

# Low-Level Volatile Organic Compounds in Active Public Supply Wells as Ground-Water Tracers in the Los Angeles Physiographic Basin, California, 2000

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U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 01-4188

Prepared in cooperation with the

CALIFORNIA STATE WATER RESOURCES CONTROL BOARD

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

5025-29

Sacramento, California  
2001

U.S. DEPARTMENT OF THE INTERIOR  
GALE A. NORTON, Secretary

U.S. GEOLOGICAL SURVEY  
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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. (<http://www.usgs.gov/>). 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. (<http://water.usgs.gov/nawqa>). 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 and priorities. NAWQA results can contribute to informed decisions that result in practical and effective water-resource management and strategies that protect and restore water quality.

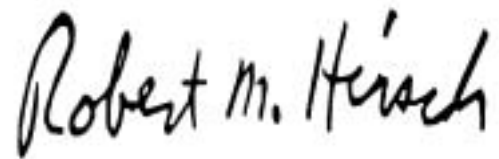
Since 1991, the NAWQA Program has implemented interdisciplinary assessments in more than 50 of the Nation's most important river basins and aquifers, referred to as Study Units. (<http://water.usgs.gov/nawqa/nawqamap.html>). Collectively, these Study Units account for more than 60 percent of the overall 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. (<http://water.usgs.gov/nawqa/natsyn.html>).

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

## CONTENTS

Abstract .....	1
Introduction .....	2
Hydrogeologic Setting .....	3
Coastal Los Angeles Basin .....	4
Coastal Santa Ana Basin .....	6
Study Design and Methods .....	6
Well Selection .....	6
Sample Collection and Analysis .....	8
Quality-Control Data for VOCs .....	9
Active Public Supply Wells Frequently Contain Low Concentrations of VOCs .....	10
VOC Distribution Indicates Enhanced Recharge and Ground-Water Pumping are Primary Controls on	
Ground-Water Flow System .....	13
Stable Isotope Data Relate Source of Recharge Water to VOC Occurrence .....	19
Assessment of Relation Between VOC Distribution and Potential Sources of VOCs .....	21
Surface Water .....	21
Population Density .....	22
Leaking Underground Fuel Tank Density .....	23
Hydrogeologically Vulnerable Areas .....	24
Summary and Conclusions .....	26
References Cited .....	28

## FIGURES

1. Major hydrogeologic features of the Los Angeles physiographic basin, California, showing study area and simplified cross-section showing the direction of ground-water flow .....	5
2. Public supply wells identified as candidates for sampling and resulting well network, Los Angeles physiographic basin, California .....	7
3. The sampling well network and the number of detections of volatile organic compounds above the laboratory reporting limit, Los Angeles physiographic basin, California, .....	10
4. Scatter plot of the number of detections of volatile organic compounds in samples from wells in the Coastal Los Angeles and Coastal Santa Ana forebay areas, California, as a function of distance from recharge facilities .....	14
5. Wells showing data for the most frequently detected volatile organic compound in each of four primary use categories in the Los Angeles physiographic basin, California for fuel oxygenate (MTBE), solvent (TCE), refrigerant (CFC-11), and the disinfection byproduct (chloroform). ....	16
6. Boxplot of the number of detections of volatile organic compounds above the laboratory reporting limit in samples from wells grouped by depth categories in the forebay areas of the Los Angeles physiographic basin, California, .....	18
7. Scatter plot of the delta oxygen-18 versus delta deuterium for samples from active public supply wells in the Los Angeles physiographic basin, California, showing hypothetical mixing lines for sources of recharge water to wells, and regression lines for samples with no detections and with detections above the LRL ....	20

8. Histogram of the frequency of MTBE detections in samples from all wells in the Los Angeles physiographic basin, in samples from wells in the Coastal Los Angeles Basin, and from wells in the Coastal Santa Ana Basin and the density of leaking underground fuel tanks within a 500-meter radius around the wells . . . . .	24
9. Map showing the number of detections of volatile organic compounds in samples from active public supply wells in the Los Angeles physiographic basin, California, overlain by the California State Water Resources Control Board's hydrogeologically vulnerable area . . . . .	25

## TABLES

1. Summary of well construction information for 178 active public supply wells sampled in the Los Angeles physiographic basin, California . . . . .	8
2. Volatile organic compounds detected in samples from 178 active public supply wells in the Los Angeles physiographic basin, California . . . . .	11
3. Volatile organic compounds analyzed for but not detected in samples from 178 active public supply wells in the Los Angeles physiographic basin, California . . . . .	12
4. Volatile organic compounds detected in 7 percent or more of the samples from 178 active public supply wells in the Los Angeles physiographic basin, California . . . . .	12
5. Comparison of the six most frequently detected volatile organic compounds in ground-water samples from the Los Angeles physiographic basin, California, and from urban areas across the United States . . . . .	13
6. Volatile organic compounds detected in samples from the Santa Ana River above the uppermost recharge facility in the Coastal Santa Ana Basin and from 178 active public supply wells in the Los Angeles physiographic basin, California . . . . .	22

## CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS, AND ABBREVIATIONS

Multiply	By	To obtain
kilogram (kg)	2.205	pound avoirdupois (lb avdb)
kilometer (km)	0.6214	mile (mi)
cubic kilometer (km <sup>3</sup> )	0.0008107	acre-foot (acre-ft)
meter (m)	3.281	foot (ft)
square kilometer (km <sup>2</sup> )	0.3861	square mile (mi <sup>2</sup> )

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

*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.

## Acronyms and Abbreviations

δ, delta

μg/L, microgram per liter

acre-ft, acre-foot

mL, milliliter

ft, foot

CAS, California Aquifer Susceptibility

CFC-11 (Freon 11), trichlorofluoromethane

CFC-113 (Freon 113), 1,1,2-trichloro-1,2,2-trifluoroethane

D, deuterium

DCE, 1,1-dichloroethene

DHS, California Department of Health Services

GAMA, Ambient Ground Water Monitoring and Assessment Program

GWSI, Ground Water Site Inventory

HCl, hydrochloric acid

LLNL, Lawrence Livermore National Laboratory

LRL, laboratory reporting limit

LUFT, leaking underground fuel tank

LUST, leaking underground storage tank

MCL, maximum contaminant level

MTBE, methyl *tert*-butyl ether

NAWQA, National Water-Quality Assessment (Program)

NWQL, National Water Quality Laboratory

<sup>18</sup>O, Oxygen-18

OCWD, Orange County Water District

PCE, tetrachloroethene (or tetrachloroethylene)

SWRCB, California State Water Resources Control Board

TCA, 1,1,1-trichloroethane

TCE, trichloroethene (or trichloroethylene)

USGS, U.S. Geological Survey

UST, underground storage tank

VOC, volatile organic compound

WRD, Water Replenishment District of Southern California

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## ABSTRACT

Data were collected to evaluate the use of low-level volatile organic compounds (VOC) to assess the vulnerability of public supply wells in the Los Angeles physiographic basin. Samples of untreated ground water from 178 active public supply wells in the Los Angeles physiographic basin show that VOCs were detected in 61 percent of the ground-water samples; most of these detections were low, with only 29 percent above 1  $\mu\text{g/L}$  (microgram per liter). Thirty-nine of the 86 VOCs analyzed were detected in at least one sample, and 11 VOCs were detected in 7 percent or more of the samples. The six most frequently detected VOCs were trichloromethane (chloroform) (46 percent); trichloroethene (TCE) (28 percent); tetrachloroethene (PCE) (19 percent); methyl *tert*-butyl ether (MTBE) (14 percent); 1,1-dichloroethane (11 percent); and 1,1,1-trichloroethane (TCA) (11 percent). These VOCs were also the most frequently detected VOCs in ground water representative of a wide range of hydrologically conditions in urban areas nationwide. Only two VOCs (TCE and PCE) exceeded state and federal primary maximum contaminant levels (MCL) for drinking water in a total of seven samples. Because samples were collected prior to water treatment, sample concentrations do not represent the concentrations entering the drinking-water system.

Ground water containing VOCs may be considered to be a tracer of postindustrial-aged water—water that was recharged after the onset of

intense urban development. The overall distribution of VOC detections is related to the hydrological and the engineered recharge facilities in the Coastal Los Angeles Basin and the Coastal Santa Ana Basin that comprise the Los Angeles physiographic basin. Most of the ground-water recharge occurs at engineered recharge facilities in the generally coarse-grained northeastern parts of the study area (forebay areas). Ground-water recharge from the land surface is minimal in the southwestern part of the basins, distal from the recharge facilities, where clay layers impede the vertical migration of ground water (pressure areas).

VOCs are not uniformly distributed over the study area. Most of the wells with multiple VOC detections, which also have the highest concentrations, are in the forebay areas and are clustered proximal to the recharge facilities. In addition, the number of VOC detections and VOC concentrations decrease beyond about 10–15 kilometers from the recharge facilities. The distribution of individual VOCs is also related to their history of use. MTBE traces ground water recharged during about the last decade and is detected almost exclusively in the forebay areas. Chloroform, which has been used since the 1920s, is more widely distributed and is detected at the greatest distances from the recharge facilities.

Downward migration of VOCs from the land surface may be a viable process for VOCs to reach aquifers in parts of the forebay areas, but there is little indication that the same process is active in

the pressure area. The lack of contrast in the number of VOC detections between wells of different depths over most of the study area suggests that the downward migration from the land surface is not a dominant pathway for VOCs to travel to the capture zones of public supply wells. Isolated occurrences of multiple VOC detections and high concentrations of VOCs in individual wells may indicate rapid vertical transport from a localized source.

Stable isotope data indicate that ground water containing VOCs is a mixture of local precipitation and runoff with water that is isotopically lighter (more negative) than the local sources. The isotopically lighter water could either be Colorado River water or State Water Project water, both of which are imported to the basin and used as a source of recharge to the ground-water flow system. The stable isotope data support the interpretation that VOCs in ground water are associated with the engineered recharge facilities.

Two of the most frequently detected VOCs in ground water, MTBE and chloroform, were detected more frequently and at higher concentrations in the Santa Ana River than in ground-water samples from active public supply wells, suggesting that the Santa Ana River may be a source of these compounds. In contrast, the maximum concentrations and frequency of detection of TCE and PCE are much higher in the ground-water samples than in the Santa Ana River. The VOCs detected in surface water sampled in the present time are only an approximation of past surface-water quality, which likely varied as a complex function of urbanization, water-quality regulations, and climate; and current surface-water quality alone can not explain VOC occurrence in ground water.

Correlations between VOC occurrence and sources of VOCs on the land surface do not explain VOC occurrence in this study. The overall lack of correlation between these surficial features and the spatial distribution of VOCs in active public supply wells in this study indicates that vertical migration of contaminants is not a dominant process outside the susceptible forebay areas. Hydrogeology and the acceleration of the lateral rate of ground-water flow produced by engineered recharge and ground-water pumping in the Coastal Los Angeles Basin

and the Coastal Santa Ana Basin appear to be the dominant factors in controlling the distribution of VOCs in active public supply wells in these coastal basins. Overall, the data show that active public supply wells in the forebay areas are more vulnerable to contamination than those in the pressure area in the Los Angeles physiographic basin study area.

## INTRODUCTION

During 1995, 14.5 billion gallons per day of ground water were extracted in California for a variety of uses, including 2.7 billion gallons per day for public supply used primarily for domestic purposes (Solley and others, 1998). Ground water supplies an estimated 30 to 60 percent of California's drinking water (Solley and others, 1998; Association of California Water Agencies, 2001), about half of which is used in the heavily urbanized parts of the southern California region (William E. Templin, U.S. Geological Survey, written commun., 2000). The quality of drinking-water resources is potentially susceptible to contamination from point- and nonpoint-source contaminants released into the urban environment. One specific class of chemicals—volatile organic compounds (VOC)—have a wide variety of uses and may be released into the urban environment during their production, distribution, storage, and use. Of particular concern is the long-term affect of the gasoline additive methyl *tert*-butyl ether (MTBE) from point sources, such as leaking underground storage tanks and spills.

In addition to the high number of potential contaminant sources, the potential susceptibility of these drinking-water resources is also heightened by the intense engineering of ground-water recharge. In general, the ground-water systems in southern California have been engineered to greatly increase the amount of water recharged (often focused in small areas) and the ground-water pumpage in public supply wells to provide water for a growing population. The vertical rate of ground-water movement also has been increased by the presence of abandoned or improperly constructed wells in some areas. An acceleration of the rate of ground-water recharge and movement increases the susceptibility of a public supply well to contamination by decreasing the travel time between potential contaminant sources and the well. There is a compelling need to understand the factors that control the occurrence, distribution, and transport of contaminants in urban ground-water systems and the degree of susceptibility





*Public supply well (photograph by Scott Hamlin, U.S. Geological Survey).*

of drinking-water resources in contrasting hydrogeologic settings.

In response to concern for future ground-water quality, the California State Water Resources Control Board (SWRCB) has implemented the California Aquifer Susceptibility (CAS) assessment to determine the water quality and susceptibility of ground water that serves as a source for public water supplies to potentially contaminating activities. CAS is part of the Ambient Groundwater Monitoring and Assessment (GAMA) Program that employs ground-water age dating techniques and low-level analyses for VOCs. The GAMA Program was developed by the SWRCB as a result of a mandate by the California State Legislature (California Legislative Analyst's Office, 1999) to develop a comprehensive ambient ground-water monitoring plan after public supply wells were closed because of the detection of MTBE and various industrial solvents. Under the GAMA Program, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program is collaborating with the SWRCB, the California Department of Health Services (DHS), the California Department of Water Resources, and the Lawrence Livermore National Laboratory (LLNL) to implement the CAS assessment.

