Stable Isotopes and Volatile Organic Compounds Along Seven Ground-Water Flow Paths in Divergent and Convergent Flow Systems, Southern California, 2000

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Stable Isotopes and Volatile Organic Compounds Along Seven Ground-Water Flow Paths in Divergent and Convergent Flow Systems, Southern California, 2000

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ABSTRACT compounds introduced at land surface. The

Ground water is a major source of drinking water in southern California. In an effort to understand factors influencing the susceptibility of ground water tapped by public supply wells, the U.S. Geological Survey has undertaken studies in cooperation with the California State Water Resources Control Board. The vertical and lateral distribution of stable isotopes (deuterium and oxygen-18) and volatile organic compounds (VOC) were examined along seven ground-water flow paths in three urban ground-water basins in southern California: Central Basin in Los Angeles County, Main Basin in Orange County, and Bunker Hill Basin in San Bernardino County. Forty-seven monitoring wells and 100 public supply wells were sampled.

The results of this study suggest that the direction of flow and perhaps the degree of confinement in an aquifer system are important controls on the distribution of VOCs. Groundwater flow in the Central and Main Basins in the southern California coastal plain is characterized as radially divergent, with ground-water flow directions moving outward from focused areas of recharge in the unconfined part of the aquifer system toward dispersed areas of discharge in the more confined part. In these basins, there is a volume of water containing VOCs that extends out into a volume of water containing no VOCs. This pattern suggests that radially divergent flow systems disperse VOCs in distal areas. The overall pattern also suggests that ground water in the pressure area is generally insulated from

compounds introduced at land surface. These two factors—dispersion of VOCs due to divergence of flow and insulation from land-surface inputs suggest that the susceptibility of public supply wells to surface contamination decreases with distance in radially divergent, well confined ground-water flow system.

In the inland Bunker Hill Basin, groundwater flow is characterized as radially convergent; ground-water flow directions move inward from dispersed recharge areas in the unconfined part of the aquifer system, toward an area of focused discharge in the more confined part. The number of VOCs increased and the concentrations of individual VOCs increased, or remained the same, with increasing travel distance. Methyl tert-butyl ether was detected only in wells in the confined part of the aquifer system, suggesting that the confining units present in the distal part of the Bunker Hill Basin do not prevent VOCs from reaching ground water. These results suggest that VOCs in the Bunker Hill Basin are collected and concentrated as ground water moves downgradient because of radial convergenence of flow. They also suggest that ground water in the Bunker Hill Basin has an increasing opportunity to pick up VOCs introduced at land surface as it moves along a flow path. Some of the downgradient increase in VOC occurrence and concentration may be due to pumping that selectively removes cleaner ground water, thus leaving ground water containing more VOCs in the aquifer. These two factors collection of VOCs due to convergence of flow and increasing opportunity to collect surficial contaminants perhaps due to a relative absence of

confinement—suggest that the susceptibility of public supply wells to surface contamination increases with distance in radially convergent ground-water flow systems, particularly those that are unconfined.

INTRODUCTION

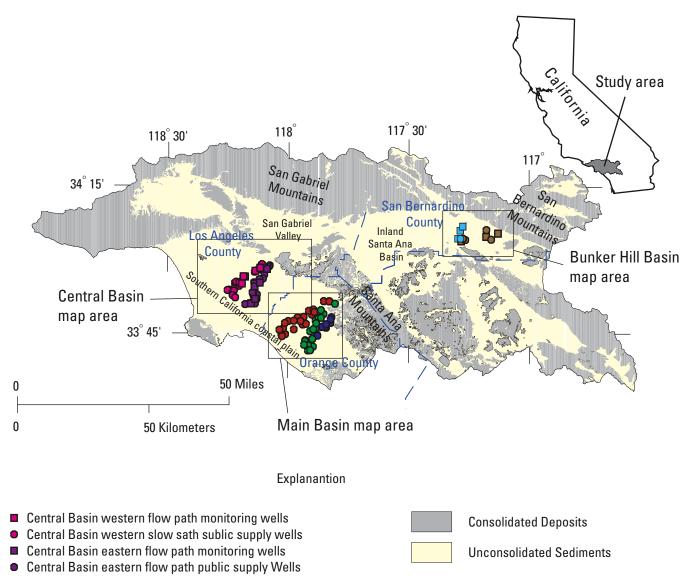
Ground water is a major source of drinking water in southern California. Some of the areas of heaviest ground-water use are in intensively urbanized areas: the Los Angeles-Orange County Coastal Plain and the San Bernardino Valley. The ground water is intensively managed in these areas: recharge has been engineered to increase the amount of water entering aquifers that supply drinking water and that have been historically depleted by pumping. While this engineering was undertaken to increase the available ground water and maintain ground-water levels, there is some concern about the effects on the quality of ground water. Compounds associated with urban land use that are known health risks, such as volatile organic compounds (VOC), are present in drinking water supplies, in some cases, over the drinking-water standards of the federal and state environmental protection agencies. Currently, no statewide program evaluates ground-water quality between the shallow, contaminated ground water near land surface (monitored by shallow monitoring wells) and the deeper zones tapped by public supply wells (monitored by California Department of Health Services).

In response to concerns about the ground-water quality, the California State Water Resources Control Board (SWRCB) has implemented the California Aquifer Susceptibility (CAS) assessment to determine the factors influencing the susceptibility of ground water tapped by public supply wells to contamination. CAS studies evaluate the distribution and occurrence of VOCs, deuterium, oxygen-18, tritium, helium-3, and helium-4 in aquifers used for public supply, and relate that distribution to ground-water flow. CAS is part of the Ambient Groundwater Monitoring and Assessment (GAMA) Program, a multiagency program that is developing a comprehensive ambient ground-water monitoring plan. Under the GAMA Program, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program is collaborating with SWRCB, the California Department of Health Services, the California Department of Water Resources, and the Lawrence Livermore National Laboratory to implement the CAS assessment.

This report examines the vertical and lateral distribution of VOCs and stable isotopes along selected ground-water flow paths from ground-water recharge areas to public supply wells in three urban groundwater basins in southern California. Tritium and helium isotope data were collected and analyzed during this study, but were not used in this analysis and are beyond the scope of this report. These data were interpreted and published by Hudson and others (2002). Relatively high numbers or concentrations of VOCs are considered indications of increased susceptibility of the ground water to contamination from land-use activities. These compounds are used in this study as tracers of ground water that has recharged since VOCs began to be used in large amounts during the 1940s. Shelton and others (2001) CAS study on the use of VOCs as tracers of ground-water movement in the southern California coastal plain found VOCs in aquifers over most of the coastal plain and determined that VOC occurrence is due primarily to lateral transport rather than vertical migration from the land surface.

Study Area

Three southern California ground-water basins were selected to assess VOC occurrence along groundwater flow paths: the Central Basin in Los Angeles County, the Main Basin in Orange County, and the Bunker Hill Basin in San Bernardino County (<u>fig. 1</u>). The Central and Main Basins are located in the southern California coastal plain, and Bunker Hill Basin is located in the inland Santa Ana Valley.



- Main Basin Santa Ana River east flow path public supply wells
- Main Basin Santa Ana River west flow path public supply wells
- Main Basin Santiago Flow path public supply wells
- Bunker Hill Basin Newmark flow path public supply wells
- Bunker Hill Basin Santa Ana River flow path public supply wells
- Bunker Hill Basin Santa Ana River flow path monitoring wells
- Bunker Hill Basin Newmark flow path monitoring wells

Figure 1. Study area, basin, and well locations in Southern California.

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The aquifers in the southern California coastal plain consist of Recent to Pleistocene unconsolidated alluvial and marine sediments. Ground-water flow in the coastal plain moves from the forebay (also referred to in this report as proximal) areas into the pressure (also referred to as distal) areas. The ground-water flow systems in the coastal plain are divergent; ground water moves radially away from a focused point of recharge (proximal) into the rest of the basin (distal). The change from forebay to pressure area is based on the relative abundance of finer-grained deposits and is not well defined. Aquifers in the forebay areas are generally unconfined and more connected to overlying land use and each other than in the pressure areas; clay and silt lenses generally do not significantly impede vertical ground-water flow. The aquifers in the pressure area consist of sands and gravels separated by relatively continuous layers of silt and clay that act as confining layers. The pressure area covers roughly 60 percent of the area in the Central Basin and in the Main Basin. Ground-water pumping is generally from about 50 to 300 m (meter) below land surface (California Department of Water Resources, 1961; Herndon and others, 1997).

The valley-fill aguifers in the inland Santa Ana Basin consist of alluvial fan and stream deposits eroded from the surrounding mountains. These deposits consist of sands and gravels with layers of silt and clay. Faults in the sediment act as barriers to ground-water flow in places, and divide the valley into several ground-water basins. The flow paths selected for this study are located in the Bunker Hill Basin, which is bounded by faults in the northeastern part of the Santa Ana Valley. The ground-water flow system in the Bunker Hill Basin is convergent; ground water moves radially away from dispersed recharge areas (proximal) toward an area of focused discharge (distal). The aquifer system in the Bunker Hill Basin is divided into upper, middle, and lower aquifers (Dutcher and Garrett, 1963). According to Dutcher and Garrett (1963, p. 63), the upper aquifer is confined in the distal area of the flow paths by a near-surface confining member, which "is discontinuous; it may be absent, thinner, or locally semipermeable in the vicinity of Warm Creek," and is mapped by Duell and Shroeder (1989, fig. 3) as cut by river channel deposits that are highly permeable. In the distal area, the confining units in the aquifer system are described by Duell and Schroeder (1989, p. 9) as "clay layers that act as leaky confining beds." The confined

(pressure) area covers roughly 20 percent of Bunker Hill Basin (Dutcher and Garrett, 1963; Duell and Schroeder, 1989).

Study Design

Ground-water flow paths originating near engineered recharge facilities were chosen on the basis of available ground-water-level data and the location of existing USGS monitoring wells in the selected ground-water basins (fig. 1). Along the flow paths in the Central and Bunker Hill Basins, 47 USGS monitoring wells at 12 sites were chosen for sampling. One hundred public supply wells were selected in all three basins from the wells sampled and described in Shelton and others (2001) and Hamlin and others (2002). Public supply wells were originally selected for those studies using a grid-based, random method (Scott, 1990) in each basin. In this report, well numbers along each flow path are ordered from upgradient to downgradient; monitoring wells at each site were given the same well number with a decimal number ordered from shallowest to deepest (for example, the shallowest monitoring well at the fifth well site along a flow path was well number 5.1). Ground-water samples collected from the USGS monitoring wells and public supply wells were analyzed for the stable isotopes deuterium (^{2}H) and oxygen-18 (^{18}O) , and for 86 VOCs. Stable isotope, VOC, well depth, and distance data were analyzed using graphical and statistical methods to determine spatial distribution and trends, and to compare VOC occurrence in three different groundwater flow systems.

Field Methods

Ground-water samples were collected from the selected wells using USGS protocols (U.S. Geological Survey, 1998) and the protocols described in Shelton and others (2001). Monitoring wells were sampled using portable, stainless-steel submersible pumps attached to Teflon tubing with stainless-steel fittings. Some public supply wells were sampled using Teflon tubing attached to a sampling point on the well discharge pipe as close to the well as possible, using brass and stainless-steel fittings; others were sampled using silicon or copper tubing and brass faucets attached to a sampling point. All equipment was cleaned after each use and stored in plastic bags, except the silicon and copper sampling lines, which were cleaned before use and then discarded after a single sampling.

Laboratory Methods

Stable isotope samples were analyzed for deuterium and oxygen-18 at the USGS Isotope Laboratory in Reston, Va., using the methods described in Epstein and Mayeda (1953) and Coplen and others (1991). Deuterium and oxygen-18 are reported as ratios per mill (%, or per thousand) of ${}^{2}H / {}^{1}H (\delta D)$ and $^{18}O / ^{16}O (\delta^{18}O)$, respectively, and are referenced to Vienna Standard Mean Ocean Water (VSMOW, 8D and δ^{18} O = 0 %). In the discussion of stable isotopes, the term "lighter" refers to waters with less deuterium and oxygen-18 (more negative per mil values), whereas the term "heavier" refers to waters that have more deuterium and oxygen-18 (less negative per mil values). VOCs were analyzed at the USGS National Water Quality Laboratory (NWQL) in Denver, Colo., using the methods described in Connor and others (1998); VOC concentrations are reported in micrograms per liter (μ g/L). All chemical constituents were determined from unfiltered water samples.

NWQL uses two thresholds for reporting analytical results: (1) laboratory reporting level (LRL), which is set to minimize the reporting of false negatives (not detecting a compound when it is actually present in a sample) to less than 1 percent, and (2) long-term method detection level (LT-MDL), which is set to minimize the reporting of false positives (reporting a detection of a compound that is not actually in the sample) to less than 1 percent (Childress and others, 1999). The LT-MDL is calculated annually from data collected throughout the year for selected analytical methods; the LRL is set at two times the LT-MDL. Detections below the LRL are reported as estimated concentrations (designated with an "E" before the value in tables and text, and shown on graphs as open symbols). For information-rich methods (including the VOC method used in this study), detections below LT-MDL also are reported as E-values. E-values also result for detections outside the range of calibration standards, for detections that did not pass laboratory quality-control analyses, or from diluted samples.

