20 microliters (Connor and others, 1998). Spike recovery was calculated according to protocols of the National Water Quality Laboratory (Mueller and others, 1997). Spike recovery calculations were not included for estimated values. Critical constituents are in **bold**. No. samples, number of samples where recovery values could be calculated]

Volatile organic compound	No. samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
1,1,1,2-Tetrachloroethane	2	77	87	82	82
1,1,1-Trichloroethane	5	52	104	95	88
1,1,2,2-Tetrachloroethane	2	98	113	106	106
1,1,2-Trichloroethane	2	94	110	102	102
1,1,2-Trichloro-1,2,2-trifluoroethane	2	70	77	73	73
1,1-Dichloroethane	2	95	100	98	98
1,1-Dichloroethene	5	45	90	82	78
1,1-Dichloropropene	2	80	83	81	81
1,2,3,4-Tetramethylbenzene	0	Compound not in spike			
1,2,3,5-Tetramethylbenzene	2	82	101	92	92
1,2,3-Trichlorobenzene	2	76	94	85	85
1,2,3-Trichloropropane	2	84	101	93	93
1,2,3-Trimethylbenzene	2	85	106	95	95
1,2,4-Trichlorobenzene	2	62	76	69	69
1,2,4-Trimethylbenzene	2	83	99	91	91
1,2-Dibromo-3-chloropropane	2	84	103	94	94
1,2-Dibromoethane	2	80	85	83	83
1,2-Dichlorobenzene	2	85	100	93	93
1,2-Dichloroethane	5	60	117	100	96
1,2-Dichloropropane	2	82	96	89	89
1,3,5-Trimethylbenzene	1	92	92	92	92
1,3-Dichlorobenzene	2	78	95	86	86
1,3-Dichloropropane	2	88	99	93	93
1,4-Dichlorobenzene	5	58	92	83	79
2,2-Dichloropropane	2	84	89	86	86
2-Butanone	2	83	102	92	92
2-Chlorotoluene	2	69	80	75	75
2-Hexanone	2	80	95	87	87
3-Chloro-1-propene	2	77	79	78	78
4-Chlorotoluene	2	70	82	76	76
p-Isopropyltoluene	2	73	89	81	81
4-Methyl-2-pentanone	1	98	98	98	98
Acetone	2	118	120	119	119
2-Propenenitrile	2	119	129	124	124
Benzene	2	86	92	89	89
Bromobenzene	2	69	78	73	73
Bromochloromethane	2	88	93	90	90
Bromodichloromethane	5	59	105	97	91
Bromoethene	2	69	84	77	77
Tribromomethane	5	68	100	89	87
Bromomethane	0	Estimated values			
n-Butylbenzene	2	68	84	76	76
Carbon disulfide	2	58	71	65	65

Table 20. Recovery of field matrix spikes for volatile organic compounds from Sacramento River Basin, California, surface-water samples, 1996–1998—Continued

Volatile organic compound	No. samples	Spike recovery in percent			
		Minimum	Maximum	Median	Mean
Chlorobenzene	2	66	77	71	71
Chloroethane	2	69	91	80	80
Trichloromethane	2	101	111	106	106
Chloromethane	0	Estimated values			
Chlorodibromomethane	5	65	101	95	89
Dibromomethane	2	91	100	96	96
Dichlorodifluoromethane	0	Estimated values			
Dichloromethane	2	104	109	107	107
Diethyl ether	2	79	84	82	82
Diisopropyl ether	2	73	83	78	78
Ethyl methacrylate	2	68	83	75	75
Ethyl *tert*-butyl ether	2	64	73	68	68
Ethylbenzene	5	53	96	70	74
Hexachlorobutadiene	2	76	91	83	83
Hexachloroethane	2	91	103	97	97
Isopropylbenzene	2	67	76	72	72
Methyl acrylate	2	81	84	83	83
Methyl acrylonitrile	2	82	89	86	86
Iodomethane	0	Estimated values			
Methyl methacrylate	2	57	67.3	62	62
Naphthalene	2	65	80	72	72
Styrene	2	78	90	84	84
Tetrachloroethene	5	52	114	100	90
Tetrachloromethane	5	49	99	90	85
Tetrahydrofuran	1	84	84	84	84
Methylbenzene	2	118	135	127	127
Trichloroethene	5	52	102	89	84
Trichlorofluoromethane	2	78	96	87	87
Chloroethene	5	36	83	71	62
cis-1,2-Dichloroethene	2	81	86	84	84
cis-1,3-Dichloropropene	2	68	75	71	71
1,4-Dimethylbenzene	2	73	85	79	79
n-Propylbenzene	2	75	85	80	80
2-Ethyltoluene	2	77	92	85	85
1,2-Dimethylbenzene	2	66	80	73	73
sec-Butylbenzene	1	92	92	92	92
Methyl *tert*-butyl ether	**5**	**64**	**93**	**85**	**82**
tert-Butylbenzene	1	104	104	104	104
tert-Amyl methyl ether	2	66	75	71	71
trans-1,2-Dichloroethene	2	86	89	88	88
trans-1,3-Dichloropropene	2	66	81	73	73
trans-1,4-Dichloro-2-butene	1	105	105	105	105