This study was part of the pilot investigation of the feasibility of developing standard methodology for screening public supply wells to assess the ground-water age and source of recharge. Data were collected from a network of wells in the Los Angeles physiographic basin to evaluate the use of ground-water age (using tritium-helium analysis) and low-level

concentrations of VOCs as indicators of the potential susceptibility of public supply wells and, by inference, specific aquifers to potential contamination. Age dating techniques used during this study provide information on the presence of young water (less than 50 years since recharged) in the well, and analysis of low concentrations of VOCs may provide an early warning of potential VOC contamination moving toward a public supply well. For example, the presence of young ground water in a public supply well indicates that the producing zone of the aquifer may be expected to be more susceptible to potential contamination because of the short travel time of water from the land surface to a well. Low-level analysis for VOCs such as MTBE will also allow water managers to identify trends in ground-water quality in their region and respond before concentrations exceed water-quality criteria. The data were evaluated in combination with the locations of potential contaminant sources and existing knowledge of the hydrogeology to determine the dominant factors that control vulnerability of the ground-water resource in the Los Angeles physiographic basin.

This report presents an analysis of the distribution and occurrence of VOCs in active public supply wells sampled prior to water treatment in the Los Angeles physiographic basin, and relates the distribution of VOCs to the hydrogeologic framework and the potential contaminant sources to assess the susceptibility of active public supply wells. During August through November 2000, the USGS collected untreated ground-water samples from a network of 178 active public supply wells. Samples were analyzed for a suite of 86 VOCs and stable isotopes. Stable isotope ratios of the ground water assisted in identifying the sources of recharge water contributed to the wells. Samples were collected for tritium/helium-3 and shipped to the LLNL for analysis to determine ground-water age; results of the analyses will be presented in a subsequent report. The authors thank the many water purveyors in the study area who allowed USGS personnel access to their wells for sampling.

## **HYDROGEOLOGIC SETTING**

The study area covers the Los Angeles physiographic basin (fig. 1A), a 2,700 km<sup>2</sup> northwest-trending alluviated lowland plain, which is bounded on the north, east, and southeast by mountains and hills, and is sometimes referred to as the coastal plain (Yerkes and others, 1965). Ground-water flow is largely controlled by engineered recharge along the San Gabriel,

the Rio Hondo, and the Santa Ana Rivers, and by ground-water pumping from the many hundreds of wells distributed across the area. The direction of ground-water flow is primarily lateral and radial from the recharge facilities toward the coast (fig. 1B). Along the coast near the seawater intrusion barriers, the direction of ground-water flow is inland owing to pumping.

The Los Angeles physiographic basin is subdivided into two basins determined by the sources of recharge water—the Coastal Los Angeles Basin and the Coastal Santa Ana Basin. These basins have historically been delineated by the Los Angeles County–Orange County line (fig. 1A) (Poland and others, 1956; California Department of Water Resources, 1961). Although the hydrogeologic setting is similar between the Coastal Los Angeles Basin and the Coastal Santa Ana Basin, each of these basins has distinct radial flow paths originating from the engineered recharge facilities. Each basin can be further subdivided into two areas—forebay and pressure areas—based on the texture and permeability of aquifer materials (Eckis, 1934; California Department of Water Resources, 1961). The forebay areas are in the northeastern part of the Los Angeles physiographic basin along and adjacent to the rivers (fig. 1A). The sediments in the forebay areas consist of unconsolidated, interbedded sands and gravels with occasional lenses of silt and clay material. The relatively small amount of fine-grained sediments in the forebay areas are laterally discontinuous and generally do not impede the vertical movement of ground water. The forebay areas are the primary areas in which ground-water recharge occurs. The pressure area extends from the southwestern edge of the forebay to the Pacific Ocean; it occupies most of the land area in the basin and is characterized by sand, gravel, and thick lenses of silt and clay. The laterally extensive and thick lenses of fine-grained sediments in the pressure area can impede vertical movement of ground water.

## **Coastal Los Angeles Basin**

The hydrogeology of the Coastal Los Angeles Basin was characterized using the extensive amount of hydrologic and geologic data collected as part of an ongoing study between the USGS and the Water Replenishment District of Southern California (WRD). The simplified cross section shown in figure 1B illustrates the regional flow path in the study area.

The Coastal Los Angeles Basin occupies the northern half of the study area (fig. 1A). The

fresh-water-bearing deposits are up to 900-m thick and consist of gravel, sand, silt, and clay of fluvial and marine origin. Depth to water ranges from about 100 m to near land surface adjacent to the ground-water recharge facilities (Water Replenishment District of Southern California, 2001).

The Coastal Los Angeles Basin is composed of several smaller basins, the two largest of which are the Central Basin and West Coast Basin. The Central and West Coast Basins are delineated by the Newport–Inglewood Uplift (fig. 1A), the Pacific Ocean, and by surrounding hills. Ground water flows primarily laterally and radially from the recharge facilities in the Central Basin and eastward from the Pacific Ocean in the West Coast Basin (Water Replenishment District of Southern California, 2001). The primary sources of engineered recharge water differs in these basins: the Central Basin receives recharge water from the ground-water recharge facilities in the forebay areas, and the West Coast Basin receives recharge water from injection wells that form the seawater intrusion barriers (fig. 1A) (Water Replenishment District of Southern California, accessed June 13, 2001).

The forebay areas in the Coastal Los Angeles Basin are in the Central Basin and can be subdivided into two areas: the Los Angeles forebay and the Montebello forebay (fig. 1A). The Los Angeles forebay is located along and adjacent to the Los Angeles River as it flows from the San Fernando Valley. Intense urban development and lining of the Los Angeles River has greatly limited the amount of natural ground-water recharge in this western forebay area. The Montebello forebay is located along and adjacent to the Rio Hondo and the San Gabriel Rivers downgradient from the Whittier Narrows Flood Basin in the San Gabriel Valley (fig. 1A). Recharge facilities in the Montebello forebay receive a combination of water from the San Gabriel Valley, treated wastewater, and imported water, and serve as the primary source of recharge to the Coastal Los Angeles Basin. The large Whittier Narrows Flood Basin just north of the study area boundary in the San Gabriel Valley is not actively managed for ground-water recharge purposes. However, the flood basin receives storm-water runoff from the San Gabriel Valley, which can recharge the aquifer. Additional recharge occurs at a series of injection wells operated to restrict seawater intrusion along parts of the coast. Injection wells receive a combination of highly treated wastewater and imported water.

Replenishment and management of the ground-water resources necessary to offset historic overdraft began during the early 1960s by the WRD, although



artificial recharge of ground water has taken place in the Los Angeles area since about 1920 (Peterson, 1961; Water Replenishment District of Southern California, 2001). The primary sources of recharge are from engineered ground-water recharge, which includes water that is spread at the recharge facilities and injected into wells that form seawater intrusion barriers. For the 2000 water year (October 1999 through September 2000), about 0.227 km<sup>3</sup> (184,300 acre-ft) of water was recharged. About 77 percent (0.174 km<sup>3</sup> or 141,700 acre-ft) of the total was from engineered ground-water recharge (Water Replenishment District of Southern California, 2001): about 0.139 km<sup>3</sup> (113,000 acre-ft) at recharge facilities in the forebay area, and about 0.035 km<sup>3</sup> (28,700 acre-ft) at injection wells that form the seawater intrusion barriers. Other sources of recharge include underflow from adjacent basins, recharge along the margins of mountains and hills, and precipitation.

Outflow or ground-water production is from ground-water pumping primarily from the pressure area. About 0.310 km<sup>3</sup> (251,525 acre-ft) of ground water was pumped during the 2000 water year, most of which was from the Central Basin (79 percent), and the remainder was from the West Coast Basin. The main production zones generally range from 120 to 370 m (400 to 1,200 ft) below land surface (Michael Land, U.S. Geological Survey, unpublished data, 2000).

## Coastal Santa Ana Basin

The hydrogeology of the Coastal Santa Ana Basin was characterized using data collected by the Orange County Water District (OCWD) and the USGS's Santa Ana River Basin study team of the NAWQA Program. Similar to the flow path in the Coastal Los Angeles Basin, ground-water studies indicate that regional ground-water flow in the Santa Ana River Basin extends laterally and radially outward from the ground-water recharge facilities toward the coast (Orange County Water District, 1997).

The Coastal Santa Ana Basin occupies the southern half of the study area. The thickness of fresh-water-bearing deposits is as much as 1,200 m (Orange County Water District, 1996). These deposits consist of alluvium derived from the mountains to the east and southeast and from marine deposits. Similar to the Coastal Los Angeles Basin, depth to water ranges from about 100 m below land surface to near land surface

along the rivers, creeks, and ground-water recharge facilities (Orange County Water District, 1996).

The forebay area occupies about 130 km<sup>2</sup> along and adjacent to the Santa Ana River after it leaves the Santa Ana Mountains (fig. 1A). Recharge facilities in the forebay area receive a combination of treated wastewater, Santa Ana River water, and imported water, providing the primary source of recharge to the ground-water basin.

Since the formation of OCWD in 1933, ground-water recharge and pumpage from public supply wells have been intensively managed to offset historic ground-water overdraft (Orange County Water District, accessed June 13, 2001). In 1999, 0.342 km<sup>3</sup> (278,000 acre-ft) was recharged primarily at facilities along the Santa Ana River. Lesser amounts of recharge to the aquifer system occur along Santiago Creek from natural infiltration along the margins of the hills that surround the coastal plain and from vertical leakage through the confining layers. In 1999, about 0.438 km<sup>3</sup> (356,000 acre-ft) was pumped from the aquifer system primarily in the confined pressure area of the basin. The upper aquifer zone is generally from 90 to 450 m (300 to 1,500 ft) below land surface, with most of the pumpage from 150 to 300 m (500 to 1,000 ft) below land surface. In the confined pressure area, the upper aquifer zone is overlain by 90 to 150 m (300 to 500 ft) of deposits that consist primarily of silts and clays, which typically impede vertical movement of ground-water (Orange County Water District, 1996).

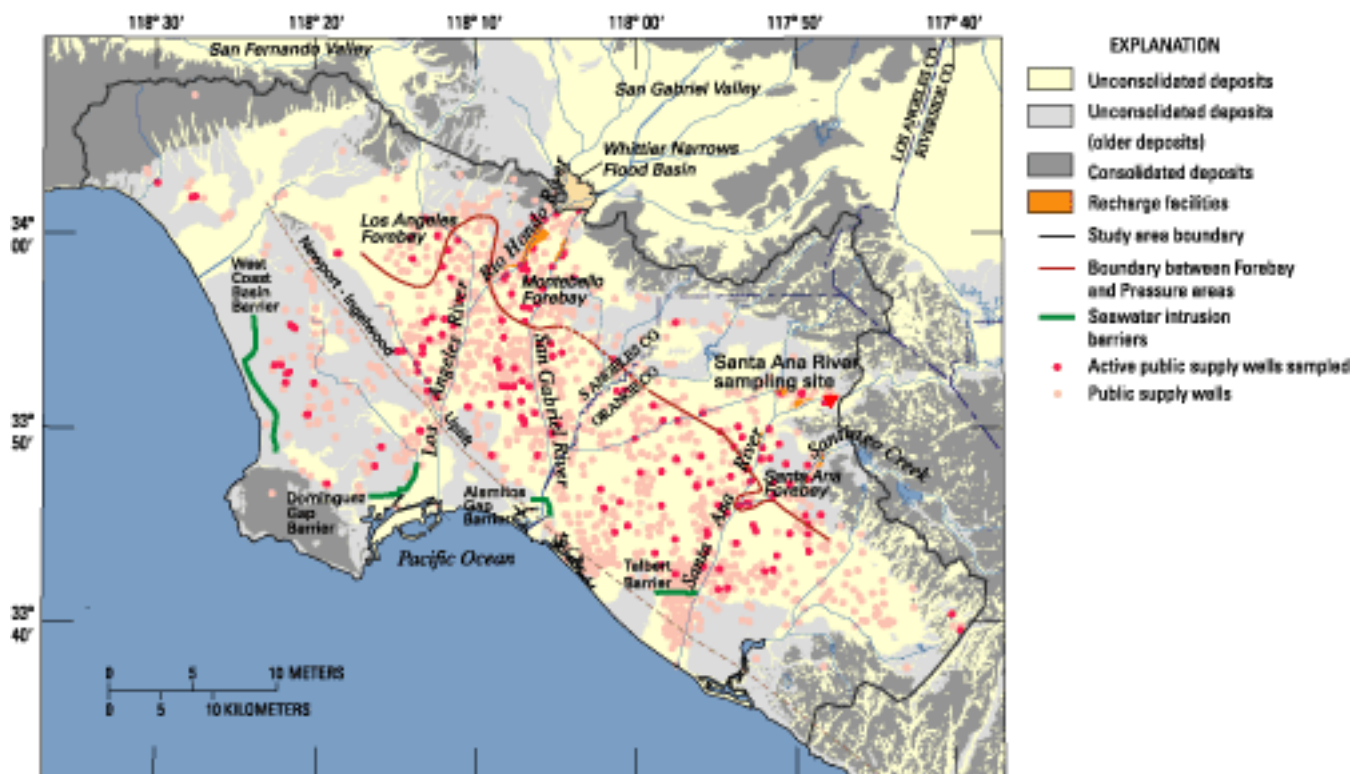
## STUDY DESIGN AND METHODS

Design of this study is based on established protocols and methods developed for the NAWQA Program (Leahy and others, 1990; Gilliom and others, 1995). Equally important was an understanding of the hydrogeology of the Coastal Los Angeles Basin and the Coastal Santa Ana Basin developed by prior research (Orange County Water District, 1997; U.S. Geological Survey, 1998a, 2000a; Hamlin and others, 1999; Water Replenishment District of Southern California, 2001), which made it possible to incorporate the hydrogeologic and geochemical framework of each aquifer system into the study design.

### Well Selection

A network of 178 wells were selected for sampling by using a grid-based random sampling approach (Scott, 1990), and by selecting wells screened in the





**Figure 2.** Public supply wells identified as candidates for sampling and resulting well network, Los Angeles physiographic basin, California

dominant producing zones tapped by most public supply wells. Candidate wells were identified using a systematic inventory of data provided by the WRD, OCWD, USGS Ground Water Site Inventory (GWSI) database, DHS, and the LLNL. The inventory produced a total of 1,691 candidate public supply wells, of which active public supply wells were preferentially selected when well status was identified (fig. 2). Public supply wells that were inactive, abandoned, or destroyed—some of which may contain constituents in violation of drinking water standards—were not selected. The active public supply wells are representative of the ground-water resources currently used for drinking water.