Quality Control

Quality-control (QC) samples were collected to evaluate the bias of VOC data introduced during sample collection, processing, transportation, and laboratory analysis. Blank samples (blanks) of organicfree water were analyzed by the same methods used for ground-water samples. Two types of blanks were used in this analysis: field and source solution. Twenty-two pairs of field and source solution blanks were collected, which is 15 percent of the number of ground-water samples collected. Field blanks measure the overall bias of the water-chemistry data. Source-solution blanks measure bias in the field blanks. QC sample data collected in 2000 in each of the three groundwater study areas described in this report were used for this QC analysis.

Field blanks were collected using specially prepared water that was certified to contain less than the LRL of the selected constituents. The blank water was pumped or poured through clean sampling equipment, processed, and analyzed using the same methods as for the ground-water samples. Because of the variation in VOCs detected in field blanks, the data was grouped by basin and by well type for QC analyses. The concentrations detected in public supply well field blanks were compared to the concentrations detected in ground-water samples from the same basin. Concentrations detected in monitoring well field blanks were compared to concentrations detected in groundwater samples from monitoring wells in the same basin.

A constituent was of potential QC concern when it was detected in one or more field blanks, in groundwater samples, and when the minimum concentration detected in ground-water samples was lower than the maximum concentration detected in the field blanks. When a VOC was of potential OC concern, the concentration detected in the field blank was compared with the concentration detected in the associated source-solution blank. The VOC was not of OC concern in the field blanks when the VOC was also detected in the source solution at a similar concentration. If the VOC was not detected in the source solution, the concentration in the field blank then was compared with the concentrations detected in ground-water samples collected before that blank sample. Detections in the field blank that are the same or higher than previous ground-water detections indicate carry-over contamination-introduction of a

VOC into a new sample from the sample equipment, in spite of cleaning, after sampling a well with a detection of that VOC. If carry-over contamination was identified as the cause of the detection in the field blank, subsequent ground-water samples and field blanks also were evaluated for evidence of carry-over contamination. For ground-water detections determined to be from carry-over contamination, a less-than LRL value was substituted for the measured concentration and counted as a nondetection.

Contamination was assumed to be limited to the blank and not to have affected the ground-water samples when a detection in a blank was at or above the LRL and accompanied by many nondetections in ground-water samples obtained prior to and subsequent to the field-blank. When detections in a blank could not be related to the source solution, to carry-over contamination, or to contamination limited to the blank, all ground-water samples with concentrations lower than the maximum blank value were considered contaminated.

On the basis of these criteria, ground-water data for the following compounds may have been affected by sample contamination in this study: benzene, ethyl benzene, methyl benzene (toluene), tetrachloroethene (PCE), and trichloroethene (TCE). Detections of benzene and ethyl benzene in one ground-water sample from the Bunker Hill Basin were determined to be from carry-over contamination; the LRLs were substituted in the results and counted as nondetections. Toluene was detected in blank samples at similar concentrations to ground-water samples in all three study areas; therefore, toluene detections in ground water are summarized, but were not used for detection frequency calculations or statistical analyses. Detections of PCE and TCE at monitoring well sites in the Central Basin were determined to be carry-over contamination from high concentrations in previous ground-water samples. For these wells, the measured values that were less than or equal to the highest blank detection (0.01 μ g/L for PCE and $0.054 \mu g/L$ for TCE) were converted to a less-than value at the LRL and counted as nondetections.

Data Analysis Methods

Distance along each flow path was measured downgradient from the first well on each cross section in the Central and Main Basins. In the Bunker Hill Basin, the distance downgradient was measured from a point of flow path convergence selected on the San Jacinto Fault. The depth used for statistical tests was the depth to the midpoint of well openings. The terms "depth" and "well depth" refer to the depth from land surface to the midpoint of well openings. Inferences of ground-water age (time since recharge) were made on the basis of presence or absence of VOCs and position along a flow path. Ground water containing VOCs was inferred to have at least partially recharged since the 1940s. Ground water that was closer to a recharge area or shallower in the aquifer system was inferred to be younger than ground water that was further from a recharge area and deeper in the aquifer system. In the Main and Bunker Hill Basins, locations of wells were compared to known locations of high TCE concentrations (TCE plumes) in ground water that resulted from a point-source contamination (Orange County Water District, 1991a, fig. 9; Orange County Water District, 1991b, fig. 7; Wildermuth Environmental, Inc., 2000b, fig. 3). In this report, wells in the mapped area of the TCE plumes are considered associated with the TCE plumes; well openings may not be at the same depth as the TCE plume in the ground water.

The four ways used in this investigation to count the number of VOC detections are based on the LRLs set by NWQL. The first count is a total of all VOC detections, regardless of whether the detected concentrations were above or below LRL. The second count is the number of only those VOC detections above LRL; this is the most reliable count of VOC detections to use for comparison between wells, as the certainty of detecting a VOC at the LRL is 99 percent or greater. The third count is the number of VOC detections below LRL. The fourth count is a new variable defined in this report as the VOC score.

The VOC score is a number with the count of VOC detections above LRL put to the left of the decimal point, and the count of detections below LRL put to the right of the decimal point. For example, a VOC score of 3.2 means that 3 VOCs were detected in that sample at concentrations above the LRL and 2 VOCs were detected in that sample at concentrations below the LRL. This way of counting gives the number of detections above LRL 10 times the weight of detections below LRL.

The one-tenth weight given to the below LRL detections is subjective. In all cases where the different counts of VOC detections were statistically tested, the

strength of the tests were nearly the same for the VOC score, the number of detections above LRL, and the total number of VOCs detected. The number of detections below LRL did not correlate with any of the variables tested. VOC score is used in this report as a method to show and classify all of the VOC detections when plotting the data. When detections were censored at the LRL, much of the information on VOC occurrence and distribution was lost, as roughly half of all the VOC detections in the investigation were below LRL. In this report, VOC score will be used to analyze the number of VOC detections in each well and along flow paths.

The VOCs selected for comparison in this report were trichloromethane (chloroform), a by-product of water chlorination; methyl-*tert*-butyl-ether (MTBE), a gasoline additive; trichloroethene (TCE), a solvent widely used in metal degreasing; tetrachloroethene (PCE), a solvent widely used in textile industry and dry cleaning; and trichlorofluoromethane (CFC-11), a refrigerant. These compounds are among the most frequently detected VOCs in ground water in the study areas (Shelton and others, 2001; Hamlin and others, 2002).

Spatial patterns in the distribution of VOC detections (number and concentration) were identified by graphical analysis. Statistical tests were used to identify significant monotonic trends and relations in the data. Nonparametric tests were used because many of the data have nonnormal distributions and many outliers. For statistical tests on data with censored values (less-than values), three values were substituted for the less-than value: zero, the LT-MDL, and half of the LT-MDL. In all tests, the results were nearly identical. On graphs, detected values are plotted at the measured concentrations; nondetections are plotted at half of the LT-MDL. The results of statistical tests are reported using half of the LT-MDL. For constituents with two LT-MDLs, the lower value was raised to the higher value. Raised LRLs were discarded and not used for data plotting or analysis.

The Spearman rank correlation test was used to determine the degree of correlation between two variables; the assumption, or the null hypothesis, is that there is no correlation (Helsel and Hirsch, 1995). The linear correlation coefficient rho (Spearman's rho) was computed on the ranks of the data; rho varies between -1 and 1, with values closer to -1 indicating an inverse correlation, values closer to 1 indicating a positive correlation, and values closer to 0 indicating no

correlation (Helsel and Hirsch, 1995). The rank-sum test (also known as the Mann–Whitney or Wilcoxon rank-sum test) was used to determine whether one group of data had statistically different values from a second group; the null hypothesis is that the groups are the same (Helsel and Hirsch, 1995).

A significance level of 90 percent was used for all statistical tests in this report. For each statistical test, the *p*-value was used to determine the significance of the test. The *p*-value is the probability of the null hypothesis being true on the basis of the data used (Helsel and Hirsch, 1995). All tests resulting in a *p*value equal to or less than 0.10 were considered to significantly show that the null hypothesis was not true. The terms "significant" and "correlation" are always used in terms of statistical results.

Accessing Data

Users of the data discussed in this report are encouraged to access information through the USGS's National Water Information System (NWIS) web page (NWISWeb) located at http://water.usgs.gov/nwis/. NWISWeb serves as a public interface to the USGS NWIS database of site information, real-time, groundwater, surface-water, and water-quality data collected from locations throughout the 50 states and elsewhere. Data on NWISWeb are updated from the NWIS database on a regularly scheduled basis. Users can retrieve data by category, geographic area, specific location, and parameter field. NWISWeb is able to output data tables (in HTML and ASCII tab formats), water-level and water-quality graphs, and to develop site-selection lists. Additional site and sample information not contained in NWIS are kept on file at the USGS offices in San Diego and Sacramento, California. (Formal requests for specific data should be directed to the U.S. Geological Survey, California District Office, Hydrologic Data Center, 6000 J Street, Sacramento, California, 95819-6129.)

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CENTRAL BASIN, LOS ANGELES COUNTY

Hydrogeology

Two ground-water flow paths were selected in the Central Ground Water Basin of the Los Angeles Coastal Plain (California Department of Water Resources, 1961), hereinafter referred to as the Central Basin; both flow paths begin in the Montebello forebay area upgradient of the Rio Hondo and San Gabriel recharge facilities and end in the Central Basin pressure area upgradient of the Newport-Inglewood fault zone (fig. 2). The western flow path is 21 km (kilometer) long and is located near and west of the Rio Hondo and the Los Angeles Rivers. The eastern flow path is 22 km long and is located near and west of the San Gabriel River. Both flow paths were selected to follow groundwater gradients based on water-level contours (fig. 3) (Water Replenishment District of Southern California, 2000).

Historically, about two thirds of ground-water recharge to the Central Basin was from the Rio Hondo and the San Gabriel Rivers as they entered the basin at the Whittier Narrows from the inland San Gabriel Valley to the northeast; minor recharge resulted from ground-water flow through the Whittier Narrows (California Department of Water Resources, 1961). Other sources of recharge include irrigation, local precipitation, and runoff from the surrounding hills. Ground-water recharge has been engineered since the 1930s at recharge facilities on the Rio Hondo and San Gabriel Rivers southwest of the Whittier Narrows (Water Replenishment District of Southern California, 2001). A variety of water sources have been used historically for engineered recharge, including storm flow and treated wastewater from the San Gabriel Valley and imported water from northern California and the Colorado River (Water Replenishment District of Southern California, 2001). Nearly all ground-water discharge from the basin is by pumping from the forebay and pressure areas (Water Replenishment District of Southern California, 2001).

Ground-water levels measured in wells tapping the main pumping zone range from more than 40 m above sea level near the recharge facilities, to more than 20 m below sea level near the Newport–Inglewood fault zone (fig. 3) (Water Replenishment District of Southern California, 2000). The water-level contour pattern in most of the Central Basin is semicircular and centered on the Whittier Narrows. The ground-water flow system in the Central Basin is divergent; ground water moves radially away from a common area of recharge below the Whittier Narrows into the rest of the basin.

The two flow paths for the 68 wells sampled in the Central Basin (table 1) begin at a well upgradient of the Rio Hondo and the San Gabriel recharge facilities (fig. 2). Twenty-five sites—23 are public supply wells and 2 are USGS monitoring sites with 4 to 6 individual wells of varying depths—were on the western flow path; 33 wells were sampled (fig. 2). Twenty-two sites—19 are public supply wells and 3 are USGS monitoring sites with 5 to 6 individual wells of varying depths-were on the eastern flow path; 36 wells were sampled. Geologic, hydrologic, and additional waterquality data from the USGS monitoring wells are described in Land and others (2002). The wells on the western flow path ranged from 49 to 409 m deep, and wells on the eastern flow path ranged from 27 to 366 m deep. There was no significant difference between well depths or distances on the western and eastern flow paths (table 2) and no correlation between distance and well depth on either Central Basin flow path (table 3).