SUMMARY AND CONCLUSION

Quality-control data discussed in this report are intended for use in conjunction with the environmental data collected during the ground- and surface-water components of the Sacramento River Basin cycle 1 study. Quality-control data can be used to quantify bias and variability resulting from sample collection, processing, or analytical practices, and to add appropriate qualifications to interpretations of the environmental data. Data from blank samples collected during the ground-water study revealed levels of ammonia and dissolved organic carbon (DOC) contamination that would affect the interpretation of ground-water data. Residual cleaning media was the likely source of DOC contamination in the blanks, but purging the sampling lines with three casing volumes of ground water likely would have removed residue. Therefore, the environmental samples would not have been exposed to the contamination detected in the DOC blanks. The source of ammonia in blank samples was undetermined. However, because of the frequency and levels of detection in the blank samples, at least some of the measured detections of ammonia in ground-water samples, especially those near the detection limit, may be due to contamination; interpretations using these data should include qualifying statements. Aluminum and copper contamination in blank samples indicate a bias in ground-water samples. Surface-water data have a positive bias based on aluminum contamination in the blank samples. The source of copper contamination is unknown. Additional testing is needed before any corrective measures can be taken to mitigate contamination. Adjustments to the cleaning procedures should result in fewer detections of DOC and suspended organic carbon in blank samples, and the use of polypropylene vials to dispense nitric acid preservative should reduce the number of detections of aluminum. Blank samples collected for pesticide and volatile organic compound analyses revealed no systematic contamination that would affect ground- or surface-water environmental data.

Replicate samples for ground and surface water indicate that variability resulting from sample collection, processing, and analysis is generally low. In addition, some of the larger relative percentage differences for replicate samples were between samples having lowest absolute concentration differences and(or) between samples having concentrations near the reporting limit.

Overall, surrogate recoveries for pesticides and volatile organic compounds in ground- and surface-water samples were within acceptable limits. As expected from laboratory method performance and from results published in the methods of analysis report, the greatest variability, least consistency among recoveries, and a tendency toward a negative bias were reported for the surrogate compound analyzed using high performance liquid chromatography (HPLC).

Field matrix spikes submitted for pesticide analysis by gas chromatography/mass spectrometry (GC/MS) during the ground- and surface-water studies had recovery values for critical constituents that were comparable with published recoveries. Carbofuran, a critical constituent for the ground- and surface-water studies, and desethyl atrazine, a critical constituent for the ground-water component, had only estimated concentrations and could not be evaluated. These compounds also performed poorly during the laboratory methods of analysis study and were published as estimates. Field matrix spikes also were submitted for pesticide analysis using HPLC during ground- and surface-water sampling. Again, results for both ground- and surface-water samples were comparable with published results in the methods of analysis studies, including results for critical constituents. Recovery values indicate a predominately negative bias for all constituents analyzed with this method. In addition to the negative bias, there were instances where the spiked compound was not detected (22 nondetects in surface-water samples), compounds for which values could only be estimated, or cases of laboratory-deleted data. Neither the ground- nor surface-water pesticide data analyzed by the GC/MS or HPLC methods will be qualified in the database as a result of field spike recovery calculations. However, lack of detection of some compounds may be due to poor analytical performance, and the environmental data should be used with caution because results may be underreported.

Field matrix spikes for VOCs generally showed acceptable recovery results for both ground- and surface-water samples. Problems affecting recoveries appear to be related to errors in the field, such as double spiking or using a spike solution past the expiration date, rather than problems with the analytical method. Because the adjustments made to the method of spike delivery and the amount of spike solution added to a sample during the Sacramento River Basin NAWQA did not affect measured recoveries, data for both protocols were combined in this report.

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