The unconsolidated deposits in the study area were partitioned into a grid of 100 equal-area cells (20 km²). Wells were then randomly chosen to be representative of the well depths and screened intervals in each cell to obtain a statistical representation of the ground-water quality captured by most active public supply wells. Candidate wells occupied 94 of these cells. Each well in a cell was randomly assigned a rank based on the number of wells in an individual cell. In addition, each well was assigned a priority code based on the information on well construction, state

well number, and well owner. Well construction information (well depth or depth below land surface, and top and bottom of screened intervals reported in depth below land surface) was identified for 685 of the candidate wells. When possible, well owners also were contacted to obtain construction information for wells with a high rank.

The aquifer depth tapped by the public supply wells that have well screened-interval information ranged from 4 m (the most shallow of the top of screened intervals) to 667 m (the deepest of the bottom of the screened intervals). Wells in individual cells were separated into three depth categories based on well depth and top and bottom of screened interval: shallow wells (well depth less than or equal to 152 m), deep wells (top of screened interval greater than 122 m and well depth greater than 152 m), and composite wells (top of screened interval less than or equal to 122 m and well depth greater than 152 m) that were screened in both the shallow and deep parts of the aquifer. Two wells from each cell were prioritized for selection according to the highest rank and screened interval depths that were most representative of the shallow and deep producing zones where possible (table 1). Wells were selected for sampling in 84 of the

100 equal-area cells. When there were no public supply wells in a cell or access could not be obtained, wells in adjacent cells were identified for sampling to maintain a spatially distributed network in the study area. After all possible wells were identified in candidate cells, 40 additional wells were selected from those where permission to sample was obtained. The resulting network contains 176 active public supply wells, 1 irrigation well, and 1 industrial well. Because the two irrigation/industrial wells are screened in the same part of the aquifer tapped by active public supply wells, no further distinction will be made between them and the 176 active public supply wells in this report. This network provides a representative sampling of the 1,691 public supply wells in the study area (fig. 2).

### Sample Collection and Analysis

Samples were collected from 178 active public supply wells by USGS personnel from August through November 2000 and analyzed for VOCs, stable isotopes, and tritium/helium-3. Sample equipment, collection, and cleaning procedures were used to collect a representative sample from the aquifer prior to water treatment, to minimize airborne contamination and volatilization of VOCs during sample collection, and to minimize carry-over contamination between wells. In general, standard USGS and NAWQA protocols were followed (Koterba and others, 1995; U.S. Geological Survey, 1998b).

Samples were collected prior to water treatment and after a minimum of three casing volumes were extracted, which help ensure that a representative sample was obtained from the aquifer. Active public supply wells that are continuously pumped required no additional pumping prior to sampling the wells, but several public supply wells in standby status were pumped to evacuate a minimum of three casing

volumes prior to sample collection. Three types of sampling lines were used to adapt the access ports available for sampling and to minimize airborne contamination and volatilization of VOCs during sample collection. Most of the samples (148 of the 178) were collected using sampling lines made of either copper or high-purity Tygon tubing, and the remaining 30 samples were collected using sampling lines made of Teflon. All three sampling lines were cleaned prior to use following a procedure similar to methods used by the NAWQA Program (Koterba and others, 1995), except that the copper lines were baked at 100°C for about 4 hours to remove any volatiles. Tygon sampling lines were used only once and discarded to avoid cross-contamination between sampling sites.

Prior to VOC sample collection, the sampling line was placed at the base of the 40-mL sample vials until overflow to displace the air from the vial. Unfiltered water then was collected in vials, preserved with hydrochloric acid (HCl) that has been analyzed for impurities, capped without headspace, and chilled to 4°C. All VOC samples were sent to the USGS National Water Quality Laboratory (NWQL) and analyzed for 86 compounds using purge and trap capillary-column gas chromatography/mass spectrometry (Connor and others, 1998). Unfiltered water collected in 60-mL bottles were sent to the USGS isotope laboratory in Reston, Virginia, and analyzed for stable isotopes using hydrogen equilibration (Coplen and others, 1991). Tritium/helium-3 samples were sent to the LLNL for analysis.

Laboratory reporting limits (LRL) for the 86 VOCs analyzed represent the minimum concentration that can be identified, measured, and reported with 99 percent confidence (Connor and others, 1998; Childress and others, 1999). However, some VOC concentrations were reported below the LRL when specific analytical identification criteria were met, and these

**Table 1.** Summary of well construction information for 178 active public supply wells sampled in the Los Angeles physiographic basin, California

[Depth category: shallow, well depth less than or equal to 152 meters (m); composite, top of screened interval less than or equal to 122 m and well depth greater than 152 m; deep, top of screened interval greater than 122 m and well depth greater than 152 m. Well depths and screened interval depths are in meters below land surface. No., number; \*, screened interval data not available for 1 well]

Depth category	No. of wells	Top of screened intervals		Bottom of screened intervals		Screened interval lengths		Well depths	
		Range	Median	Range	Median	Range	Median	Range	Median
Shallow	47	12–130	72	43–149	108	3–117	30	43–152	112
Composite	64	24–139*	93*	93–472*	204*	5–440*	139*	154–472	220
Deep	67	123–324	154	149–512	299	8–328	122	153–512	311
All wells	178	12–324*	107*	43–512*	200*	3–440*	89*	43–512	210

concentrations are qualified as estimated (“E” remark code). The NWQL collects quality-control data on a continuing basis to establish LRLs, and reevaluates the LRLs annually. The LRL controls the probability of falsely reporting a nondetection. The chance of falsely reporting a nondetection for a sample that contained a VOC at a concentration equal to or greater than the LRL is less than 1 percent (Childress and others, 1999). The chance of falsely reporting a detection for a sample that does not contain a VOC is much less than 1 percent.

Throughout this report, two types of analytical results are reported: detection of a VOC above the LRL and detection of a VOC below the LRL. The LRL is different for every VOC because it is dependent on chemical behavior and, hence, laboratory quality-control data. Therefore, VOC detections were screened at the LRL for comparisons of the number of VOCs detected between sites. Alternately, all detections were reported for comparisons of the detection or concentration of a single VOC between sites instead of only reporting detections above the LRL. Thus, the effect of falsely reporting a detection or nondetection on the data interpretation is minimized, and the amount of information obtained from the data is maximized. VOC concentrations are reported to the same number of significant digits as the NWQL reports for the LRL.

The LRLs changed (reduced by about half) for nine VOCs after 33 of the 178 wells were sampled; only four of these VOCs were detected (trichloromethane; 1,1-dichloroethane; dichloromethane; and chloromethane). Almost all of the samples with concentrations of these VOCs between the two LRLs were collected after the LRLs were changed or lowered. Therefore, the LRL that was active when the sample was analyzed was used to determine the number of VOCs detected above the LRL.

## Quality-Control Data for VOCs

Quality-control samples were collected and analyzed to qualify the interpretation of environmental data (samples from wells) and to identify the sources and magnitude of bias and variability in the data associated with sample collection, processing, transportation, and laboratory analysis. Blank samples (blanks), consisting of organic-free water (blank water) certified by the NWQL to be free of VOCs, were analyzed by the same methods used for environmental samples. Four different types of blanks were collected: field (14 samples); source-solution (18 samples); equipment

(2 samples); and trip (11 samples). Field blanks measure the overall bias of the environmental data, and the other types of blanks measure specific sources of bias associated with the blank water and with various aspects of sampling, processing, transportation, and laboratory analysis.

Five VOCs (methylbenzene, chloromethane, ethylbenzene, trichloromethane, and dichloromethane) that were detected in environmental samples were also detected below the LRL in field blanks. Trichloromethane and dichloromethane were each detected in one field blank; however, these detections could be attributed to blank water contamination because they were detected in source-solution blanks at higher concentrations than environmental samples and thus do not affect the interpretation of the environmental data. Methylbenzene was detected in 1 equipment blank and in 7 of the 11 trip blanks at similar concentrations as in the three field blanks, possibly indicating that the source of contamination may be from transportation or shipment of samples. Chloromethane was detected in a source-solution blank and in one lot of HCl preservative (reported in the Certificate of Analysis from the NWQL) used during 1 week of sampling. Consequently, chloromethane was detected in seven environmental samples at a concentration similar to that in the two field blanks, indicating that the preservative may be the source of contamination for the low-level detections. Ethylbenzene also was detected in one trip blank at a concentration similar to that in one field blank, indicating that the source of contamination may be from transportation or shipment of samples.

VOC concentrations detected in environmental samples were censored at or below the maximum concentration detected in a field blank sample and, subsequently, were not reported as a detection. This censoring reduced the number of environmental detections of methylbenzene from 9 to 0, of ethylbenzene from 1 to 0, and of chloromethane from 13 to 8. VOCs were not detected more frequently in any of the different types of sampling lines in either blank or environmental samples.

Overall, the data show that VOC sample collection, processing, and field-cleaning procedures were successful in minimizing environmental sample contamination or carryover. Further, on the basis of the trip and source-solution blank data, most of the detections in the field blanks could be attributed to contamination during transportation or preservation.

The NWQL also routinely analyzes internal quality-control samples to monitor analytical method

performance. Results of quality-control data were evaluated from laboratory samples processed by NWQL at the same time as the samples submitted from this study, and from long-term historical data on method precision and recoveries. It is beyond the scope of this report to present all of the quality-control data collected and analyzed by the NWQL, but short- and long-term quality-control data is available for the NWQL (U.S. Geological Survey, 2000b).

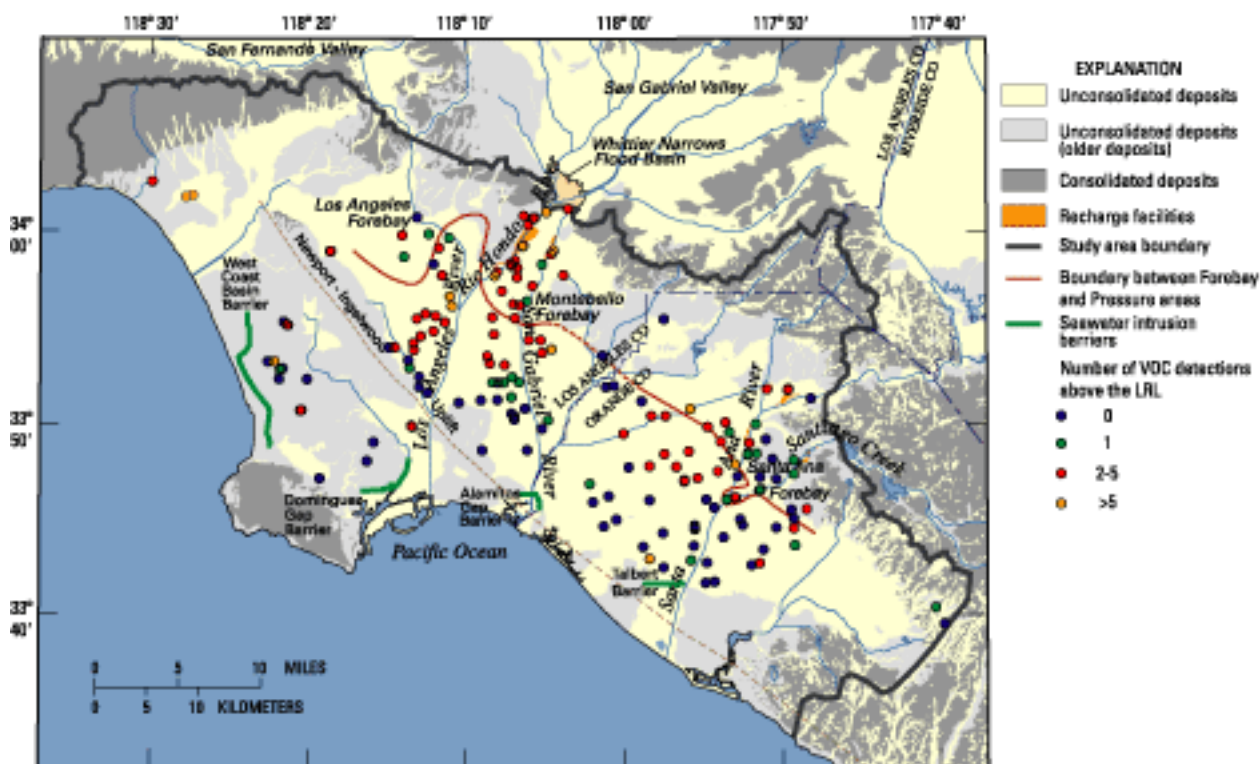
## ACTIVE PUBLIC SUPPLY WELLS FREQUENTLY CONTAIN LOW CONCENTRATIONS OF VOCs

Ground-water samples from 108 (61 percent) of the 178 wells contained one or more VOCs at concentrations above the LRL (fig. 3). Most of these detections were at low-levels, with only 29 percent above 1 µg/L. Six or more VOCs were detected at concentrations above the LRL in samples from 7 percent of the wells. Most of the wells with the highest number of VOC detections also contained the highest concentrations of individual compounds.

Thirty-nine of the 86 VOCs analyzed were detected: 29 were detected at concentrations above the

LRL, and 10 were only detected at concentrations below the LRL and are reported as estimated. This report will focus on VOCs detected at concentrations above the LRL because the LRL is based on quality-control data, which, as noted earlier, greatly reduces the probability of falsely reporting a nondetection. However, the 11 most frequently detected VOCs are the same regardless of whether the number of VOC detections above the LRL or the total number of VOC detections are counted (table 2). Forty-seven of the 86 VOCs analyzed were not detected (table 3).