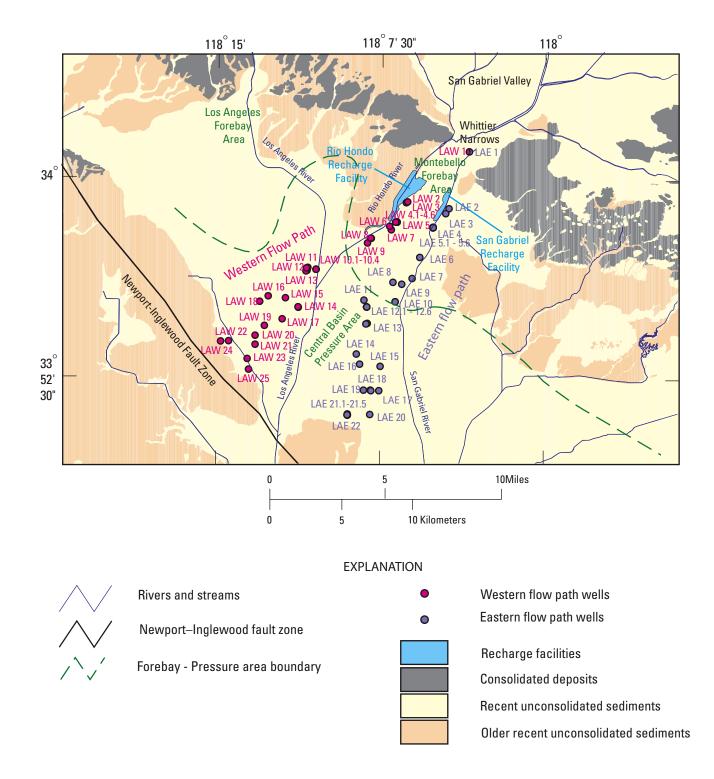
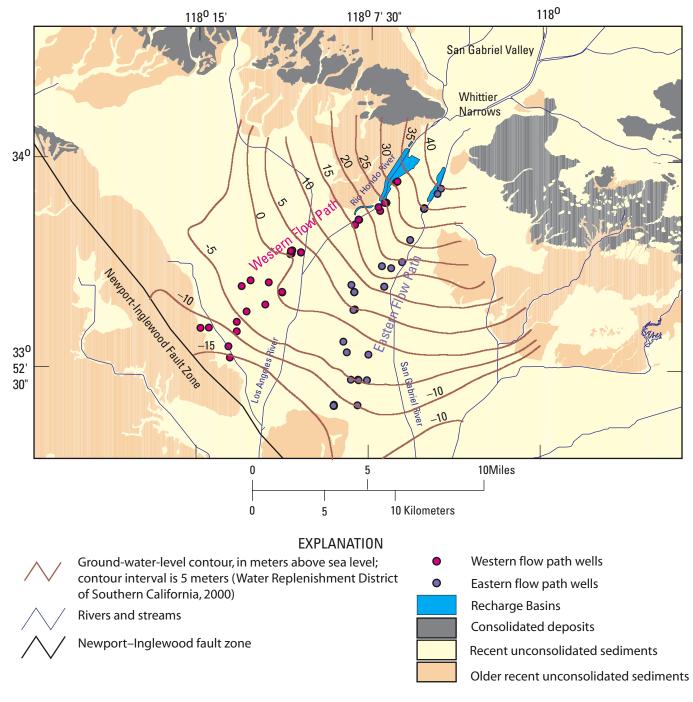


Figure 2. Locations of the western and eastern ground-water flow paths, wells samples, and major hydrologic features of the Central Basin, Los Angeles County, California.





Site Number	USGS Site ID	State well number	Distance down gradient, in kilometers	Depth to middle of openings, in meters below land surface
LAW 1	340112118033701	002S011W05N004S	0.0	87
LAW 2	335914118062501	002S012W23B004S	5.6	133
LAW 3	335915118062401	002S012W23B008S	5.7	130
LAW 4.1	335829118065206	002S012W26D014S	7.1	46
LAW 4.2	335829118065205	002S012W26D013S	7.1	88
LAW 4.3	335829118065204	002S012W26D012S	7.1	134
LAW 4.4	335829118065203	002S012W26D011S	7.1	219
LAW 4.5	335829118065202	002S012W26D010S	7.1	280
LAW 4.6	335829118065201	002S012W26D009S	7.1	341
LAW 5	335826118164601	002S012W26D007S	7.6	127
LAW 6	335821118070801	002S012W27A005S	7.7	203
LAW 7	335817118070701	002S012W27H001S	7.8	154
LAW 8	335752118080201	002S012W28J006S	9.3	194
LAW 9	335745118081701	002S012W28Q001S	9.6	135
LAW 10.1	335642118103705	003S012W06B008S	13.6	70
LAW 10.2	335642118103704	003S012W06B007S	13.6	175
LAW 10.3	335642118103703	003S012W06B006S	13.6	280
LAW 10.4	335642118103702	003S012W06B005S	13.6	405
LAW 11	335643118105801	003S012W06D004S	14.1	207
LAW 12	335645118105601	003S012W06D002S	14.2	212
LAW 13	335635118110001	003S012W06D001S	14.3	207
LAW 14	335515118112101	003S013W12J001S	16.4	209
LAW 15	335537118115701	003S013W12E004S	16.6	149
LAW 16	335542118124701	003S013W11C001S	17.3	89
LAW 17	335452118121601	003S013W13D001S	17.8	169
LAW 18	335529118130901	003S013W11E001S	18.0	188
LAW 19	335433118125701	003S013W14F015S	19.1	177
LAW 20	335411118132001	003S013W15R001S	19.9	75
LAW 21	335350118132001	003S013W22H002S	20.5	74
LAW 22	335357118143501	003S013W21B001S	21.5	94
LAW 23	335318118134401	003S013W22Q004S	21.5	98
LAW 24	335356118145801	003S013W21C006S	21.9	83
LAW 25	335302118072201	003S013W27G001S	22.0	145
LAE 1	340112118033701	002S011W05N004S	0.0	87
LAE 2	335859118043101	002S011W19F001S	4.3	114
LAE 3	335849118043701	002S011W19M001S	4.7	134
LAE 4	335817118051301	002S012W25G001S	5.9	105
LAE 5.1	335818118051206	002S012W25G008S	5.9	34
LAE 5.2	335818118051205	002S012W25G007S	5.9	75
LAE 5.3	335818118051204	002S012W25G006S	5.9	101
LAE 5.4	335818118051203	002S012W25G005S	5.9	174
LAE 5.5	335818118051202	002S012W25G004S	5.9	256
LAE 5.6	335818118051201	002S012W25G003S	5.9	363
LAE 6	335712118054901	002S012W36M006S	8.1	131
LAE 7	335810118070201	003S012W02H004S	9.6	100

 Table 1.
 Wells sampled in Central Basin, Los Angeles County, California, 2000.

Site Number	USGS Site ID	State well number	Distance down gradient, in kilometers	Depth to middle of openings, in meters below land surface
LAE 8	335609118064001	003S012W02L001S	10.4	186
LAE 9	335612118070101	003S012W03J001S	10.7	136
LAE 10	335529118065501	003S012W11E001S	11.6	149
LAE 11	335532118082401	003S012W09G001S	13.0	152
LAE 12.1	335517118081306	003S012W09J006S	13.2	30
LAE 12.2	335517118081305	003S012W09J005S	13.2	79
LAE 12.3	335517118081304	003S012W09J004S	13.2	116
LAE 12.4	335517118081303	003S012W09J003S	13.2	180
LAE 12.5	335517118081302	003S012W09J002S	13.2	290
LAE 12.6	335517118081301	003S012W09J001S	13.2	360
LAE 13	335440118081101	003S012W16H001S	14.4	170
LAE 14	335330118083901	003S012W21L001S	16.6	78
LAE 15	335209118082001	003S012W33B001S	17.2	190
LAE 16	335313118083101	003S012W28C001S	17.3	44
LAE 17	335208118073801	003S012W34F001S	18.9	322
LAE 18	335209118080101	003S012W33A007S	19.1	190
LAE 19	335301118073401	003S012W27C002S	19.1	255
LAE 20	335108118080301	004S012W04J003S	20.7	100
LAE 21.1	335112118090406	004S012W05H010S	20.9	24
LAE 21.2	335112118090405	004S012W05H009S	20.9	46
LAE 21.3	335112118090404	004S012W05H008S	20.9	88
LAE 21.4	335112118090403	004S012W05H007S	20.9	140
LAE 21.5	335112118090402	004S012W05H006S	20.9	198
LAE 22	335113118090801	004S012W05J001S	21.0	229

Table 1. Wells sampled in C	entral Basin, Los Angeles County	, California, 2000—Continued
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[VOC, volatile organic compound]	
Variable	Rank-sum test <i>p</i> -value
Distance	0.71
Depth to top of openings	0.96
Depth to mid-point of openings	0.47
Depth to bottom of openings	0.23
δ Oxygen-18	0.17
δ Deuterium	0.45
VOC Score	² 0.03
Number of detections above LRL	² 0.03
Total number of VOCs detected	¹ 0.08
Trichloromethane (Chloroform)	³ 0.004
Tetrachloroethene (PCE)	² 0.02
Trichloroethene (TCE)	0.30
1,1-Dichloroethane	² 0.03
Methyl <i>tert</i> -butyl ether (MTBE)	0.49
cis-1,2-Dichloroethylene	² 0.05
Chloromethane	³ 0.006
1,1,1-Trichloroethane	¹ 0.10
Trichlorofluoromethane (CFC-11)	0.89
1,1-Dichloroethylene	0.35
Bromodichloromethane	0.22
Carbon disulfide	0.57
1,4-Dichlorobenzene	0.62
Dichlorodifluoromethane	¹ 0.09
trans-1,2-Dichloroethylene	0.98
1,1,2-Trichlorotrifluoroethane	0.98
Diisopropyl ether	0.18
Benzene	0.17
Dichloromethane	0.13
1,2-Dichloroethane	0.35
Dibromochloromethane	0.35
Ethylbenzene	0.31
Isopropylbenzene	0.35
m- and p-Xylene	0.31

 Table 2.
 Statistical differences between the western and eastern ground-water
 flow paths, Central Basin, Los Angeles County, California, 2000.

 $\label{eq:green} \begin{array}{l} ^1 \mbox{ blue, } p = 0.10 \mbox{ to } 0.06 \\ ^2 \mbox{ green, } p = 0.05 \mbox{ to } 0.02 \\ ^3 \mbox{ yellow, } p = 0.01 \mbox{ to } < 0.0001 \end{array}$

Table 3. Statistical correlations along ground-water flow paths in the Central Basin, Los Angeles County, California, 2000.

[n, number of ground-water samples]

		Western Flow Path	h, n = 33		Eastern Flow Pat	h, n = 36
Variable	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlation	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlatior
Correlations with distance down gr	adient:			1		
Depth to top of openings	0.23	-0.21	No	0.30	0.18	No
Depth to mid-point of openings	0.47	-0.13	No	0.73	0.06	No
Depth to bottom of openings	0.65	-0.08	No	0.77	-0.05	No
δDeuterium	² 0.04	² 0.39	Positive ²	² 0.05	² 0.34	Positive ²
δOxygen-18	0.24	0.22	No	0.70	-0.07	No
VOC Score	¹ 0.07	¹ -0.32	Inverse ¹	³ 0.0002	³ -0.61	Inverse ³
Number of detections above LRL	0.07	-0.32	No	³ 0.0002	³ -0.62	Inverse ³
Total number of VOCs detected	0.13	-0.27	No	³ 0.0005	³ -0.59	Inverse ³
Trichloromethane (Chloroform)	0.86	-0.03	No	² 0.04	² -0.35	Inverse ²
Methyl <i>tert</i> -butyl ether (MTBE)	³ <0.0001	³ -0.75	Inverse ³	³ <0.0001	³ -0.84	Inverse ³
Trichloroethene (TCE)	0.95	0.01	No	² 0.02	² -0.39	Inverse ²
Tetrachloroethene (PCE)	0.92	0.02	No	³ 0.004	³ -0.48	Inverse ³
Trichlorofluoromethane (CFC-11)	0.72	0.06	No	0.52	-0.11	No
Correlations with depth to the mid-	point of opening	s:				
Distance down gradient	0.47	-0.13	No	0.71	0.06	No
δDeuterium	³ 0.0002	³ -0.70	Inverse ³	0.51	-0.12	No
δOxygen-18	³ <0.0001	³ –0.79	Inverse ³	0.84	-0.04	No
VOC Score	0.19	0.23	No	0.85	-0.03	No
Number of detections above LRL	0.28	0.19	No	0.91	-0.02	No
Total number of VOCs detected	¹ 0.09	¹ 0.30	Positive ¹	0.97	-0.01	No
Trichloromethane (Chloroform)	³ 0.008	³ 0.47	Positive ³	0.74	0.06	No
Methyl tert-butyl ether (MTBE)	0.34	-0.17	No	0.83	-0.04	No
Trichloroethene (TCE)	0.88	0.03	No	0.66	-0.07	No
memoroeulene (TCE)						
Tetrachloroethene (PCE)	$^{1}0.07$	¹ 0.32	Positive ¹	0.55	-0.10	No

¹ blue, p = 0.10 to 0.06 ² green, p = 0.05 to 0.02 ³ yellow, p = 0.01 to < 0.0001

Stable Isotopes

A plot of δ^{18} O in relation to δ D for the western and eastern Central Basin ground-water flow paths is shown in figure 4; ground-water values plot along and slightly below the Global Meteoric Water Line (Craig. 1961). Stable isotope values from both Central Basin flow paths were statistically the same (<u>table 2</u>). Along both flow paths, δD showed a significant increase with distance (table 3). No correlation was found between δ^{18} O and distance. Along both flow paths, δD showed a significant increase with distance, and no correlation was found between δ^{18} O and distance (table 3). However, statistical differences were found between the flow paths in correlations with depth: along the western flow path δD and $\delta^{18}O$ showed an inverse correlation with depth, while no correlation was found on the eastern flow path between depth and δD , or between depth and $\delta^{18}O$ (table 3). A more detailed analysis of stable isotopes in the Central Basin indicates a mixture of sources to ground water in the Central Basin and differences between the eastern and western flow paths (M.T. Land, U.S. Geological Survey, written comm., 2002). However, these differences are not greater than the overall range of values, which is in contrast to the stable isotope values along flow paths in the Main and Bunker Hill Basins.