Eleven VOCs were detected at concentrations above the LRL in 7 percent or more of the samples (table 4), and 6 VOCs were detected at concentrations above the LRL in 11 percent or more of the samples. Trichloromethane (chloroform), a disinfection byproduct and the most frequently detected VOC, had concentrations above the LRL in 82 (46 percent) of the samples. The solvents trichloroethene (TCE); tetrachloroethene (PCE); 1,1-dichloroethane; and 1,1,1-trichloroethane (TCA) were detected at concentrations above the LRL in 50 (28 percent), 34 (19 percent), 20 (11 percent), and 20 (11 percent) of the samples, respectively. The fuel oxygenate MTBE was detected at concentrations above the LRL in 25 (14 percent) of



**Figure 3.** The sampling well network and the number of detections of volatile organic compounds above the laboratory reporting limit, Los Angeles physiographic basin, California. VOC, volatile organic compound; LRL, laboratory reporting limit.



**Table 2.** Volatile organic compounds detected in samples from 178 active public supply wells in the Los Angeles physiographic basin, California

[LRL, laboratory reporting limit; 2 LRLs used during sampling period. µg/L, microgram per liter]

Compound name (common name)	LRL (µg/L)	Number of detections above LRL	Number of detections below LRL	Total number of detections
Trichloromethane (Chloroform)	0.052*, 0.024	82	20	102
Trichloroethene (TCE)	0.038	50	19	69
Tetrachloroethene (PCE)	0.10	34	28	62
Methyl <i>tert</i> -butyl ether (MTBE)	0.17	25	18	43
1,1-Dichloroethane	0.066*, 0.035	20	14	34
1,1,1-Trichloroethane (TCA)	0.032	20	20	40
Bromodichloromethane	0.048	18	5	23
Trichlorofluoromethane (CFC-11)	0.09	16	20	36
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)	0.060	16	4	20
<i>cis</i> -1,2-Dichloroethene	0.038	13	11	24
1,1-Dichloroethene (DCE)	0.044	12	10	22
Chlorodibromomethane	0.18	5	1	6
1,2-Dichloroethane	0.13	4	0	4
Tribromomethane (Bromoform)	0.06	4	0	4
Tetrachloromethane (Carbon tetrachloride)	0.06	3	5	8
Carbon disulfide	0.07	2	5	7
<i>trans</i> -1,2-Dichloroethene	0.032	2	1	3
Bromochloromethane	0.044	2	0	2
Dichloromethane (Methylene chloride)	0.38*, 0.16	1	1	2
1,2,3,4-Tetramethylbenzene	0.23	1	0	1
1,2,3,5-Tetramethylbenzene	0.20	1	0	1
2-Ethyltoluene	0.06	1	0	1
1,2,3-Trimethylbenzene	0.12	1	0	1
1,2,4-Trimethylbenzene	0.056	1	0	1
1,3,5-Trimethylbenzene	0.044	1	0	1
Chlorobenzene	0.028	1	0	1
<i>n</i> -Propylbenzene	0.042	1	0	1
<i>sec</i> -Butylbenzene	0.032	1	0	1
Diisopropyl ether	0.10	1	0	1
Dichlorodifluoromethane (CFC-12)	0.27	0	9	9
Chloromethane (Methyl chloride)	0.5*, 0.25	0	8	8
Isopropylbenzene	0.032	0	3	3
1,4-Dichlorobenzene	0.05	0	2	2
Benzene	0.035	0	2	2
<i>n</i> -Butylbenzene	0.19	0	1	1
<i>p</i> -Isopropyltoluene	0.07	0	1	1
Tetrahydrofuran	2.2	0	1	1
1,3 and 1,4-Dimethylbenzene (meta and para-Xylene)	0.06	0	1	1

the samples. The other VOCs detected in 7 percent or more of the samples include the disinfection byproduct bromodichloromethane; the refrigerants trichlorofluoromethane (CFC-11 or Freon 11) and 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113 or Freon 113); 1,1-dichloroethene (DCE), which is used in the synthesis of organic chemicals; and the solvent *cis*-1, 2- dichloroethene.

This group of frequently detected VOCs is similar to those found in ground water in urban areas

representative of a wide range of hydrogeologic conditions across the United States (Squillace and others, 1999). This group also is similar to VOCs detected in drinking water in the Northeast and mid-Atlantic regions of the United States (Grady and Casey, 2001), and of ground-water samples from monitoring and public supply wells in southern New Jersey (Stackelberg and others, 2000). The six VOCs detected most frequently in this study were also the most frequently detected VOCs in a study of urban areas across the

**Table 3.** Volatile organic compounds analyzed for but not detected in samples from 178 active public supply wells in the Los Angeles physiographic basin, California

[LRL, laboratory reporting limit; \*, 2 LRLs used during sampling period. µg/L, microgram per liter]

Compound (common name)	LRL (µg/L)	Compound (common name)	LRL (µg/L)
1,1,1,2-Tetrachloroethane	0.03	Bromoethene	0.10
1,1,2,2-Tetrachloroethane	0.09	Bromomethane	0.26
1,1,2-Trichloroethane	0.06	Chloroethane	0.12
1,1-Dichloropropene	0.026	Chloroethene	0.11
1,2,3-Trichlorobenzene	0.27	<i>cis</i> -1,3-Dichloropropene	0.09
1,2,3-Trichloropropane	0.16	Dibromomethane	0.05
1,2,4-Trichlorobenzene	0.19	Diethyl ether	0.17
1,2-Dibromo-3-chloropropane	0.21	Ethylbenzene	0.03
1,2-Dibromoethane	0.036	Ethyl methacrylate	0.18
1,2-Dichlorobenzene	0.031*, 0.048	Ethyl <i>tert</i> -butyl ether (ETBE)	0.054
1,2-Dichloropropane	0.029*, 0.068	Hexachlorobutadiene	0.14
1,2-Dimethylbenzene ( <i>ortho</i> -Xylene)	0.038	Hexachloroethane	0.19
1,3-Dichlorobenzene	0.03*, 0.054	Iodomethane (Methyl iodide)	0.12
1,3-Dichloropropane	0.12	Methyl acrylate	1.4
2,2-Dichloropropane	0.05	Methyl acrylonitrile	0.6
2-Butanone	1.6	Methylbenzene (Toluene)	0.05
2-Chlorotoluene	0.026*, 0.042	Methyl methacrylate	0.35
2-Hexanone	0.7	Naphthalene	0.25
2-Propenenitrile	1.2	Styrene	0.042
3-Chloro-1-propene	0.07*, 0.2	<i>tert</i> -Amyl methyl ether (TAME)	0.11
4-Chlorotoluene	0.06	<i>tert</i> -Butylbenzene	0.06
4-Methyl-2-pentanone	0.37	<i>trans</i> -1,3-Dichloropropene	0.09
Acetone	7	<i>trans</i> -1,4-Dichloro-2-butene	0.7
Bromobenzene	0.036		

**Table 4.** Volatile organic compounds detected in 7 percent or more of the samples from 178 active public supply wells in the Los Angeles physiographic basin, California

[E, estimated; LRL, laboratory reporting limit; No., number; \*, 2 LRLs used during sampling period. µg/L, microgram per liter]

Compound name (common name)	LRL (µg/L)	Percentage of samples with a detection above the LRL	No. of detections above the LRL	Detected concentrations (µg/L)			Primary use
				Minimum	Median	Maximum	
Trichloromethane (Chloroform)	0.052*, 0.024	46	82	E 0.011	0.060	11	Disinfection byproduct
Trichloroethene (TCE)	0.038	28	50	E 0.0089	0.095	69	Solvent
Tetrachloroethene (PCE, PERC)	0.10	19	34	E 0.0099	0.14	11	Solvent
Methyl <i>tert</i> -butyl ether (MTBE)	0.17	14	25	E 0.052	0.18	0.85	Fuel oxygenate
1,1-Dichloroethane	0.066*, 0.035	11	20	E 0.012	0.046	0.50	Solvent
1,1,1-Trichloroethane (TCA)	0.032	11	20	E 0.0063	0.032	0.33	Solvent
Bromodichloromethane	0.048	10	18	E 0.019	0.069	5.5	Disinfection byproduct
Trichlorofluoromethane (CFC-11)	0.09	9	16	E 0.01	0.06	8	Refrigerant
1,1,2-Trichloro-1,2,2-trifluoroethane (CFC-113)	0.060	9	16	E 0.014	0.13	2.5	Refrigerant
<i>cis</i> -1,2-Dichloroethene	0.038	7	13	E 0.016	0.040	1.4	Solvent
1,1-Dichloroethene (DCE)	0.044	7	12	E 0.012	0.047	3.3	Organic synthesis

United States (table 5), when both data sets are censored at a reporting limit of 0.20 µg/L (Squillace and others, 1999).

Most VOCs were detected at low concentrations, but maximum concentrations varied greatly (table 4). The three most frequently detected VOCs also had the highest maximum concentrations. Eight of the 11 most frequently detected VOCs had maximum concentrations greater than 1 µg/L in a total of 25 samples. Two VOCs exceeded the state and federal primary maximum contaminant level (MCL) for drinking water (U.S. Environmental Protection Agency, 1996) in a total of seven samples. Trichloroethene (TCE) concentrations exceeded the MCL (5 µg/L) in four samples with a maximum concentra-

**Table 5.** Comparison of the six most frequently detected volatile organic compounds in ground-water samples from the Los Angeles physiographic basin, California, and from urban areas across the United States

Compound name (common name)	Percentage of detections censored 0.2 micrograms per liter	
	Urban areas across the United States (Squillace and others, 1999)	Los Angeles physio- graphic basin, California
Trichloromethane (Chloroform)	26	10
Tetrachloroethene (PCE)	17	15
Methyl <i>tert</i> -butyl ether (MTBE)	17	11
Trichloroethene (TCE)	12	14
1,1,1-Trichloroethane (TCA)	10	1
1,1-Dichloroethane	6	1

tion of 69 µg/L, and tetrachloroethene (PCE) concentrations exceeded the MCL (5 µg/L) in five samples with a maximum concentration of 11 µg/L. Water purveyors were aware of these MCL exceedances in the ground water from their routine monitoring, and the water was already being treated to remove these compounds. In this study, samples were collected prior to water treatment and, thus, sample concentrations do not represent the concentrations entering the drinking-water system. More than half of the remaining samples with TCE and PCE detections contained concentrations between 0.5 and 5 µg/L.

## VOC DISTRIBUTION INDICATES ENHANCED RECHARGE AND GROUND-WATER PUMPING ARE PRIMARY CONTROLS ON GROUND-WATER FLOW SYSTEM

As a simple approximation, the ground-water flow system can be conceptualized as a radial wedge or pie-slice with the apex at the recharge facilities in the forebay and flow paths extending outward toward the coast. Within the wedge is water bearing the fingerprint of urbanization—that is, water containing VOCs. Outside the wedge is native ground water. VOCs might be introduced in the coarse-grained forebay areas either at the recharge facilities or in other sources of recharge that encounter point or nonpoint contaminant sources. This radial pattern of flow is reflected in the distribution of VOCs (fig. 3), which act as tracers of postindustrial-aged water (water recharged since the onset of intense urban development). Inspection of water-level contour maps (Orange County Water District, 1996) also indicates flow originating at the engineered recharge facilities and radiating outward. However, because of changes in the source and quality of recharge water over time, ground-water quality in the flow system is not the same as the quality of water presently recharged at the forebay areas and the recharge facilities. This radial wedge concept of the ground-water flow system, however, does not describe the flow system west of the Newport–Ingelwood Uplift in the West Coast Basin of the Coastal Los Angeles Basin. The Newport–Inglewood Uplift separates the Central Basin from the West Coast Basin and impedes lateral ground-water flow, thus the West Coast Basin receives more water from the seawater intrusion



*Recharge facility in the Coastal Santa Ana Basin (photograph by Carmen Burton, U.S. Geological Survey).*

barriers than from recharge in the forebay areas (Water Replenishment District of Southern California, 2001).

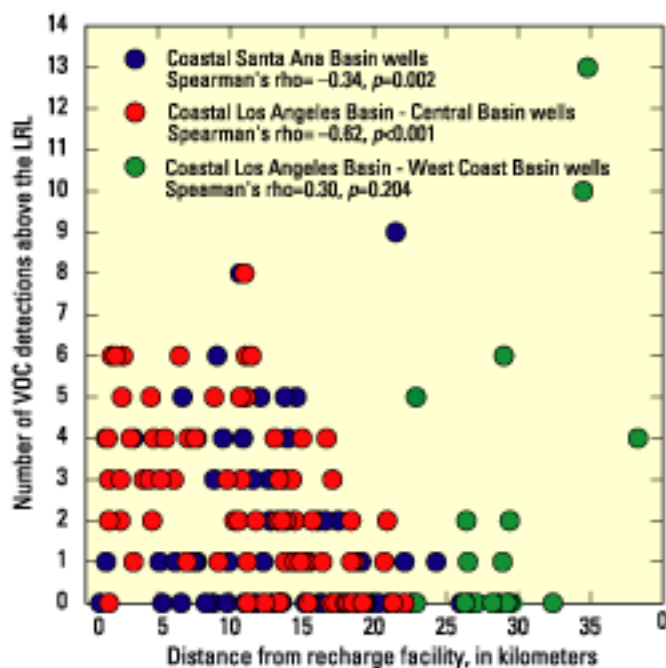
The spatial distribution of the VOCs detected above the LRL can be quantified in terms of the distance between the recharge facility and the location of the well. This distance represents distance along the radial flow path and is a surrogate for the time of travel. The distance from the recharge facilities is negatively correlated with the number of VOCs detected above the LRL in the Central Basin of the Coastal Los Angeles Basin and in the Coastal Santa Ana Basin ( $p < 0.001$  and  $p = 0.002$ , respectively; Spearman's rank correlation) (fig. 4). This analysis shows samples with the most VOC detections are from wells located within 15 km of the recharge facilities, with a few exceptions. The wells with VOCs detected above the LRL almost form a line at approximately 10–15 km of the recharge facilities beyond which few or no VOCs were detected (fig. 3). Thus, the low-level concentrations of VOCs seem to act as a reasonable groundwater tracer for postindustrial-aged water and indicate the distance water has traveled from where it was recharged in the forebay areas.

The most notable exceptions to this generalization are the four wells in which more than five VOCs

were detected outside the wedge of postindustrial-aged water: one is in the southern part of the Coastal Santa Ana Basin, one is in the West Coast Basin of the Coastal Los Angeles Basin, and two are in the extreme north-western corner of the Coastal Los Angeles Basin (fig. 3). The VOCs in wells located in the older unconsolidated deposits and outside the radial flow paths are probably not derived from the water recharged in the forebays. The injection wells that make up the seawater intrusion barriers contribute to water recharged in areas along the coast and may be a potential low-level source of VOCs to public supply wells in those areas.

Although the recharge facilities along the Rio Hondo, the San Gabriel, and the Santa Ana Rivers are the major sources of recharge, they are not the only sources. The Los Angeles River, prior to being lined with concrete, and Santiago Creek are also sources of recharge water. In addition, there are a variety of potential point and nonpoint sources of VOCs in urban areas. The coarse-grained sediments and discontinuous silt and clay lenses in the forebay areas also allow vertical migration of precipitation, infiltration from excess landscape watering, storm-water runoff, chemical spills, leaky underground fuel tanks, and leaky sewer and water distribution lines to recharge the aquifer. Age dating from the tritium/helium-3 analyses may assist in the interpretation of potential sources of recharge water and VOCs.

The use of VOCs as tracers of postindustrial-aged ground water may be further examined by evaluating the most frequently detected VOCs with reference to when these VOCs were introduced into the environment. Figure 5 shows the distribution of sample concentrations of four of the most frequently detected VOC in each of four primary use categories (table 4). The spatial distribution of the fuel oxygenate MTBE, which has the most recent history of use, is shown in figure 5A. MTBE was used to enhance octane levels in gasoline during the late 1970s (Zogorski and others, 1996), and the use of MTBE increased significantly during the early 1990s after fuel oxygenates were mandated by the Clean Air Act amendments to reduce atmospheric concentrations of carbon monoxide. In 1996, about 10.6 billion liters (2.8 billion gallons) of MTBE were produced in the United States, over 95 percent of the gasoline used in California was blended with MTBE, and the annual production capacity of MTBE in California was about 719 million liters (190 million gallons) (Gomez and others, 1998). MTBE has the most localized distribution of detections with all but two of the detections at concentrations above the LRL in wells close to the recharge



**Figure 4.** Scatter plot of the number of detections of volatile organic compounds in samples from wells in the Coastal Los Angeles and Coastal Santa Ana forebay areas, California, as a function of distance from recharge facilities. VOC, volatile organic compound; LRL, laboratory reporting limit; <, less than.

facilities in the forebay (fig. 5A). This nearly exclusive occurrence of MTBE close to the area of recharge is consistent with the relatively recent introduction of MTBE as a fuel additive, the concept of the radial-flow system, and the use of VOCs as ground-water tracers for postindustrial water.

Most of the MTBE detections and the highest MTBE concentrations are found in samples from wells close to the recharge facilities and the Rio Hondo or the San Gabriel Rivers in the Montebello forebay area in the Coastal Los Angeles Basin. The reason for this higher frequency of occurrence and concentration in the Coastal Los Angeles Basin than in the Coastal Santa Ana Basin is unknown. Perhaps it is due to inflow from adjacent basins or the greater amount of surface area of recharge facilities or unlined reaches of rivers in the Montebello forebay than in the Coastal Santa Ana Basin. Approximately 3.4 km<sup>2</sup> (850 acres) of recharge facilities or unlined reaches of the Rio Hondo and the San Gabriel Rivers are in the Montebello forebay area. The rapid infiltration of large volumes of surface water potentially could provide a more rapid way for MTBE to be transported to the aquifer.

TCE has been in use longer than MTBE and is more widely distributed. TCE has been produced in large quantities since the 1960s (Stackelberg and others, 2000) and is considered to be a high production volume chemical in that over 450,000 kg (1 million pounds) are produced annually in the United States (Environmental Defense, 2001a). In contrast with MTBE, TCE is detected farther from the recharge facilities and at about the same frequency in the forebay areas as it is detected in the pressure areas (fig. 5B). Because TCE has been in production longer than MTBE, TCE has traveled with recharge water a greater lateral distance from the forebay. Similar to MTBE, TCE is detected more frequently and occurs at higher concentrations in the Coastal Los Angeles Basin than in the Coastal Santa Ana Basin. However, unlike MTBE, some of the highest concentrations of TCE are isolated and are not in proximity to the recharge facilities (fig. 5B); these detections may be due to rapid vertical migration from a localized source of contamination.

The spatial distribution of the most frequently detected refrigerant, CFC-11, is shown in figure 5C. CFC-11 was frequently used in air conditioners and coolants during the 1970s and is also considered a high production volume chemical (Environmental Defense, 2001b). In July 1992, producers of CFC-11 were required to gradually reduce production, and

production was to be completely phased out by January 1, 2000 (U.S. Environmental Protection Agency, 1999). This reduction may have decreased the amount of chlorofluorocarbon that enters the ground-water system and explain the lack of detections in the forebay areas and the higher frequency of detections in the pressure areas. Most of the detections of CFC-11 above the LRL (0.09 µg/L) are from wells in the pressure areas.

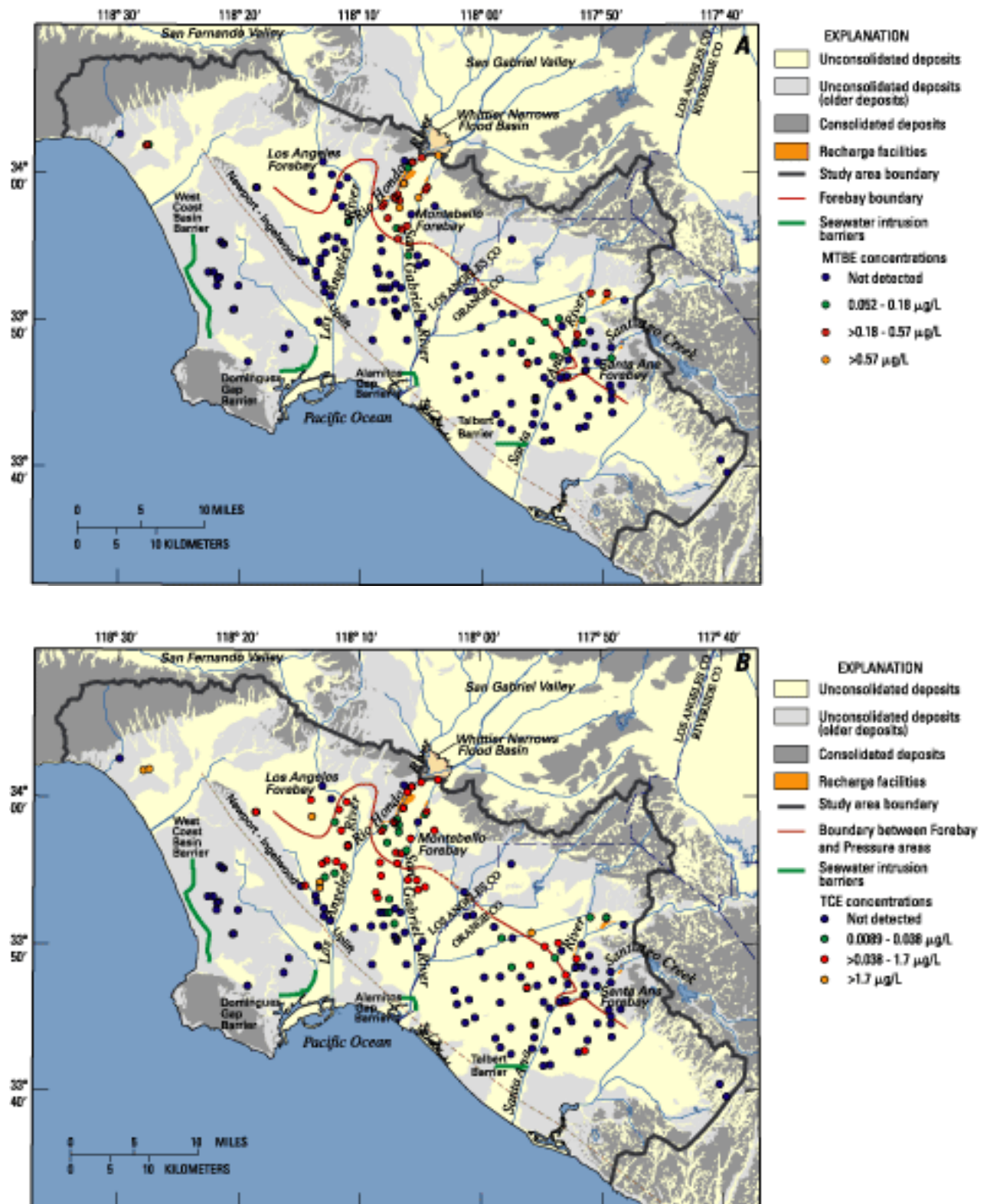
Unlike the spatial distribution of MTBE and TCE, CFC-11 is more frequently detected and occurs at higher concentrations in the Coastal Santa Ana Basin than in the Coastal Los Angeles Basin (fig. 5C). The second most frequently detected refrigerant, CFC-113, has a similar pattern and spatial distribution. The reasons for the increased frequency of refrigerant detections in the Coastal Santa Ana Basin are unknown, but could potentially result from localized sources.

The distribution of chloroform (fig. 5D) is similar to the overall distribution of VOCs. Chloroform, often produced as a byproduct of the disinfection of drinking water, has been produced since the 1920s for many uses, including manufacturing of pharmaceuticals, dry cleaning, fire extinguishers, fumigants, and as an anesthetic (Stackelberg and others, 2000; U.S. Department of Health and Human Services, 2001). Most of the chloroform detections are above the LRL (0.024 µg/L) and are found in almost equal numbers in both the Coastal Los Angeles and the Coastal Santa Ana Basins. Sources of chloroform that would result in a wide distribution of this disinfection byproduct include chlorination of drinking water, leaks in drinking water distribution systems, lawn irrigation, and recharge of large volumes of treated wastewater and State Water Project water at recharge facilities. Chloroform detections close to the coast may be related to injection of treated wastewater into the wells that form the seawater intrusion barriers.

Degradation along ground-water flow paths could also result in lower concentrations of VOCs at greater distances from where ground water is recharged. Assuming the spatial distribution of VOCs is dominated by lateral flow from the forebay, then the current extent of any specific VOC is minimal because loss of VOC mass from sorption and degradation along the ground-water flow path have not been accounted for in this study.

An alternative to the radial flow concept of the flow system is that the VOC distribution could be