Volatile Organic Compounds

Sixteen VOCs were detected at concentrations above LRL in ground water along the Central Basin flow paths; an additional 8 VOCs were detected at concentrations only below LRL (<u>table 4</u>). Eighty-four percent (57 of 68) of the wells sampled in the Central Basin had one or more detections of any VOC above the LRL. Four percent (3 of 68) of wells had detections of VOCs only below LRL, and 15 percent (10 of 68) of the wells had no VOC detections.

Three VOCs were detected at concentrations above a federal or state maximum contaminant level (MCL) (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001): PCE, TCE, and *cis*-1,2-dichloroethylene (<u>table 4</u>). Most of the VOCs detections were well below their respective MCLs; 62 percent of all detected VOC concentrations were less than 1 percent of the MCL.

Chloroform, TCE, and PCE were the most frequently detected compounds in the Central Basin. The five compounds discussed in this report (chloroform, MTBE, TCE, PCE, and CFC-11), were all detected above LRL on both flow paths, and are among the 10 most frequently detected compounds (<u>table 5</u>).

VOC Score

VOC scores were significantly higher on the western flow path than on the eastern flow path (<u>table 2</u> and <u>fig. 5</u>). VOC score showed a slight statistical decrease with distance on the western flow path and strong statistical decrease with distance on the eastern flow path (<u>fig. 5</u>). The highest VOC scores occurred around 15 km on both flow paths. No correlation was found on either Central Basin flow path between VOC score and well depth (<u>table 3</u>).

Wells with VOC detections are at all depths throughout the forebay and most of the pressure area. In contrast, wells with no VOC detections (VOC scores of 0.0) were deep monitoring wells or the most distal wells on the flow paths (fig. 6). This suggests that ground-water recharged since the use of VOCs began (in the 1940s) has migrated along most Central Basin flow paths and mixed with older ground water containing no VOCs.

The distribution of VOC scores on the western and eastern flow paths suggests that the number of VOCs introduced to ground water was higher in the past. Wells with the highest VOC score were at middle distances (in the proximal pressure area) and at middle depths along both flow paths (fig. 6). Low VOC scores were detected in shallow wells near the recharge facilities on the eastern flow path, in the more distal wells on both flow paths, and dispersed throughout both flow paths. High VOC scores were in both the forebay and pressure areas and in the well upgradient of the recharge facilities, suggesting that ground water containing multiple VOCs enters the Central Basin through the Whittier Narrows.

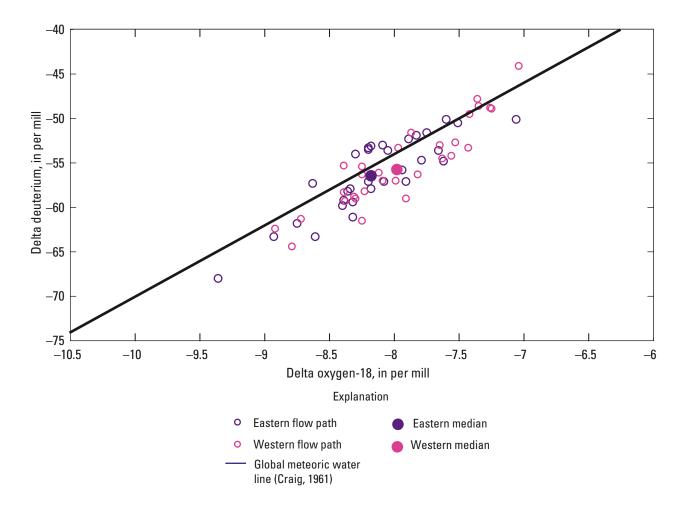


Figure 4. Relation between delta oxygen-18 and delta deuterium in ground water along flow paths in the Central Basin, Los Angeles County, California.

Table 4. Volatile organic compounds detected in 68 ground-water samples from selected wells in the Central Basin, Los Angeles County, California, 2000.

[LRL, laboratory reporting limit; µg/L, micrograms per liter; MCL, maximum contaminant level; ---, no value available or applicable; E -concentration estimated]

oncentration estimated] Constituent	LRL, in µg/L		detections	Minimum detection, in µg/L	Median detection, i µg/L	Maximum n detection, in µg/L	MCL, in µg/L	Number of wells exceeding a MCL
Total number of VOCs detected	_	_	_	0	4	13	_	_
VOC score		—	—	0.0	2.5	8.5	—	—
Trichloromethane (Chloroform)	0.052, 0.024 ⁵	39	7	E0.014	0.080	0.623	80 ^{1,3}	0
Tetrachloroethene (PCE)	0.1	29	17	E0.03	0.150	16.4	5^{1}	5
Trichloroethene (TCE)	0.038	35	8	E0.009	0.095	8.780	5^{1}	2
1,1-Dichloroethane	0.066, 0.035 ⁵	12	10	E0.009	0.053	0.285	5 ²	0
Methyl tert-butyl ether (MTBE)	0.17	22	7	E0.05	0.37	0.85	13 ²	0
cis-1,2-Dichloroethylene	0.038	13	6	E0.016	0.083	8.820	6 ²	1
Chloromethane	$0.5, 0.25^5$	0	18	E0.05	E0.07	E0.15		0
1,1,1-Trichloroethane	0.032	4	12	E0.005	E0.005	E0.075	200^{1}	0
1,1-Dichloroethylene	0.04	5	8	E0.01	E0.03	0.35	6	0
Trichlorofluoromethane (CFC-11)	0.09	6	6	E0.01	0.09	0.94	150^{2}	0
Bromodichloromethane	0.048	3	4	E0.019	E0.029	0.550	801,3	0
Carbon disulfide	0.07	3	2	E0.006	0.12	0.18	_	0
1,4-Dichlorobenzene	0.05	0	5	E0.01	E0.01	E0.02	5^{2}	0
Dichlorodifluoromethane	0.27	0	3	E0.04	E0.11	E0.13	_	0
trans-1,2-Dichloroethylene	0.032	2	0	E0.033	0.190	0.347	100^{1}	0
1,1,2-Trichlorotrifluoroethane	0.06	1	1	E0.02	E0.04	E0.07	$1,200^2$	0
Diisopropyl ether	0.1	1	1	E0.1	E0.1	E0.1	_	0
Benzene	0.035	0	2	E0.008	E0.011	E0.015	1^{2}	0
Dichloromethane	0.38, 0.16 ⁵	0	2	E0.04	E0.04	E0.04	5^{1}	0
1,2-Dichloroethane	0.13	1	0	0.15	_	—	0.5^{2}	0
Dibromochloromethane	0.18	1	0	0.41		_	801,3	0
Ethylbenzene	0.03	0	1	E0.01		_	700^{1}	0
Isopropylbenzene	0.032	0	1	E0.010	_	—	_	0
m- and p-Xylene	0.06	0	1	E0.01	_	_	$1,750^{2}$	0
Methyl benzene ⁴	0.05	0	10	E0.004	E0.01	E0.02	150^{2}	0

¹ U.S. Environmental Protection Agency, 2001
 ² California Department of Water Resources, 2001
 ³ Total Trihalomethanes, as of 01/01/02 (U.S. Environmental Protection Agency, 2001)

⁴ Methyl benzene concentrations may be due to sample contamination during collection and analysis

⁵ 2 LRLs used during the sampling period

Table 5. Detection frequencies of volatile organic compounds in the 68 wells in the Central Basin, Los Angeles County, California, 2000.

[LRL, laboratory reporting limit; n, number of ground-water samples]

				Detectio	Detection Frequency, in percent	in percent			
Constituent	A	All Detections		Dete	Detections above LRL	.RL	Detec	Detections below LRL	.RL
	Combined	Western	st	Combined	Western	Eastern	Combined	Western	Eastern
	n = 68	n = 33	n = 36	n = 68	n = 33	n = 36	n = 68	n = 33	n = 36
Trichloromethane (Chloroform)	68	85	53	56	76	39	12	6	14
Tetrachloroethene (PCE)	68	<i>4</i>	58	43	61	28	25	18	31
Trichloroethene (TCE)	63	70	58	51	58	47	12	12	11
1,1-Dichloroethane	44	36	53	29	18	39	15	18	14
Methyl tert-butyl ether (MTBE)	43	48	39	32	36	31	10	12	8
cis-1,2-Dichloroethylene	28	39	19	18	30	5.6	10	9.1	14
Chloromethane	26	30	22	0.0	0.0	0.0	26	30	22
1,1,1-Trichloroethane	24	36	11	5.9	12	0.0	18	24	11
1,1-Dichloroethylene	19	27	14	7.4	12	2.8	12	15	11
Trichlorofluoromethane (CFC-11)	18	21	14	8.8	9.1	8.3	8.8	12	5.6
Bromodichloromethane	10	15	5.6	4.4	6.1	2.8	5.9	9.1	2.8
Carbon disulfide	7.4	12	2.8	4.4	9.1	0.0	2.9	3.0	2.8
1,4-Dichlorobenzene	7.4	9.1	5.6	0.0	0.0	0.0	7.4	9.1	5.6
Dichlorodifluoromethane	4.4	3.0	5.6	0.0	0.0	0.0	4.4	3.0	5.6
trans-1,2-Dichloroethylene	2.9	3.0	2.8	2.9	3.0	2.8	0.0	0.0	0.0
1,1,2-Trichlorotrifluoroethane	2.9	3.0	2.8	1.5	0.0	2.8	1.5	3.0	0.0
Diisopropyl ether	2.9	0.0	5.6	1.5	0.0	2.8	1.5	0.0	2.8
Benzene	2.9	3.0	2.8	0.0	0.0	0.0	2.9	3.0	2.8
Dichloromethane	2.9	3.0	2.8	0.0	0.0	0.0	2.9	3.0	2.8
1,2-Dichloroethane	1.5	0.0	2.8	1.5	0.0	2.8	0.0	0.0	0.0
Dibromochloromethane	1.5	0.0	2.8	1.5	0.0	2.8	0.0	0.0	0.0
Ethylbenzene	1.5	3.0	0.0	0.0	0.0	0.0	1.5	3.0	0.0
Isopropylbenzene	1.5	0.0	2.8	0.0	0.0	0.0	1.5	0.0	2.8
m- and p-Xylene	1.5	3.0	0.0	0.0	0.0	0.0	1.5	3.0	0.0

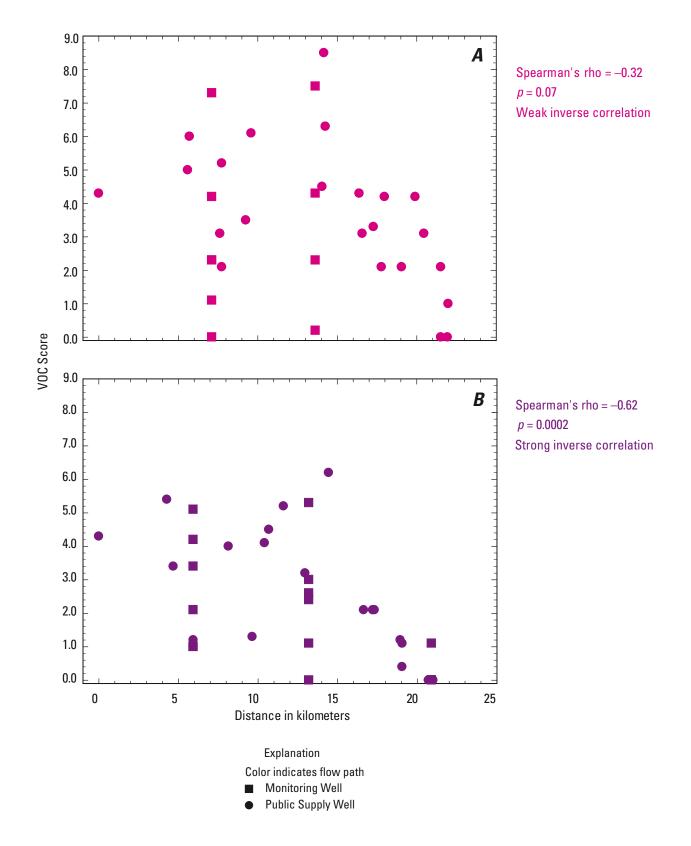


Figure 5. VOC score versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

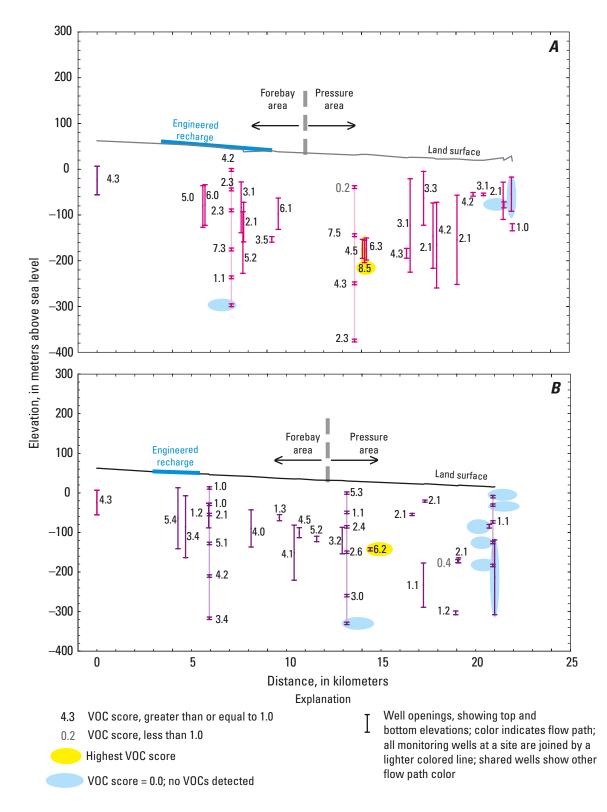


Figure 6. VOC score in wells along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

Chloroform

Chloroform was detected in ground water from 68 percent of the wells (<u>table 5</u>). Chloroform was detected more often at higher concentrations along the western flow path than the eastern (<u>table 5</u> and <u>fig. 7</u>). Chloroform concentrations did decrease significantly downgradient along the eastern flow path, but no correlation with distance was found along the western flow path (<u>fig. 7</u>). Chloroform concentrations were significantly higher in wells with deeper openings along the western flow path (<u>table 3</u>). No statistical correlation with depth was found on the eastern flow path; the highest concentrations were at mid-depth (<u>table 3</u> and <u>fig. 7</u>).