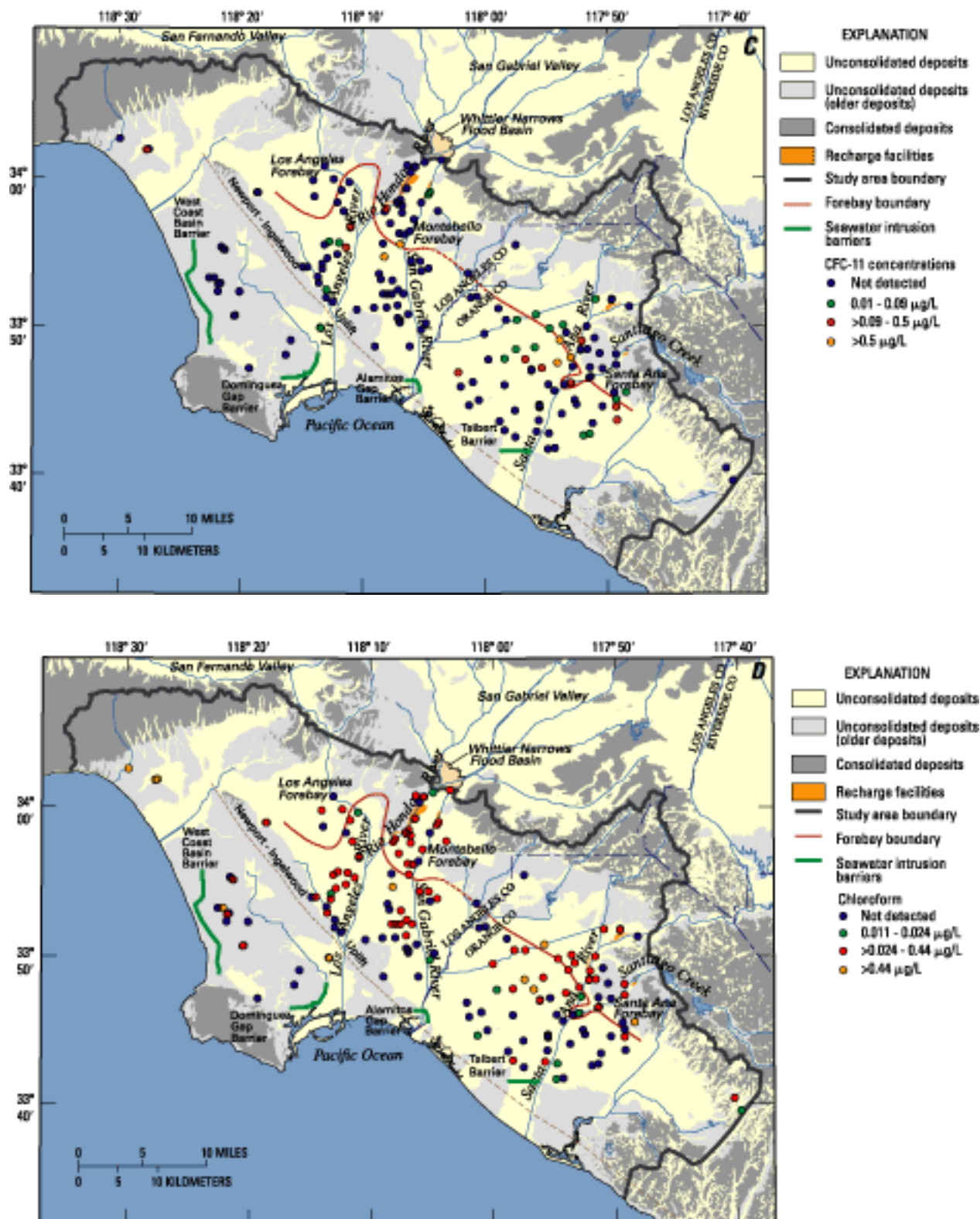


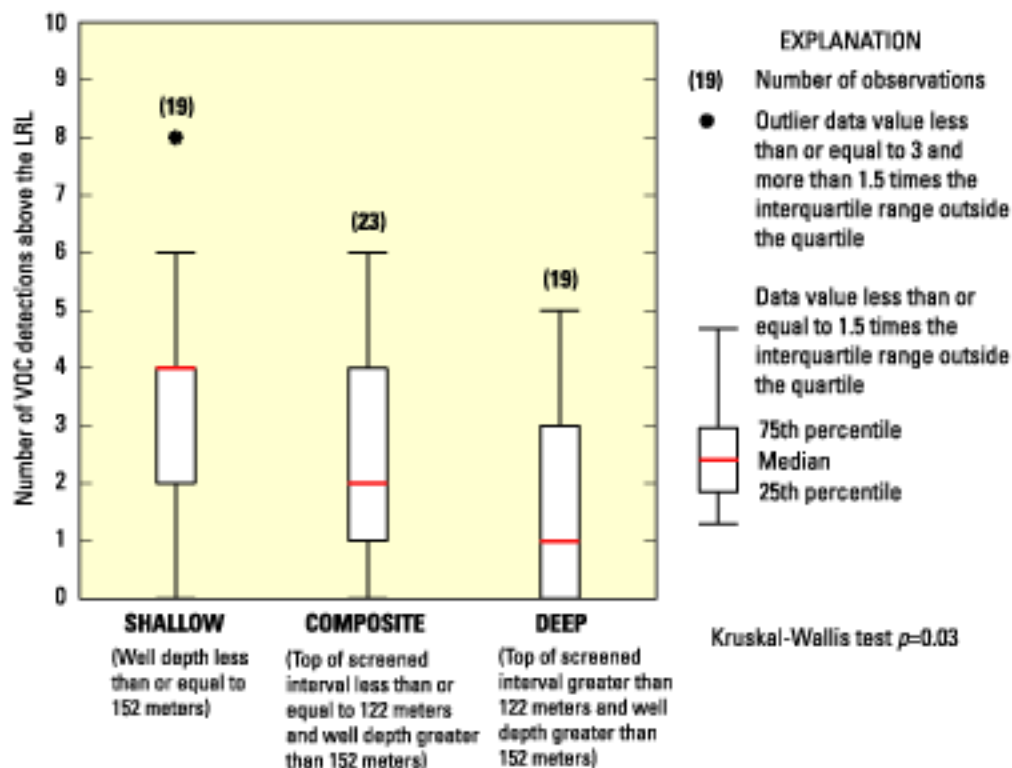
Figure 5.—Continued.

controlled by vertical movement of ground water in proximity to a well. Given that VOCs are likely to enter the ground-water system at the water table, a reasonable expectation would be that the frequency and magnitude of VOC concentrations would decrease with increased depth of a public supply well. However, this relation was not observed in the data for the entire study area. The number of VOC detections above the LRL was not significantly different ( $p = 0.72$ ; Kruskal-Wallis test) among samples from wells grouped into three depth categories—shallow, composite, and deep—and located throughout the entire study area. Conversely, the number of VOC detections above the LRL is significantly different ( $p = 0.03$ ; Kruskal-Wallis test) among samples from wells grouped by the three depth categories for the 61 wells in the forebay areas (fig. 6), and the median of the number of VOC detections above the LRL is higher in the shallow wells (4) than the deep wells (1). The number of VOC detections above the LRL is not significantly different ( $p = 0.27$ ; Kruskal-Wallis test) among samples from wells grouped by the three depth categories for the 117 wells in the pressure area. There was no difference in well depth between the forebay and pressure area. These results indicate that the greater thickness of clay

layers and other fine-grained sediment in the pressure area possibly impede the downward migration of VOCs.

The differences in the number of detections of VOCs above the LRL among the three depth categories in the forebay areas is due solely to contrasts in VOC detections among the 31 wells in the forebay of the Coastal Santa Ana Basin ( $p = 0.01$ , Kruskal-Wallis test); there are no significant differences in the number of detections of VOCs above the LRL among depth categories in the forebay in the Coastal Los Angeles Basin ( $p = 0.88$ ; Kruskal-Wallis test). The contrast in the number of VOC detections with depth in the Coastal Santa Ana Basin forebay indicates that there could be a vertical component of transport affecting the distribution in this area. Rapid vertical transport could result from several mechanisms; for example, a leaking well casing, inter-borehole flow, or local high vertical gradients from pumping. More data is necessary to determine the significance of these mechanisms and to distinguish the effects of lateral or vertical movement of ground water in the forebay.

The data indicate that VOC detections above the LRL are not uniformly distributed over the study area



**Figure 6.** Boxplot of the number of detections of volatile organic compounds above the laboratory reporting limit in samples from wells grouped by depth categories in the forebay areas of the Los Angeles physiographic basin, California. VOC, volatile organic compound; LRL, laboratory reporting limit.



(fig. 3). Most of the wells with multiple VOC detections, which also have the highest concentrations, are in the forebay areas and clustered proximal to the recharge areas. In addition, there appears to be a distance of about 10–15 km from the recharge facilities beyond which the number of VOC detections above the LRL (figs. 3 and 4) and VOC concentrations (fig. 5) decrease. The pattern of VOC distribution is related to the history of use. For example, chloroform has the longest history of use and is the most widely distributed when compared with MTBE, which has the most recent history of use and is detected at concentrations above the LRL almost exclusively in the forebay areas. This distribution and the history of introduction of the most frequently detected VOCs into the urban landscape indicate that engineered recharge and ground-water pumping are the dominant controls on the flow system; VOCs travel along radial flow paths to a distance that is indicative of the age of the recharge water or the time in which the VOC was introduced into the environment.

The data also suggests that downward vertical migration of VOCs from the water table may be a viable process for contaminating aquifers in the forebay areas but there is little evidence that the same process is active and affecting the occurrence of VOCs in many wells in the pressure areas. The significant difference in the number of VOC detections above the LRL between different depth categories in the forebay areas suggests that vertical downward migration of VOCs is a potential pathway to the capture zone of public supply wells in the Coastal Santa Ana forebay. The lack of contrast in the number of VOC detections between well depth categories basinwide and the nonuniform distribution of VOCs basinwide suggests that vertical migration is not the dominant pathway. The data are insufficient, however, to exclude the possibility that (1) VOCs traveling vertically from near-surface have not yet reached the wells or (2) VOCs are present but not detectable in the uppermost fraction of the well screens because of the mixing over the large lengths of the screened intervals. Additional data along the ground-water flow paths collected from discrete zones in the aquifer at various depths may aid in assessing the transport of VOCs to public supply wells.

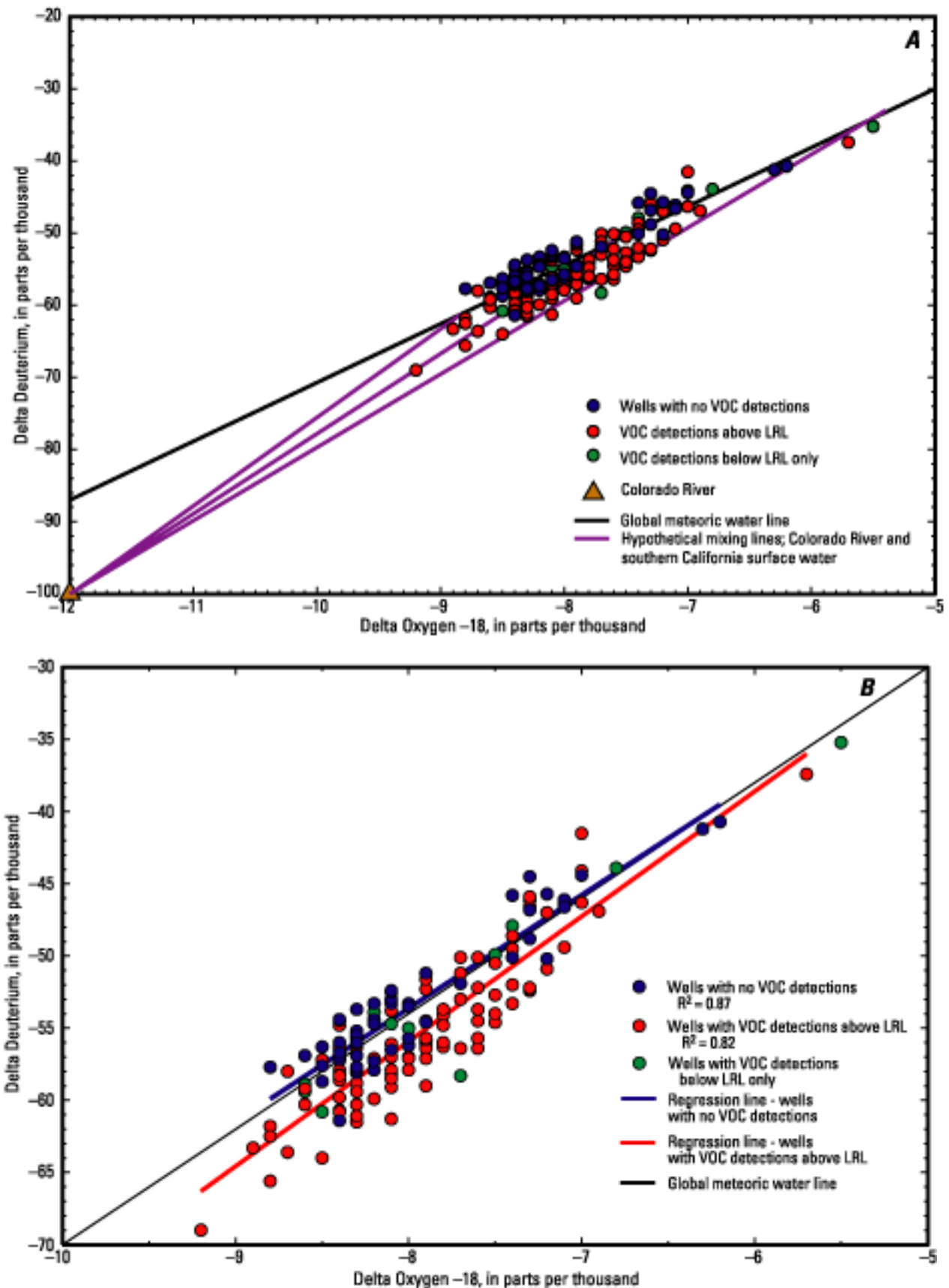
## STABLE ISOTOPE DATA RELATE SOURCE OF RECHARGE WATER TO VOC OCCURRENCE

The presence of recharge from precipitation; urban runoff; Santiago Creek; and the Santa Ana, the

San Gabriel, and the Los Angeles Rivers can be partly discerned from analysis of stable isotope ratios in ground- and surface-water samples. Oxygen-18 ( $^{18}\text{O}$ ) and deuterium (D) are naturally occurring stable isotopes of oxygen and hydrogen, respectively. The abundance of these isotopes in water is generally expressed as a ratio in delta ( $\delta$ ) notation, and on a global scale the relation between  $\delta^{18}\text{O}$  and  $\delta\text{D}$  is linear, plotting along the global meteoric water line (Craig, 1961). Deviations from the global meteoric water line can occur as a consequence of several hydrologic processes, including evaporation and mixing.

Figure 7 shows plots of the isotopic composition of water samples from active public supply wells in the Los Angeles physiographic basin. The samples are differentiated on the basis of the occurrence of VOCs: samples with no detections, samples with one or more detections above the LRL, samples with detections only below the LRL. Also shown in both figures is the global meteoric water line. In general, the ground-water samples plot along and to the right of (below) the global meteoric water line.

Figure 7A illustrates hypothetical mixing lines for mixtures of imported Colorado River water and southern California surface water. The isotopic composition of Colorado River water plots to the right of (below) the global meteoric water line owing to evaporation. The isotopic composition of southern California surface water plots over a range of values, but is consistently heavier than Colorado River water. For the purposes of illustration, three hypothetical southern California surface water end-members are considered that may represent the source of the ground-water sampled in the active public supply wells: one that is isotopically light (more negative), one that is isotopically heavy (less negative), and one that is intermediate. Each of the mixing lines illustrates the plotting positions of water samples that represent varying amounts of the Colorado River end-member and one of the southern California end-members. A sample with a relatively high proportion of Colorado River water would plot relatively close to the Colorado River end-member. A sample with a relatively low proportion of Colorado River water would plot relatively close to the global meteoric water line. Overall, mixing of imported Colorado River water with southern California surface water results in a shift in the isotopic composition away from the global meteoric water line. Along any particular mixing line, the shift is downward and to the left towards the Colorado River end-member. For a group of samples obtained from a set of



**Figure 7.** Scatter plot of the delta oxygen-18 versus delta deuterium for samples from active public supply wells in the Los Angeles physiographic basin, California, showing (A) hypothetical mixing lines for sources of recharge water to wells, and (B) regression lines for samples with no detections and with detections above the LRL. VOC, volatile organic compound; LRL, laboratory reporting limit.

mixing lines, however, the net effect is for the set of samples to plot to the right of the global meteoric water line.

The second of the two isotope plots (figure 7B) includes two regression lines: one for the samples with no VOC detections ( $R^2 = 0.87$ ), and one for the samples with VOC detections above the LRL ( $R^2 = 0.82$ ). The regression line for the samples with no VOC detections plots nearly coincident with the global meteoric water line, indicating that the source of the water in these wells is southern California precipitation and runoff. Nearly all of the wells with no VOC detections at concentrations above the LRL are located in the pressure areas, away from the forebay areas where most of the ground-water recharge occurs (fig. 3); thus, samples from wells in the pressure areas likely represent predominantly older ground water than samples from wells in the forebay areas. The ground-water samples from wells in the pressure areas with no VOC detections at concentrations above the LRL were likely from water recharged prior to the onset of intense urban development and from large-scaled engineered recharge and ground-water pumping. This source of water would likely be from natural inputs to the ground-water systems, so it would have originated from precipitation and runoff.

The regression line for the samples with VOC detections above the LRL plots below, and at an angle to, the global meteoric water line, suggesting that the water in these wells is a mixture of local sources and water that is isotopically lighter (more negative) than the local sources. The isotopically lighter water could either be Colorado River water or State Water Project water, both of which are imported to the basin and used as a source of recharge to the ground-water flow system. Overall, the regression lines suggest that the occurrence of VOCs in ground water is associated with the engineered recharge of imported surface water, which occurs in the forebay areas.

## ASSESSMENT OF RELATION BETWEEN VOC DISTRIBUTION AND POTENTIAL SOURCES OF VOCs

VOCs are widely used in urban areas and may be transported to ground water through urban runoff, atmospheric deposition and infiltration, or from other surface and below-ground sources. Potential sources of VOCs include household products, leaking fuel storage facilities, accidental spills, gasoline stations, vehicle exhaust, and industries that use VOCs as part

of manufacturing, processing, or cleaning. Lopes and Bender (1998) determined that VOCs on urban land surfaces (contributing to urban runoff) and in urban air are important sources of VOCs in drinking water. Previous studies have shown that potential sources in proximity to wells increase the likelihood that VOCs will be detected in samples of well water. Such findings indicate a component of vertical flow exists, accounting for the movement of VOCs from sources near the well to the screened interval or capture zone of the well. In this study, relations between the occurrence of potential sources near wells generally were not significantly correlated with the occurrence of VOCs in well samples. This finding further indicates that the primary factor governing the distribution of VOCs is lateral transport of VOCs from the recharge facilities and other sources in the forebay areas.

## Surface Water

The limited amount of data on current VOC concentrations in surface water that recharge the forebay area show that some of the most frequently detected VOCs in ground-water samples were also detected in surface-water samples. Sources of surface water entering the aquifer system in the Los Angeles physiographic basin are precipitation; Coast Range runoff; water from the Los Angeles, the Rio Hondo, the San Gabriel, and the Santa Ana Rivers; water from Santiago Creek; stormwater runoff; and imported and treated wastewater spread at the recharge facilities in the forebay areas and injected into wells along the sea-water intrusion barriers. The predominant sources, however, are from imported and treated wastewater spread at the recharge facilities along the Rio Hondo, the San Gabriel, and the Santa Ana Rivers. The sources and the amounts of the different sources of water used



*Santa Ana River surface-water site (photograph by Carmen Burton, U.S. Geological Survey).*

at the recharge facilities, and the quality of those recharge waters, have changed over time; however, the presence of VOCs in surface water currently used at the recharge facilities provides some information on potential sources of VOCs in ground water. As part of the NAWQA Program, the Santa Ana NAWQA River Basin study team obtained surface-water quality data for various sites along the Santa Ana River, the primary surface-water component of ground water recharge in the Coastal Santa Ana Basin part of the flow system. Surface-water quality data from the Santa Ana River presented in this section is from a site located upstream of the uppermost recharge facility in the Coastal Santa Ana Basin (fig. 1). VOCs reported in the 40 surface-water samples from this site were collected from November 1998 through December 2000.

Two VOCs were detected more frequently and at higher concentrations in the surface-water samples than in the ground-water samples (table 6). The median concentrations of all detections of MTBE and chloroform were higher in the surface-water samples (0.24 and 0.36  $\mu\text{g/L}$ , respectively) than in the ground-water samples (0.18 and 0.060  $\mu\text{g/L}$ , respectively). The maximum MTBE concentration is also higher in the surface-water samples (1.2  $\mu\text{g/L}$ ) than in the ground-water samples (0.85  $\mu\text{g/L}$ ). These data indicate that the Santa Ana River may be a potential source of these VOCs in ground water.

In contrast, current VOC occurrence in surface water cannot account for the high concentration and frequency of detection of other VOCs in ground water. The maximum concentrations of TCE and PCE in surface-water samples were over 100 times lower (estimated 0.040 and 0.080  $\mu\text{g/L}$ , respectively) than in the ground-water samples (69 and 11  $\mu\text{g/L}$ , respectively) (table 6). These VOCs were also detected about twice

as often in the ground-water samples than in the surface-water samples. Furthermore, CFC-11, the most frequently detected refrigerant in ground-water samples, was not detected in any of the surface-water samples. These are all indications that surface water alone cannot explain the concentrations of VOCs detected in the ground water.

Extrapolation of these comparisons must be made with caution for several reasons. The Santa Ana River water is only one component of the water recharged at the Coastal Santa Ana Basin recharge facilities, and, therefore, concentrations observed in the surface-water samples are not necessarily representative of all of the water directly recharged to the ground-water system. No similar VOC analyses exist for surface water recharged in the Coastal Los Angeles Basin. The VOCs detected in surface water sampled today are only an approximation of past surface-water quality, which likely varied as a complex function of urbanization, regulation, and climate, among other factors. Nonetheless, the occurrence of VOCs in air and surface water in the study area is similar to VOC occurrence reported in other urban areas in the United States (Delzer and others, 1996; Lopes and Bender, 1998; Bender and others, 2000). Although the surface-water data are limited, the high concentrations of some VOCs in the surface water suggest that additional work is needed to evaluate the potential for surface water to contribute VOCs to ground water in this area.

## Population Density

Because the number of potential VOC sources generally increases with the number of people living in an area, and population data is readily available, population density has been used to evaluate the aggregate

**Table 6.** Volatile organic compounds detected in samples from the Santa Ana River above the uppermost recharge facility in the Coastal Santa Ana Basin and from 178 active public supply wells in the Los Angeles physiographic basin, California

[E, estimated; ND, not detected; GW, Los Angeles physiographic basin active public supply wells; SW, Santa Ana River above spreading diversion below Imperial Highway near Anaheim.  $\mu\text{g/L}$ , microgram per liter]

Compound name (common name)	Percent of samples with a detection		Detected concentrations ( $\mu\text{g/L}$ )			
			Median		Maximum	
	SW	GW	SW	GW	SW	GW
Methyl <i>tert</i> -butyl ether (MTBE)	92	24	0.24	0.18	1.2	0.85
Trichloromethane (Chloroform)	100	57	0.36	0.060	0.86	11
Trichloroethene (TCE)	18	39	E 0.014	0.095	E 0.040	69
Tetrachloroethene (PCE)	15	35	E 0.010	0.14	E 0.080	11
Trichlorofluoromethane (CFC-11)	ND	20	ND	0.06	ND	8



effect of urban activities on VOC occurrence in ground water used for drinking water (Maine Bureau of Health, 1998; Squillace and others, 1999). In the current study, however, population density was only weakly related to the occurrence of VOCs. Population density for each well was determined by locating the well on a 1-km<sup>2</sup> grid derived from the 1990 census block data (Price and Clawges, 1999). The population density ranged from 89 to 8,742 people per square kilometer in the Coastal Los Angeles Basin and from 48 to 8,773 people per square kilometer in the Coastal Santa Ana Basin. Although population density is not evenly distributed across the study area, most of the wells sampled (65 percent) are located in the areas with 2,000 to 5,000 people per square kilometer.

The population density was significantly different at wells where at least one VOC was detected above the LRL than at wells where VOCs were not detected, but only in the Coastal Los Angeles Basin ( $p = 0.048$ ; Mann–Whitney test). Conversely, population density was not significantly correlated to the total number of detections of VOCs in either the Coastal Los Angeles Basin or the Coastal Santa Ana Basin ( $p = 0.55$  and  $p = 0.76$ , respectively; Spearman's rank correlation). The weak relation between the population density and the occurrence of VOCs may be due to the narrow range in population density within each area. Previous studies (Maine Bureau of Health, 1998; Squillace and others, 1999) that found significant relations between VOC occurrence and population density made comparisons across regions with large differences in population density. For example, in a state-wide assessment of MTBE and other gasoline compounds in Maine drinking water, MTBE was detected more frequently in areas with a population density above 70 people per square kilometer (Maine Bureau of Health, 1998).

Squillace and others (1999) determined that VOCs were more likely to be detected in urban land-use settings classified as more than 386 people per square kilometer, than in rural land-use settings. Squillace and others (1999) used a logistic regression model of population density to estimate the probability of detecting VOCs in ambient ground water. The population density in the Coastal Los Angeles Basin and the Coastal Santa Ana Basin is at or above the high end of the range used to validate the model, but comparison between the data from the current study and the modeled probabilities reveals that the data from this study area fall below the expected probability of detection of a VOC above 0.2 µg/L. Because of the overall high



*Photograph by Phil Contreras (U.S. Geological Survey).*

density in population in the Coastal Los Angeles Basin and Coastal Santa Ana Basin, the influence of overlying sources may reach a threshold value beyond which the impact does not increase. In this study area, the acceleration of the lateral rate of ground-water flow produced by engineered recharge and ground-water pumping may be more important in controlling the occurrence of VOCs than the proximity of the well to local overlying sources of VOCs.

In addition to the narrow range of population density in the Coastal Los Angeles Basin and the Coastal Santa Ana Basin compared with the state of Maine (Maine Bureau of Health, 1998) and the nationwide study (Squillace and others, 1999), depth to water and consequently well depths may affect whether population density can be correlated with VOC occurrence. The public supply wells in this study likely are deeper than in Maine because ground water is generally shallower in the coarse-grained aquifers of the northeastern United States. Median well depth for this study (210 m) (table 1) was more than five times greater than the median well depth for all rural and urban wells that reported construction information (40 m) in the national study (Squillace and others, 1999).

### **Leaking Underground Fuel Tank Density**

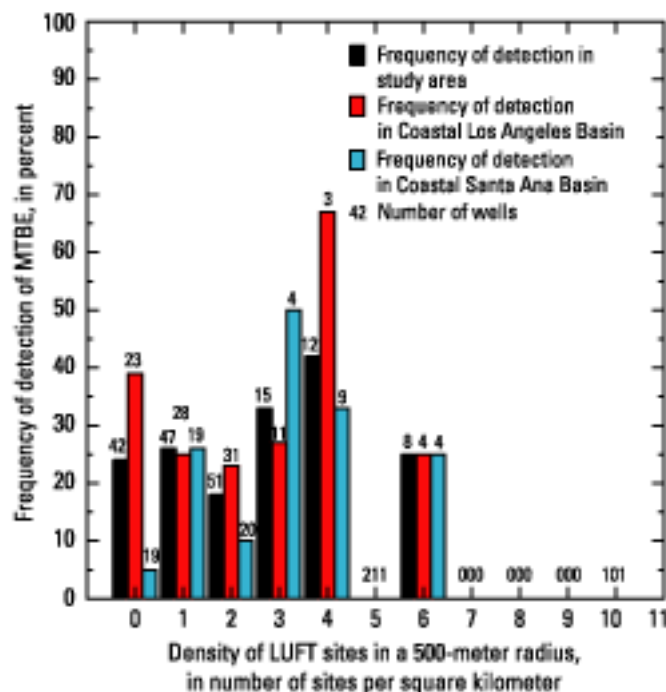
Because MTBE was widely used as a fuel oxygenate, leaking underground fuel tank (LUFT) sites are a potential source of MTBE and other gasoline compounds such as benzene, toluene, ethylbenzene, and total xylene (BTEX) in ground water used for drinking water (Moran and others, 1999; Johnson and others, 2000). A previous study found MTBE in shallow ground water at 75 percent of leaking underground storage tank (LUST) sites in California (Happel and others, 1998). The current study, however, did not find

any relation between the density of LUFT sites and the occurrence and concentration of MTBE or the number of detections of VOCs above the LRL.

The most current LUFT data were obtained in electronic files from the State Water Resources Control Board (Amy Tong, California State Water Resources Control Board, written commun., 2001). LUFT density at each well was calculated by determining the density falling within a circle centered on the well. Circles of 100, 500, and 1,000 m radius were used. For comparison, a 500-m radius is approximately equal to the California Department of Health Services (DHS) minimum radius of 1,500 ft for porous media aquifers for the 10-year time-of-travel zone as specified in the DHS Drinking Water Source Assessment and Protection Program (California Department of Health Services, 2001). The LUFT densities calculated for each radius were not significantly different between sites where MTBE was detected and sites with no MTBE detections. Further, the frequency of detection of MTBE in samples from all wells in the study area and from subsets of wells in the Coastal Los Angeles Basin and the Coastal Santa Ana Basin was not significantly correlated to LUFT density at either the 100, 500 (fig. 8), or 1,000-m radius. This data demonstrates that LUFT density is not a good predictor of the occurrence of VOCs in active public supply wells in this area.

In contrast to these findings, Squillace and Moran (2000) determined that the density of above and underground storage tanks (UST) was an effective variable in explaining the occurrence of MTBE in ambient ground water in the Northeast and mid-Atlantic regions. Univariately, or in combination with other variables, LUST density also was found to be significantly related to MTBE occurrence in certain situations. LUST density, however, was dropped out of the final multivariate logistic regression model through a stepwise elimination procedure, and ultimately was not a significant variable in estimating the probability of detecting MTBE in the final model (Michael Moran, U.S. Geological Survey, written commun., 2001).