The spatial distribution of chloroform concentrations in ground water is similar to the pattern of VOC scores. High concentrations on both Central Basin flow paths in the forebay and pressure areas are generally surrounded vertically and laterally by lower concentrations and nondetections (fig. 8). The highest chloroform concentrations were in the proximal pressure area at mid-depths at a distance of 14 km (fig. 8), surrounded vertically and laterally by lower concentrations and nondetections. This indicates that more chloroform was reaching ground water in the Central Basin in the past than at present.

MTBE

MTBE was detected in 43 percent of the wells (table 5). MTBE occurrence was not significantly different between the two Central Basin flow paths (table 2). On both Central Basin flow paths, the highest MTBE concentrations were in the forebay area, with concentrations decreasing very significantly with increasing distance along the flow paths (figs. 9 and 10). Although no correlation was found between MTBE concentration and depth for all wells (table 3), concentrations in wells in the forebay area are generally higher in the shallower wells (fig. 10).

The spatial distribution of MTBE concentrations is different than for VOC score or chloroform. The highest concentrations are in the most upgradient wells (fig. 10), and there is a strong inverse correlation between concentration and distance (table 3 and fig. 9). This suggests that MTBE is currently being introduced into ground water in the forebay area. The highest concentration is in the well upgradient from the engineered recharge facilities (fig. 10), suggesting that MTBE is associated with the Whittier Narrows ground water, as well as with water being recharged in the Central Basin. No MTBE was detected in wells greater than 15 km along the western flow path or greater than 12 km along the eastern flow path (<u>figs. 9</u> and <u>10</u>). The low concentrations in wells located in the upgradient pressure area suggest that MTBE is migrating downgradient from the forebay (<u>fig. 10</u>).

TCE

TCE was detected in 63 percent of the wells (table 5). Two detections are above the federal and state MCL of 5 μ g/L (table 4) (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001). TCE occurrence was not significantly different between the Central Basin flow paths (table 2). No correlation with distance was found along the Western flow path (table 3 and fig. 11); high concentrations were in both forebay and pressure area wells (fig. 12). Concentrations along the eastern flow path showed a statistical decrease with distance, with more nondetections in the most distal wells. No correlation was found on either Central Basin flow path between TCE concentration and depth (table 3).

The spatial distribution of TCE concentrations is similar to the patterns of VOC score. Along both flow paths, high concentrations were detected at middle to deeper depths in middle distances, and are surrounded vertically and laterally by lower concentrations (fig. 12). This suggests that relatively higher concentrations entered the basin at some time in the past. High concentrations also were in the northernmost well, upgradient of the engineered recharge facilities, an indication of the TCE contamination that continues to enter the Central Basin through the Whittier Narrows from known sources in the San Gabriel Valley (U.S. Environmental Protection Agency, 1998). Concentrations in wells beneath the recharge facilities are lower than in wells upgradient or downgradient, suggesting that the current recharge water is diluting TCE concentrations in older water.

The highest concentrations of TCE were in shallow pressure area wells (fig. 12). On the western flow path, the highest occurrence was at about 20 km in a shallow public supply well. The highest on the eastern flow path was at about 13 km in a shallow monitoring well in the pressure area. These wells are downgradient from much lower concentrations, indicating that even in the pressure area, ground water is susceptible to contamination from VOC sources.

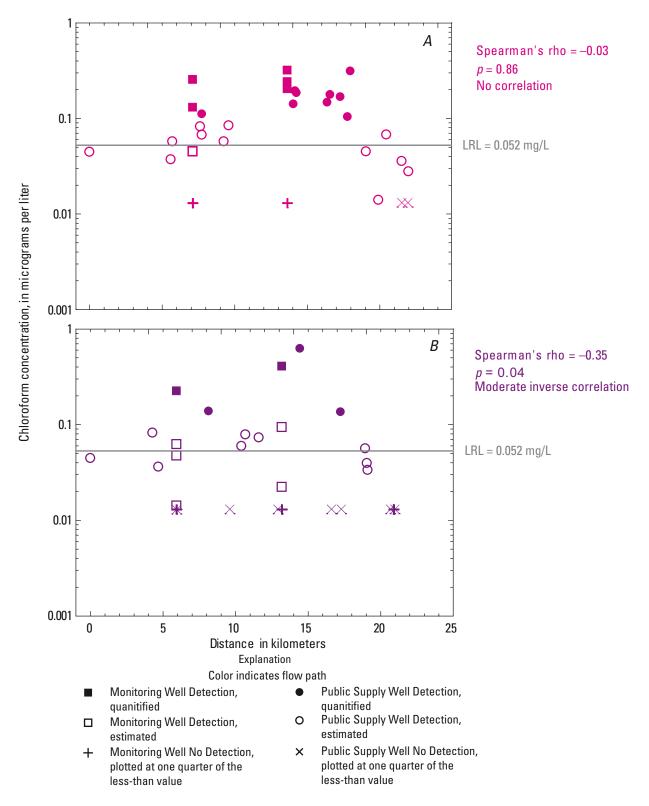


Figure 7. Trichloromethane (chloroform) concentration versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

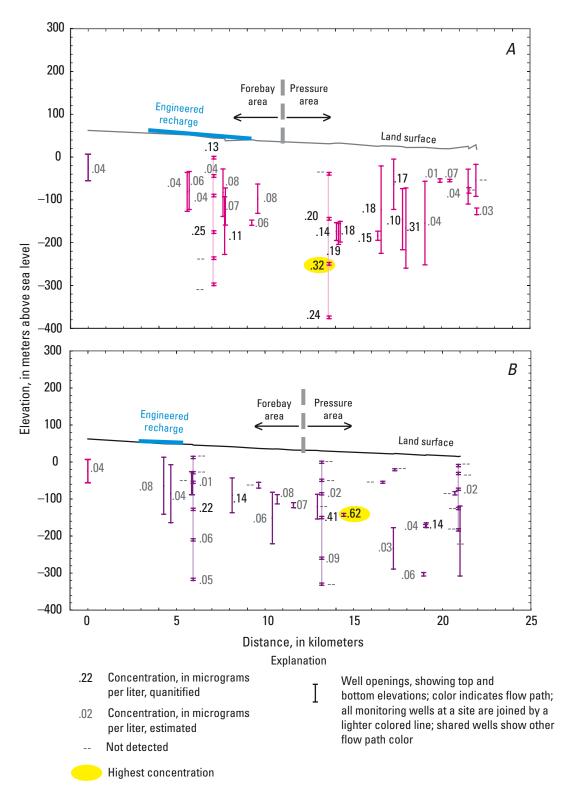


Figure 8. Trichloromethane (chloroform) concentrations in wells along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

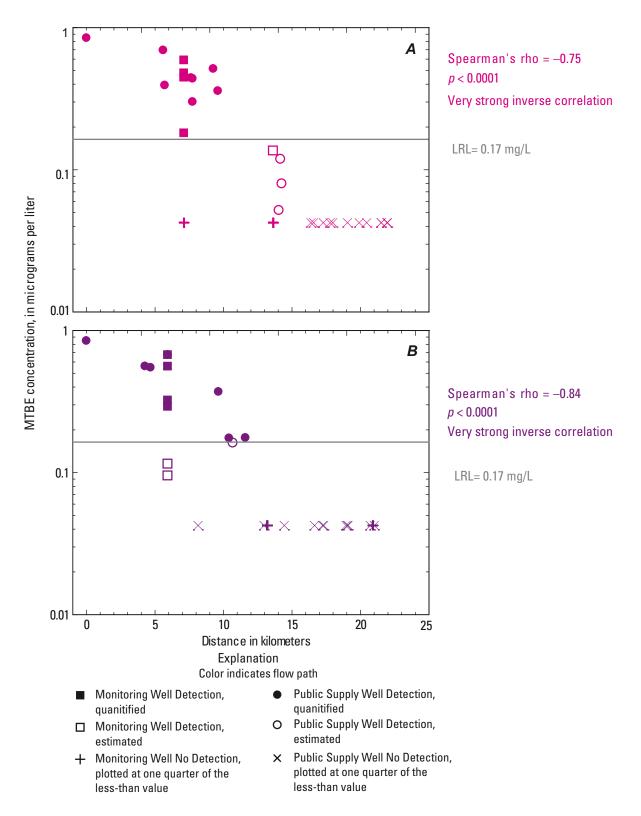


Figure 9. Methyl tert-butyl ether (MTBE) concentration versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

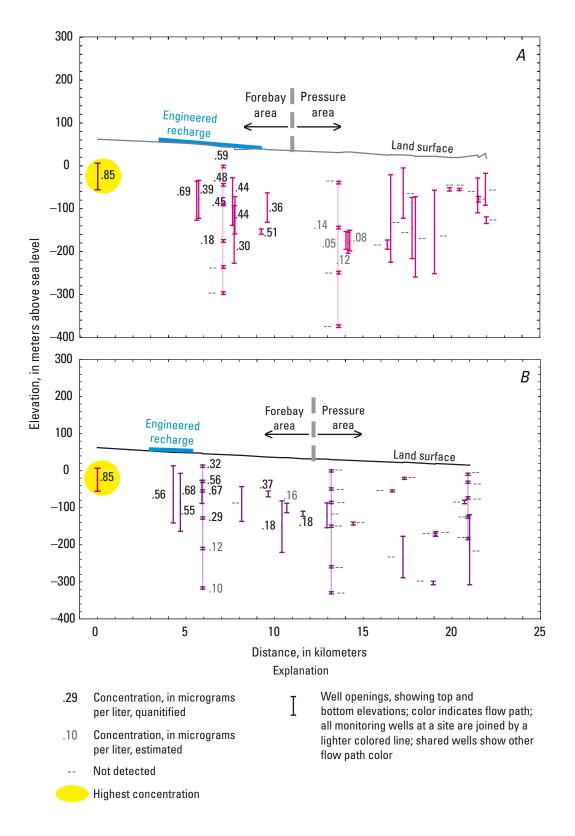


Figure 10. Methyl tert-butyl ether (MTBE) concentrations in wells along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

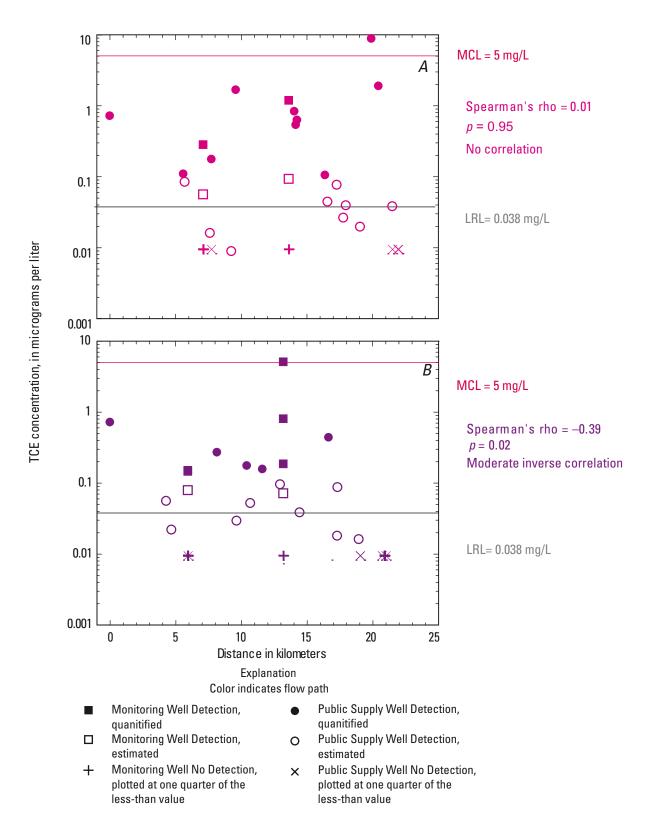


Figure 11. Trichloroethene (TCE) concentration versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

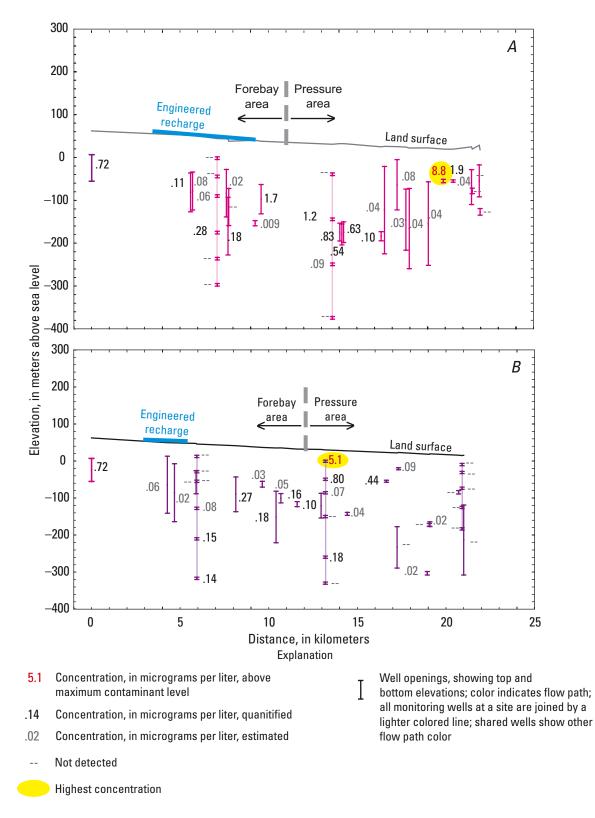


Figure 12. Trichloroethene (TCE) concentrations in wells along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

PCE

PCE was detected in 68 percent of the wells (table 5). Five detections exceeded the federal and state MCL of 5 μ g/L (table 4) (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001). Concentrations were statistically higher on the western flow path (table 2 and fig. 13); no correlation with distance was found along the western flow path (table 3). PCE concentrations along the eastern flow path decreased significantly with distance (table 3 and fig. 13). PCE concentrations were significantly higher in deeper wells on the western flow path; no correlation with depth was found along the eastern flow path (table 3).