Similar to the population density, the LUFT density does not vary widely across the Coastal Los Angeles Basin and the Coastal Santa Ana Basin. Conversely, there is a wide range of well depths (43 to 512 m) in this study (table 1). Differences in well depth or type may affect whether UST or LUFT densities are an effective variable in explaining the occurrence or frequency of detection of MTBE in ground water. The active public supply wells sampled as part of this study are likely deeper than the combination of

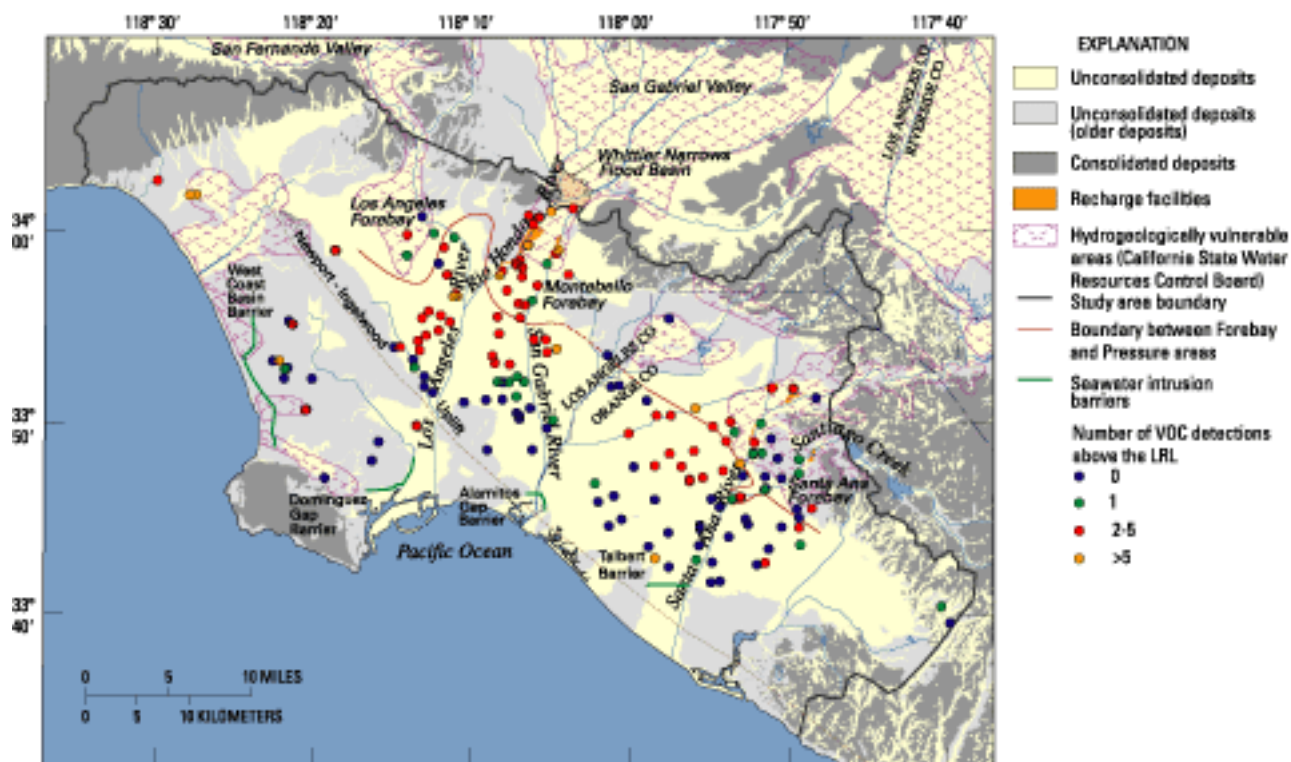


**Figure 8.** Histogram of the frequency of MTBE detections in samples from all wells in the Los Angeles physiographic basin, in samples from wells in the Coastal Los Angeles Basin, and from wells in the Coastal Santa Ana Basin and the density of leaking underground fuel tanks within a 500-meter radius around the wells. LUFT, leaking fuel tank; MTBE, methyl *tert*-butyl ether.

shallow monitoring wells, private wells, and municipal wells sampled in the Northeast and mid-Atlantic regions as part of the Squillace and Moran (2000) study.

## Hydrogeologically Vulnerable Areas

The influence of hydrogeology on VOC occurrence can be illustrated by evaluating the relative susceptibility of aquifers to potential contamination. The relative susceptibility—that is, the ease with which a contaminant present at the land surface will migrate into an aquifer—of the surficial aquifers in California have been qualified into two general categories (Jan Stepak, California State Water Resources Control Board, written commun., 2000): (1) hydrogeologically most susceptible or hydrogeologically vulnerable areas, and (2) other areas. About 10 percent of the study area is designated as hydrogeologically vulnerable. This area is generally coincident with the engineered recharge facilities and along the upper reaches of the Los Angeles, the San Gabriel, and the Santa Ana Rivers (fig. 9). The data from this study indicate that the distinction between hydrogeologically vulnerable areas and other areas does not explain the occurrence of VOCs, whereas the



**Figure 9.** Number of detections of volatile organic compounds in samples from active public supply wells in the Los Angeles physiographic basin, California, overlain by the California State Water Resources Control Board's hydrogeologically vulnerable area. VOC, volatile organic compound; LRL, laboratory reporting limit.

delineation of the forebay areas explains differences in VOC occurrence and hence may provide a reasonable approximation of areas hydrogeologically vulnerable to current contamination.

Thirty-three of the 178 wells sampled were located in the hydrogeologically vulnerable areas (fig. 9). About 73 percent of these wells had one or more detections above the LRL, a frequency of VOC detection slightly higher than the samples from wells located in the areas designated as other (58 percent); however, the number of VOC detections above the LRL are not significantly different between the hydrogeologically vulnerable and other areas ( $p = 0.12$ ; Chi-square test).

Although the high overall frequency of VOC detection above the LRL in the hydrogeologically vulnerable areas is consistent with this area's classification as most susceptible to potential contamination, the frequency of VOC occurrence is the same or greater in areas designated as other areas. For example, 45 percent of the MTBE detections, which represents some of the most recent contamination in this area (and thus the shortest travel times), were in wells outside of the hydrogeologically vulnerable areas.

This lack of distinction between hydrogeologically vulnerable and other areas is evidence that the acceleration of the lateral rate of ground-water flow produced by the engineered recharge and ground-water pumping in the Coastal Los Angeles Basin and the Coastal Santa Ana Basin is a more important factor in the occurrence of VOCs in active public supply wells than the surficial features used for mapping vulnerability. This engineered acceleration implies that areas downgradient of the recharge facilities are susceptible to contamination by any contaminant that will persist for decades.

The forebay areas represent a more consistent designation of susceptibility in the study area, possibly because they more closely reflect the zones where ground water is more likely to migrate vertically compared with the pressure areas where clay layers are more extensive and vertical migration of ground water is impeded. Sixty-one wells sampled in this study are located within the forebay, and 79 percent have one or more detections above the LRL. The number of VOC detections above the LRL is significantly different in wells in the forebay areas and in close proximity to the recharge facilities than in wells in the pressure

areas at greater distances from the recharge facilities ( $p = 0.0008$ , Kruskal-Wallis test), and the median number of VOC detections above the LRL is higher in samples from wells in the forebay areas (3) than in samples from wells in the pressure areas (1). This relation is slightly stronger when the West Coast Basin wells, which are hydrogeologically isolated from the forebay areas or recharge facilities, are removed from the data set ( $p = 0.0005$ , Kruskal-Wallis test). Only one of the wells outside the forebay area had a concentration of MTBE above the LRL, whereas 23 wells inside the forebay area had a MTBE concentration above the LRL (fig. 5A). Unlike MTBE, the concentrations of VOCs in use for decades, such as CFC-11, CFC-113, chloroform, PCE, and TCE, are not different between the forebay and the pressure areas, and the detection rates are similar.

The overall lack of correlation between population and LUFT density on the land surface and the occurrence and distribution of VOCs in active public supply wells in this study suggests that vertical migration of contaminants is not a dominant process outside the susceptible forebay areas, as evidenced by the higher number of VOC detections and the higher concentrations of MTBE in the forebay area. Although VOCs are detected in wells outside the forebay areas, these wells are further from the source of recharge and reflect a longer time of travel, as evidenced by lower MTBE concentrations. While the forebay areas may be the most susceptible to current contamination, the presence of compounds in use for decades at similar concentrations both inside and outside the forebay areas indicate that the pressure areas are susceptible to downgradient migration of persistent contaminants recharged upgradient in the forebay areas.

## SUMMARY AND CONCLUSIONS

Results of sampling untreated ground water from 178 active public supply wells in the Coastal Los Angeles and Coastal Santa Ana Basins show that volatile organic compounds (VOC) were detected in 61 percent of the ground-water samples at concentrations above the laboratory reporting limits (LRL). Thirty-nine of the 86 VOCs analyzed were detected: 29 VOCs were detected at concentrations above the LRL, and 10 VOCs were detected only at concentrations below the LRL. The most frequently detected VOC was trichloromethane (chloroform), detected at concentrations above the LRL in 82 (46 percent) of the samples.

Trichloroethene (TCE) and tetrachloroethene (PCE) were detected at concentrations above the LRL in 50 (28 percent) and 34 (19 percent) of the samples, respectively. Methyl *tert*-butyl ether (MTBE) was detected at concentrations above the LRL in 25 (14 percent) of the samples. VOCs detected in 7 percent or more of the samples also include 1,1,1-trichloroethane (TCA); 1,1-dichloroethane; *cis*-1,2-dichloroethene; bromodichloromethane; trichlorofluoromethane (CFC-11 or Freon 11); 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113 or Freon 113); and dichloromethane. The six most frequently detected VOCs—chloroform, TCE, PCE, MTBE, TCA, and 1,1-dichloroethane—were also the most frequently detected VOCs in a wide variety of hydrogeologic conditions in ground water from urban areas across the United States.

Most VOCs were detected at low-level concentrations, with only 29 percent of the detections above 1  $\mu\text{g/L}$  (microgram per liter). Two VOCs exceeded the state and federal primary maximum contaminant level (MCL) for drinking water. TCE concentrations exceeded the MCL (5  $\mu\text{g/L}$ ) in four samples with a maximum concentration of 69  $\mu\text{g/L}$ , and PCE concentrations exceeded the MCL (5  $\mu\text{g/L}$ ) in five samples with a maximum concentration of 11  $\mu\text{g/L}$ . More than half of the remaining samples with TCE and PCE detections contained concentrations between 0.5 and 5  $\mu\text{g/L}$ . Because samples were collected prior to water treatment, sample concentrations do not represent the concentrations entering the drinking-water system.

VOC detections above the LRL are not uniformly distributed over the study area. Samples from wells in the forebay areas contained significantly more VOCs than samples from wells in the pressure area downgradient of the forebay. Samples with the most VOC detections generally are from wells located within 10–15 kilometers of the recharge facilities.

Ground water containing VOCs may be considered to be a tracer of postindustrial-aged water that recharged after the onset of intense urban development. The overall distribution of VOC detections is related to the hydrogeology and the recharge facilities in the forebay, and the distribution of individual VOCs is related to their history of use. For example, chloroform has been used since the 1920s, is the most widely distributed, and is detected at the greatest distances from the recharge facilities. In contrast, MTBE has the most recent history of use and was detected almost exclusively in the forebay areas at concentrations above the LRL.



Downward migration of VOCs from the land surface may be a viable process for contaminating aquifers in parts of the forebay areas, but there is little indication that the same process is active in the pressure area. The number of VOC detections above the LRL is significantly higher in samples from shallow wells than in samples from deep wells in the forebay areas; however, effects of the processes of lateral movement and downward vertical movement of ground water in the forebay areas cannot be separated. Detections are not significantly different when wells are grouped by depth categories in the pressure area. The lack of contrast in the number of VOC detections between wells of different depths in the pressure area suggests that downward migration from the land surface is not the dominant pathway for VOCs to travel to the capture zones of public supply wells; however, the data are not sufficient to evaluate other processes that could affect the occurrence of VOCs in public supply wells, such as mixing over the long screened intervals. Isolated occurrences of multiple VOC detections and high concentrations of some VOCs, such as TCE, in individual wells may be explained by rapid vertical transport from localized sources.

Stable isotope composition indicates that ground water containing VOCs is a mixture of local precipitation and runoff and of water that is isotopically lighter (more negative) than the local sources. The isotopically lighter water could either be Colorado River water or State Water Project water, both of which are imported to the basin and used as a source of ground-water recharge. Nearly all of the wells with no VOC detections at concentrations above the LRL are located in the pressure area and likely represent predominately older ground water than samples from wells in the forebay areas. The stable isotope data support the interpretation that VOCs in ground water are associated with the recharge facilities in the forebay areas.

Two of the most frequently detected VOCs in ground water, MTBE and chloroform, were detected more frequently and at higher concentrations in the Santa Ana River upstream from a recharge facility than in ground-water samples from active public supply wells, suggesting that the Santa Ana River may be a source of these VOCs in ground water. In contrast, the maximum concentrations and frequency of TCE and PCE detections were much higher in the ground water samples than in the Santa Ana River. However, the

Santa Ana River water is only one component of the water used in the engineered recharge facilities and these data are not necessarily representative of past surface-water quality. In addition, engineered recharge water is likely not the sole source of VOCs in the forebay or the only process by which VOCs can enter the ground-water flow system. Point and nonpoint sources may enter the flow system in the forebay areas and spread radially outward.

The location of VOC sources on the land surface, such as population density and leaking underground fuel tank (LUFT) sites, or mapped susceptibility features, do not explain VOC occurrence in the study area. Population density was only weakly related to the occurrence of VOCs. The density of LUFT sites was not related to the occurrence or the frequency of MTBE detection, or the number of detections of VOCs above the LRL. The mapped surficial areas designated as hydrogeologically vulnerable areas did not encompass the area in which most of the VOCs were detected. Rather, the delineation of the forebay areas provides a reasonable approximation of areas susceptible to current contamination.

Overall, the data show that active public supply wells in the forebay areas are more vulnerable to contamination than those in the pressure area but areas downgradient of the recharge facilities are susceptible to contamination by any contaminant that will persist for decades. The lack of correlation between population density and LUFT density on the land surface and the occurrence and distribution of VOCs in active public supply wells in this study indicates that vertical migration of contaminants is not a dominant process outside the susceptible forebay areas, and the occurrence of VOCs is controlled primarily by the direction and rate of movement of water and the hydrogeology. The overall occurrence of VOCs is not a function of localized contaminant sources or well characteristics, and rapid vertical transport, while possible, is not dominant. The acceleration of the lateral rate of ground-water flow produced by engineered recharge and ground-water pumping in the Los Angeles physiographic basin appears to be the dominant factor in controlling the distribution of VOCs in active public supply wells; thus, low-level VOCs can act as tracers of postindustrial-aged water recharged in these southern California Coastal Basins.

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