The spatial distribution of PCE concentrations is similar to that of TCE. High concentrations were detected in wells at middle depths and distances, and in the first well (upgradient of recharge facilities) on the flow paths. Low concentrations and nondetections were in the most distant wells and in some shallow wells at all distances (fig. 14). As with TCE, the pattern suggests that PCE continues to enter Central Basin through the Whittier Narrows from known sources in the San Gabriel Valley (U.S. Environmental Protection Agency, 1998), that concentrations are lower than in the past, and that current recharge in the Central Basin is diluting PCE concentrations.

CFC-11

CFC-11 was detected in 18 percent of the wells (<u>table 5</u>). There was no significant difference in CFC-11 between the two flow paths (<u>table 2</u>); however, the distribution is slightly different (<u>fig. 15</u>). CFC-11 detections on the western flow path are grouped in the mid-distance wells, with higher concentrations in deeper wells (<u>fig. 16</u>). On the eastern flow path, CFC-11 detections are spread along the flow path, with higher concentrations in middle to more distal wells. No correlations with distance or depth were found (<u>table 3</u>), with the highest concentrations at middle distances and depths.

The spatial distribution of CFC-11 concentrations is similar to VOC score, chloroform, TCE, and PCE; however, overall detection frequency is lower. The nondetections in shallow wells suggest that CFC-11 is not currently reaching ground water at detectable concentrations. The pattern suggests that higher concentrations were reaching ground water in the past than at present.

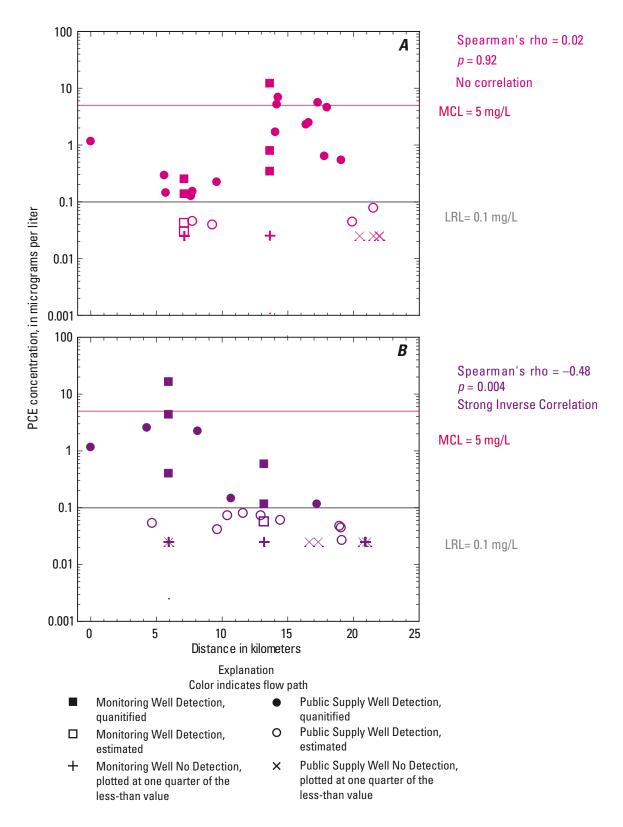


Figure 13. Tetrachloroethene (PCE) concentration versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

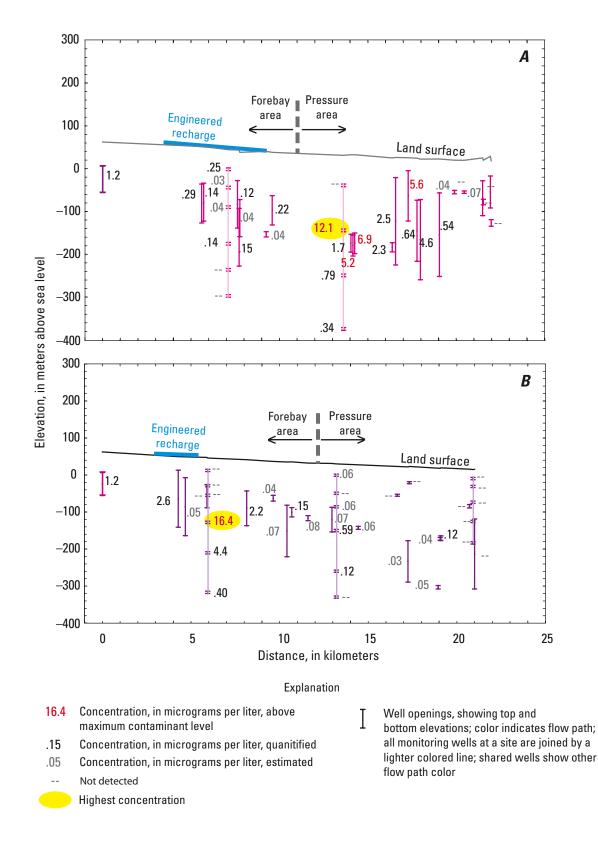


Figure 14. Tetrachloroethene (PCE) concentration versus distance along the (A) western and (B) eastern flow paths in the Central Basin, Los Angeles County, California, 2000.

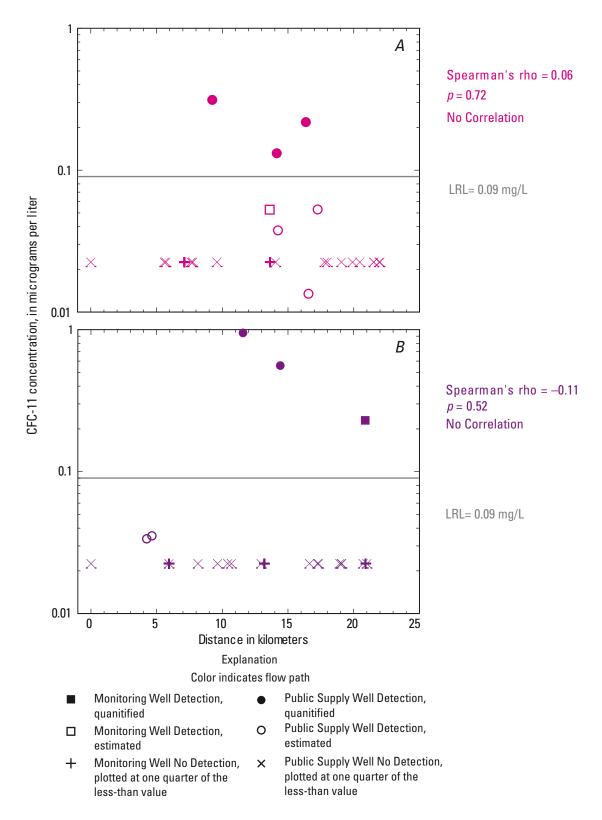


Figure 15. Trichlorofluoromethane (CFC-11) concentration versus distance along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

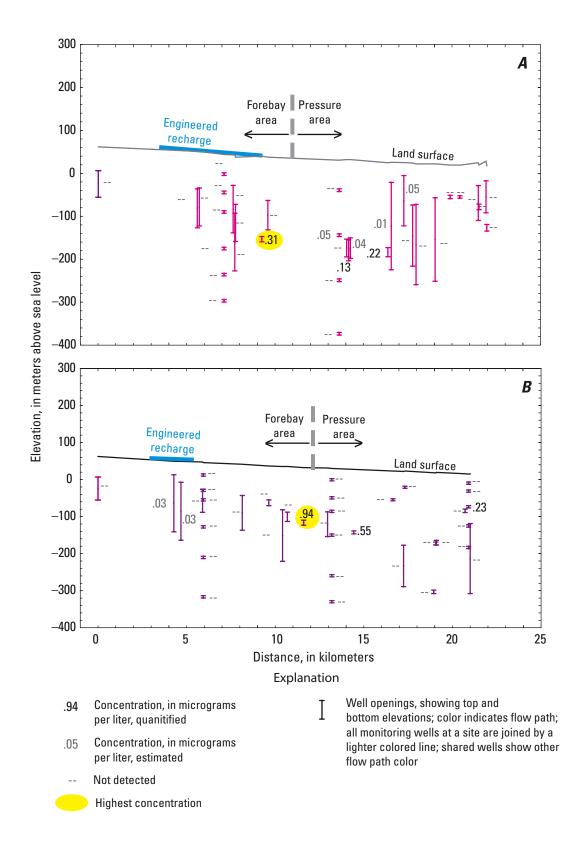


Figure 16. Trichlorofluoromethane (CFC-11) concentrations in wells along the (A) western and (B) eastern flow paths, Central Basin, Los Angeles County, California, 2000.

MAIN BASIN, ORANGE COUNTY

Hydrogeology

Three ground-water flow paths were selected in the Main Basin of the Coastal Santa Ana ground-water basin. Two flow paths, the Santa Ana River (SAR) west and SAR east, begin near the recharge facilities along the Santa Ana River in the forebay area and end in the pressure area, upgradient of the Newport–Inglewood fault zone (fig. 17). The SAR west flow path is west of the Santa Ana River, and the SAR east flow path is near and east of the Santa Ana River. The third flow path, Santiago, begins near the recharge facilities on Santiago Creek, is near and south of Santiago Creek, and ends on the SAR east flow path.

The ground-water flow system in the Main Basin includes two flow systems, one associated with the Santa Ana River and the other with Santiago Creek. As in the Central Basin, both are divergent flow systems; ground water moves radially away from a focused point of recharge (proximal) into the rest of the basin (distal). In contrast to the Central Basin, there are two main points of recharge, one along the Santa Ana River and a smaller one along Santiago Creek.

Three-fourths of ground-water recharge takes place at engineered recharge facilities in and along the Santa Ana River and at the smaller facility on Santiago Creek. Other sources of recharge include irrigation return, local precipitation, and ground-water inflow from other basins (Herndon and others, 1997). Engineered recharge facilities, in operation along the Santa Ana River since the 1940s, have used stormflow and base flow from the inland Santa Ana Basin, imported Colorado River water, and imported northern California water (Moreland and Singer, 1969; Herndon and others, 1997). The Santiago Creek recharge facility, in operation for about 10 years, uses local mountain runoff from the Santa Ana Mountains and excess stormflow diverted from the Santa Ana River recharge facilities. Additional engineered recharge is from injection wells at the Talbert and Alamitos seawater barriers (fig. 17). The Talbert barrier has been in operation since 1975 and uses a mixture of treated wastewater and deep ground water (Herndon and others, 1997; Orange County Water District, 2001). The Alamitos barrier has been in operation since 1965

and uses imported water (Herndon and others, 1997; Orange County Water District, 2001). Nearly all ground-water discharge in the Main Basin is from ground-water pumping in the pressure area.

The Main Basin flow paths were selected to approximately follow ground-water gradients based on water-level contours (fig. 18) (Wildermuth Environmental, Inc., 2000). Well information for the 51 wells sampled in the Main Basin are given in table 6. Wells were selected that tap the upper production zone (from 60 to 120 m below land surface), the lower production zone (from 150 to 300 m below land surface), and both zones.

The SAR west flow path (25 km long) follows the middle of the radial flow from the Santa Ana River recharge facilities from proximal to distal areas. Twenty-three public supply wells were sampled on the SAR west flow path (fig. 17 and table 6).

The Santiago flow path (11 km long) follows the middle of the radial flow from the Santiago Creek recharge facilities from proximal to distal areas. Although the Santiago flow path is shorter in length, it covers the same parts of that flow system as the SAR west flow path (proximal to distal). The shorter length reflects the shorter time of operation and lower recharge rates of the Santiago Creek recharge facility. Ten public supply wells were sampled on the Santiago flow path (fig. 17 and table 6).

The SAR east flow path (22 km long), which follows the eastern edge of the radial flow from the Santa Ana River recharge facilities from proximal to distal areas, is also distal to the Santiago flow path. Twenty public supply wells were sampled on the SAR east flow path (fig. 17 and table 6).

Well distances and depths are statistically similar along the SAR west and east flow paths (<u>table 7</u>). The wells on the Santiago flow path are more evenly distributed along the entire flow path than the wells on the SAR flow paths, which have more wells located in the downgradient part of the flow paths (<u>fig. 17</u>). Well depths are similar between the SAR east and Santiago flow paths (<u>table 7</u>). The bottoms of well openings are statistically deeper on the SAR west than on the Santiago flow path (<u>table 7</u>). There was no correlation between well depths and distance downgradient along either SAR flow path. The midpoints and bottoms of well openings were significantly deeper with distance downgradient along the Santiago flow path.

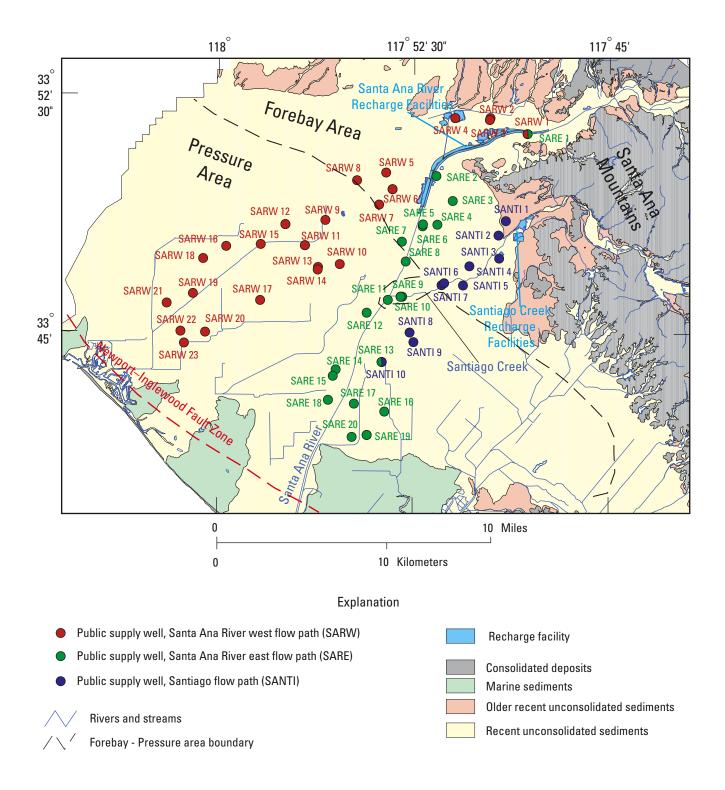


Figure 17. Geology, locations of wells sampled, and major hydrologic features of the Main Basin, Orange County, California.

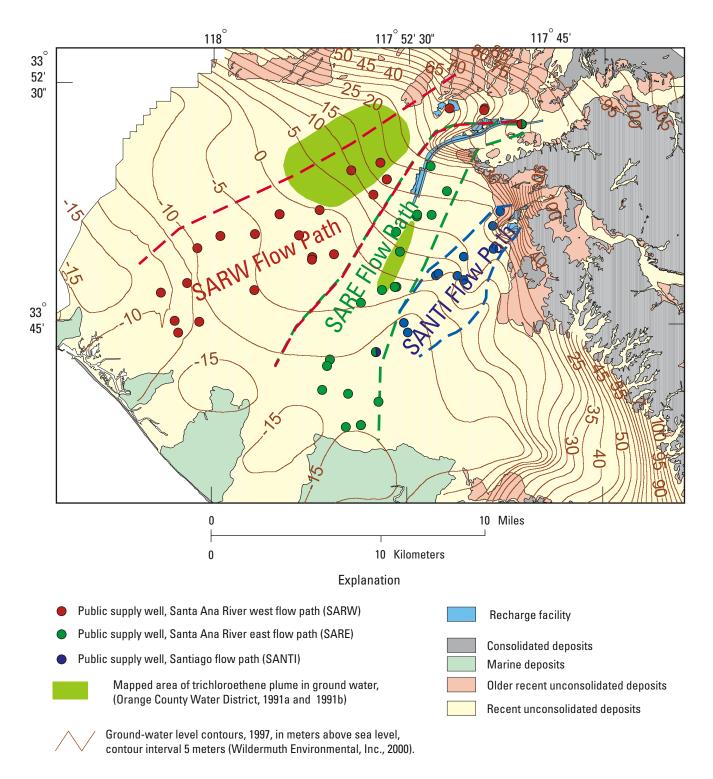


Figure 18. Ground-water level contours in the Central Los Angeles Basin, California, spring 2000.

Site Number	USGS Site ID	State well number	Distance down gradient, in kiloeters	Depth to middle of openings, in meters below land surface
SARW 1	335118117481401	004S009W03H002S	0.0	37
SARW 2	335148117494001	003S009W33K005S	2.3	88
SARW 3	335145117494101	003S009W33K006S	2.3	76
SARW 4	335148117510101	003S009W32L001S	4.4	265
SARW 5	335004117533901	004S010W11Q002S	9.5	105
SARW 6	334932117532401	004S010W14H003S	9.9	324
SARW 7	334903117535201	004S010W23B002S	11.0	101
SARW 8	334949117544301	004S010W15B005S	11.1	102
SARW 9	334833117555501	004S010W21L001S	14.1	124
SARW 10	334710117552101	004S010W34E002S	15.0	230
SARW 11	334745117564501	004S010W29K001S	15.9	261
SARW 12	334825117573101	004S010W20M001S	16.0	263
SARW 13	334704117561101	004S010W33F002S	16.2	200
SARW 14	334659117561201	004S010W33F004S	16.3	56
SARW 15	334747117582701	004S010W30E002S	17.9	256
SARW 16	334744117594601	004S011W26J002S	19.4	80
SARW 17	334601117582401	005S011W01H002S	20.1	194
SARW 18	334719118003901	004S011W26N001S	20.9	194
SARW 19	334613118005901	005S011W03C001S	22.7	134
SARW 20	334500118003001	005S011W10J004S	23.7	106
SARW 21	334552118020201	005S011W04L001S	24.3	188
SARW 22	334501118013001	005S011W09J002S	24.8	174
SARW 23	334439118011801	005S011W15D003S	25.1	85
SARE 1	335118117481401	004S009W03H002S	0.0	37
SARE 2	334958117514401	004S009W07P001S	5.9	105
SARE 3	334911117510601	004S009W17N001S	7.1	226
SARE 4	334826117514101	004S009W19K001S	8.6	222
SARE 5	334826117521401	004S010W24J002S	8.8	219
SARE 6	334822117521401	004S010W24J001S	9.0	246
SARE 7	334753117525901	004S010W25F001S	10.2	105
SARE 8	334716117525301	004S010W36C002S	11.2	213
SARE 9	334608117525601	005S010W01E002S	13.2	134
SARE 10	334609117530401	005S010W01E003S	13.2	283
SARE 11	334603117533301	005S010W02K002S	13.7	153
SARE 12	334538117541901	005S010W03R003S	14.8	291
SARE 13	334405117534701	005S010W14L001S	17.3	279
SARE 14	334350117553201	005S010W21B004S	18.5	176
SARE 15	334338117553901	005S010W21B003S	18.9	135
SARE 16	334231117534001	005S010W26L001S	20.0	283
SARE 17	334246117545001	005S010W27C002S	20.1	185
SARE 18	334253117555001	005S010W28C009S	20.4	219
SARE 19	334147117542001	005S010W34H010S	21.6	135
SARE 20	334143117545401	005S010W34F003S	22.0	142
SANTI 1	334833117490301	004S009W22M001S	0.0	128
SANTI 2	334806117492001	004S009W28A001S	1.0	181

Table 6. Wells sampled in the Main Basin, Orange County, California, 2000.

Site Number	USGS Site ID	State well number	Distance down gradient, in kiloeters	Depth to middle of openings, in meters below land surface
SANTI 3	334722117491901	004S009W28R002S	1.8	118
SANTI 4	334707117502601	004S009W32B004S	3.4	200
SANTI 5	334631117504101	004S009W32P002S	4.5	254
SANTI 6	334635117512401	004S009W31R001S	5.2	187
SANTI 7	334631117513001	004S009W31Q001S	5.3	234
SANTI 8	334501117524001	005S010W12L003S	8.7	191
SANTI 9	334443117523401	005S010W13B009S	8.9	221
SANTI 10	334405117534701	005S010W14L001S	11.0	279

 Table 6.
 Wells sampled in the Main Basin, Orange County, California, 2000—Continued

Stable Isotopes

A plot of δ^{18} O in relation to δ D for the three Main Basin ground-water flow paths is shown on figure 19. Most of the ground-water values plot along and slightly below the Global Meteoric Water Line (Craig, 1961). Stable isotope values from both SAR flow paths were statistically identical, indicating a similar source of ground water. The two lighter values on the SAR west flow path may indicate the mixing with lighter sources of recharge, such as water from the inland Santa Ana Basin, northern California aqueduct water, and Colorado river water. Stable isotope values were significantly heavier on the Santiago flow path (table 7), reflecting a greater proportion of ground water from local precipitation. Except for δD on the SAR East flow path, δ^{18} O and δ D were inversely correlated with depth on the Main Basin flow paths (table 8).

Volatile organic compounds

Of the 86 VOCs analyzed for in this study, 9 VOCs were detected at concentrations at or above LRL in ground water along the Main Basin flow paths; an additional 8 VOCs were detected below LRL (<u>table 9</u>). Fifty-one percent (26 of 51) of wells sampled contained one or more VOCs above LRL; an additional 31 percent (16 of 51) of the wells had one or more VOCs only below LRL. Twenty-two percent (11 or 51) of the wells sampled had no VOC detections. All VOCs detected along the three Main Basin flow paths were below federal and state MCLs (<u>table 9</u>) (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001).

U.S. Environmental Protection Agency, 2001).

The five compounds discussed in this report (chloroform, MTBE, TCE, PCE, and CFC-11) were all detected above LRL in the Main Basin and are among the seven compounds most frequently detected (<u>table 10</u>). Chloroform, MTBE, and TCE were detected on all three flow paths. PCE and CFC-11 were not detected on the Santiago flow path (<u>table 10</u>).

VOC Score

VOC score was statistically highest along the SAR west flow path (<u>table 7</u>). VOC scores on the SAR east flow path were significantly lower than on the SAR west flow path, but statistically similar to those on the Santiago flow path (<u>table 7</u> and <u>fig. 20</u>).

There is an inverse correlation between distance and VOC score on all three flow paths (<u>table 8</u>). The distal wells have the lowest number of VOC detections (<u>figs. 20</u> and <u>21</u>). A transition from high to low VOC scores (detections mostly above LRL to only detections below LRL) occurs on the SAR west flow path at about 18 km downgradient in the pressure area (<u>fig. 20A</u>). This transition occurs on the SAR east line slightly closer to the SAR recharge area (14 km) (<u>fig. 20B</u>). There is a monotonic decrease in VOC score along the Santiago flow path, with the most VOCs detected in the well closest to the Santiago Creek recharge facilities (<u>fig. 21C</u>). These correlations and patterns indicate that VOCs were introduced in the forebay either with engineered recharge water or from the land surface. Table 7. Statistical differences between ground-water flow paths in the Main Basin, Orange County, California, 2000.

	SARW vs SARE	SARW vs Santiago	SARE vs Santiago
Variable	Rank-sum test <i>p</i> -value	Rank-sum test <i>p</i> -value	Rank-sum test <i>p</i> -value
Distance	0.44	³ 0.001	³ 0.0007
Depth to top of openings	0.38	0.67	0.48
Depth to mid-point of openings	0.13	0.14	0.83
Depth to bottom of openings	0.13	¹ 0.06	0.52
δDeuterium	0.59	³ 0.0001	³ 0.0004
δOxygen-18	0.88	³ 0.009	³ 0.008
VOC Score	² 0.05	¹ 0.06	0.74
Number of detections above LRL	² 0.04	$^{1}0.07$	1.00
Total number of VOCs detected	² 0.02	² 0.05	0.60
Trichloromethane (Chloroform)	² 0.05	0.19	0.98
1,1,1-Trichloroethane	² 0.04	³ 0.004	0.21
1,1,2-Trichlorotrifluoroethane	³ 0.002	³ 0.0009	0.18
Methyl <i>tert</i> -butyl ether (MTBE)	0.37	0.20	0.61
Trichlorofluoromethane (CFC-11)	0.18	² 0.02	0.33
Trichloroethene (TCE)	¹ 0.07	$^{1}0.08$	0.77
Tetrachloroethene (PCE)	1.00	0.58	0.33
Bromodichloromethane	0.28	0.40	0.97
1,1-Dichloroethylene	0.84	0.58	0.61
Dichlorodifluoromethane	0.72	0.62	0.38
1,1-Dichloroethane	² 0.04	² 0.05	0.89
Chloromethane	0.10	² 0.03	0.51
Dibromochloromethane	0.49	0.14	0.12
cis-1,2-Dichloroethylene	0.49	0.60	0.97
1,2,4-Trimethylbenzene	0.87	0.37	0.33
Tetrahydrofuran	0.95	0.88	0.87

[LRL, laboratory reporting limit; SARW , Santa Ana River West; SARE, Santa Ana River East]

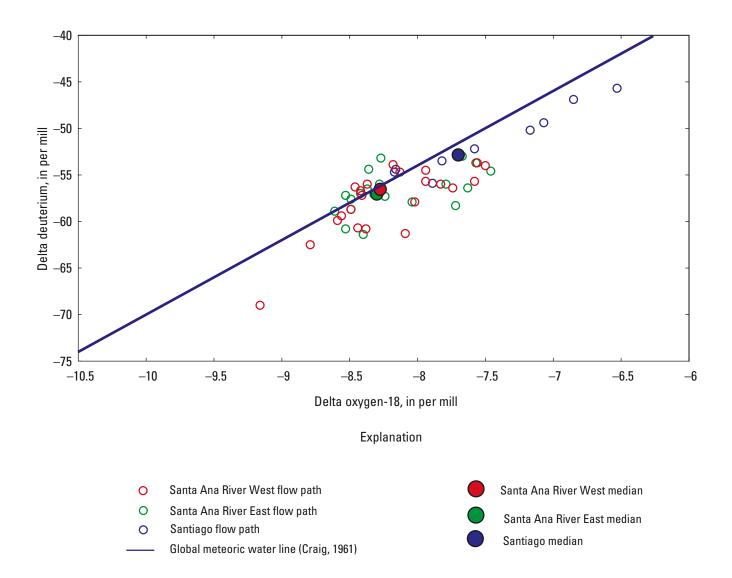


Figure 19. Relation between delta oxygen-18 and delta deuterium in ground water along flow paths in the Main Basin, Orange County, California.

Table 8. Statistical correlations along ground-water flow paths in the Main Basin, Orange County, California, 2000.

		SARW n = 2	2		SARE n = 20)		Santiago n =	10
Variable	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlation	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlation	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlation
Correlations with distance dowr	n gradient	:							
Depth to top of openings	0.51	0.14	No	0.97	0.009	No	0.94	-0.02	No
Depth to mid-point of openings	0.62	0.11	No	0.59	0.12	No	² 0.03	² 0.73	Positve ²
Depth to bottom of openings	0.95	0.01	No	0.73	0.08	No	² 0.02	² 0.78	Positve ²
δDeuterium	0.86	-0.04	No	0.72	0.08	No	¹ 0.09	¹ –0.56	Inverse ¹
δOxygen-18	³ 0.006	³ -0.59	Inverse ³	² 0.02	² -0.52	Inverse ²	² 0.04	² -0.70	Inverse ²
VOC Score	³ 0.006	³ -0.59	Inverse ³	¹ 0.08	¹ -0.40	Inverse ¹	² 0.05	² -0.64	Inverse ²
Number of detections above LRL		³ -0.58	Inverse ³	¹ 0.10	¹ -0.38	Inverse ¹	² 0.04	² -0.69	Inverse ²
Total number of VOCs detected		³ -0.56	Inverse ³	0.13	-0.35	No	¹ 0.08	¹ -0.57	Inverse ¹
Trichloromethane (Chloroform)	³ 0.01	³ -0.55	Inverse ³	0.17	-0.33	No	² 0.02	² –0.79	Inverse ²
Methyl <i>tert</i> -butyl ether (MTBE)	³ 0.003	³ –0.65	Inverse ³	0.20	-0.30	No	¹ 0.06	$^{1}-0.62$	Inverse ¹
Trichloroethene (TCE)	³ 0.002	³ –0.67	Inverse ³	0.50	-0.16	No	0.11	-0.52	No
Tetrachloroethene (PCE)	³ 0.0006	³ –0.73	Inverse ³	¹ 0.10	¹ -0.39	Inverse ¹	nd	nd	nd
Trichlorofluoromethane (CFC-11)	² 0.02	² -0.52	Inverse ²	0.60	-0.12	No	nd	nd	nd
Correlations with depth to the mid-point of openings:									
Distance down gradient	0.62	0.11	No	0.59	0.12	No	² 0.03	² 0.73	Positve ²
δDeuterium	³ 0.003	³ -0.63	Inverse ³	0.39	-0.20	No	¹ 0.09	¹ -0.56	Inverse ¹
δOxygen-18	³ 0.004	³ -0.62	Inverse ³	² 0.03	² -0.51	Inverse ²	² 0.02	² -0.76	Inverse ²
VOC Score	0.51	0.14	No	0.13	-0.35	No	0.13	-0.50	No
Number of detections above LRL	0.49	0.15	No	0.20	-0.29	No	¹ 0.07	¹ -0.60	Inverse ¹
Total number of VOCs detected	0.63	0.10	No	¹ 0.07	¹ -0.41	Inverse ¹	0.18	-0.44	No
Trichloromethane (Chloroform)	0.32	0.22	No	0.25	-0.28	No	¹ 0.06	¹ -0.62	Inverse ¹
Methyl tert-butyl ether (MTBE)	0.19	-0.28	No	0.56	-0.14	No	² 0.04	$^{2}-0.68$	Inverse ²
Trichloroethene (TCE)	¹ 0.09	¹ -0.36	Inverse ¹	¹ 0.10	¹ -0.40	Inverse ¹	0.22	-0.41	No
Tetrachloroethene (PCE)	0.15	-0.30	No	¹ 0.10	¹ -0.39	Inverse ¹	nd	nd	nd
Trichlorofluoromethane (CFC-11)	0.16	0.31	No	³ 0.01	³ –0.60	Inverse ³	nd	nd	nd
111 0.10 0.000	4								

[SARW, Santa Ana River West; SARE, Santa Ana River East; n, number of samples; nd, not detected]

¹ blue, p = 0.10 to 0.06 ² green, p = 0.05 to 0.02

³ yellow, p = 0.01 to < 0.0001

Table 9. Volatile organic compounds detected in 51 ground-water samples from selected wells in the Main Basin, Orange County, California, 2000.

[LRL, laboratory reporting limit; µg/L, micrograms per liter; MCL, maximum contaminant level; ---, no value available or applicable; E, concentration estimated]

Constituent	LRL, in μ g/L	Number of detections at or o above LRL	Number of letections below LRL	Minimum detection, in μg/L	Maximum detection, in μg/L	MCL, in μg/L	Number of wells exceeding a MCL
Total number of VOCs detected	_			0	9	_	_
VOC Score	_	_	_	0.0	6.1		_
Trichloromethane (Chloroform)	⁵ 0.052, 0.024	22	11	E0.011	1.200	^{1,3} 80	0
1,1,1-Trichloroethane	0.032	12	5	E0.004	0.334	¹ 200	0
1,1,2-Trichlorotrifluoroethane	0.06	11	4	E0.01	2.54	² 1,200	0
Methyl tert-butyl ether (MTBE)	0.17	3	10	E0.06	0.23	² 13	0
Trichlorofluoromethane (CFC-11)	0.09	5	7	E0.02	7.98	² 150	0
Trichloroethene (TCE)	0.038	6	5	E0.011	0.531	¹ 5	0
Tetrachloroethene (PCE)	0.1	2	5	E0.02	0.3	¹ 5	0
Bromodichloromethane	0.048	4	1	E0.019	0.167	^{1,3} 80	0
1,1-Dichloroethylene	0.04	2	3	E0.02	0.11	6	0
Dichlorodifluoromethane	0.27	0	4	E0.05	E0.12		—
1,1-Dichloroethane	⁵ 0.066, 0.035	0	3	E0.014	E0.019	² 5	0
Chloromethane	⁵ 0.5, 0.25	0	2	E0.04	E0.04		_
Dibromochloromethane	0.18	0	1	E0.02	E0.02	1,380	0
cis-1,2-Dichloroethylene	0.038	0	1	E0.017	E0.017	² 6	0
1,2,4-Trimethylbenzene	0.056	0	1	E0.029	E0.029		
Tetrahydrofuran	2.2	0	1	E1.3	E1.3	—	_
Methyl benzene ⁴	0.05	0	4	E0.005	E0.02	² 150	0

¹ U.S. Environmental Protection Agency, 2001
 ² California Department of Water Resources, 2001

³ Total Trihalomethanes, as of 01/01/02 (U.S. Environmental Protection Agency, 2001)

⁴ Methyl benzene concentrations may be due to sample contamination during collection and analysis ⁵ 2 LRLs used during the sampling period

Table 10. Comparison of detection frequencies of volatile organic compounds detected in 51 wells sampled in the Main Basin, Orange County, California, 2000.

	5
ILRL. laboratory reporting limit: SARW. Santa Ana River West: SARE. Santa Ana River Eastl	

		Wool, DI MALI, Dulliu I Mid AN VI Lund		frend to the	Detectio	n Freque	Detection Frequency, in percent	rcent				
		All detections	ctions		Detec	tions at o	Detections at or above LRL	RL	De	tections b	Detections below LRI	
Constituent	Com- bined n = 51	SARW n = 22	SARE n = 20	Santi- ago n = 10	Com- bined n = 51	SAR W n= 22	SARE n = 20	Santi- ago n = 10	Com- bined n = 51	SAR W n= 22	SARE n = 20	Santi- ago n = 10
Trichloromethane (Chloroform)	65	73	55	60	43	55	30	40	22	18	25	20
1,1,1-Trichloroethane	33	50	25	10	24	41	15	0.0	10	9.1	10	10
1,1,2-Trichlorotrifluoroethane	29	59	10	0.0	22	45	5.0	0.0	7.8	14	5.0	0.0
Methyl tert-butyl ether (MTBE)	25	36	15	20	9	14	0.0	0.0	20	23	15	20
Trichlorofluoromethane (CFC-11)	24	41	15	0.0	10	14	10	0.0	14	27	5.0	0.0
Trichloroethene (TCE)	22	41	5.0	10	12	18	5.0	10	10	23	0.0	0.0
Tetrachloroethene (PCE)	12	23	5.0	0.0	3.9	9.1	0.0	0.0	9.8	18	5.0	0.0
Bromodichloromethane	10	18	0.0	10	7.8	14	0.0	10	2.0	4.5	0.0	0.0
1,1-Dichloroethylene	10	14	10	0.0	3.9	0.0	10	0.0	5.9	14	0.0	0.0
Dichlorodifluoromethane	7.8	14	0.0	10	0.0	0.0	0.0	0.0	7.8	14	0.0	10
1,1-Dichloroethane	5.9	14	0.0	0.0	0.0	0.0	0.0	0.0	5.9	14	0.0	0.0
Chloromethane	3.9	4.5	5.0	0.0	0.0	0.0	0.0	0.0	3.9	4.5	5.0	0.0
Dibromochloromethane	2.0	0.0	0.0	10	0.0	0.0	0.0	0.0	2.0	0.0	0.0	10
cis-1,2-Dichloroethylene	2.0	0.0	0.0	10	0.0	0.0	0.0	0.0	2.0	0.0	0.0	10
1,2,4-Trimethylbenzene	2.0	4.5	0.0	0.0	0.0	0.0	0.0	0.0	2.0	4.5	0.0	0.0
Tetrahydrofuran	2.0	4.5	0.0	0.0	0.0	0.0	0.0	0.0	2.0	4.5	0.0	0.0

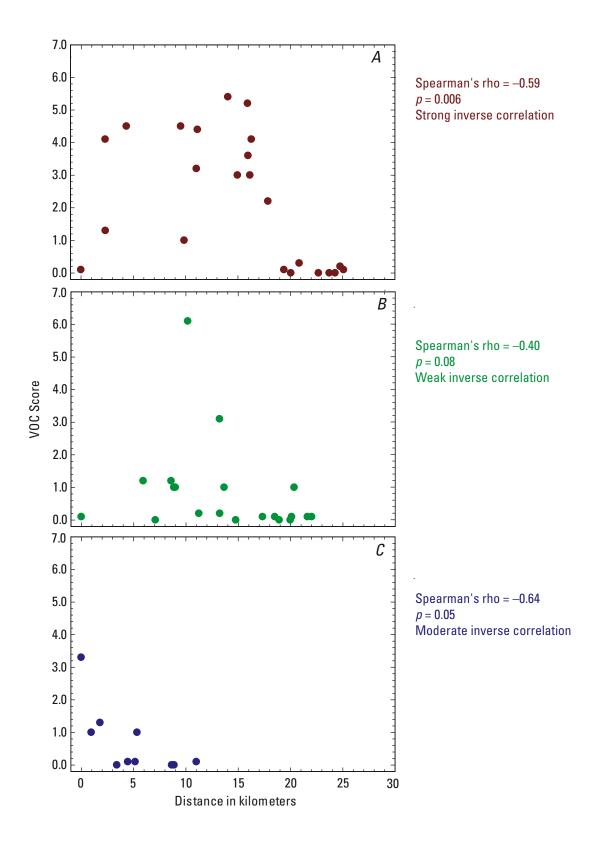


Figure 20. VOC score versus distance along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

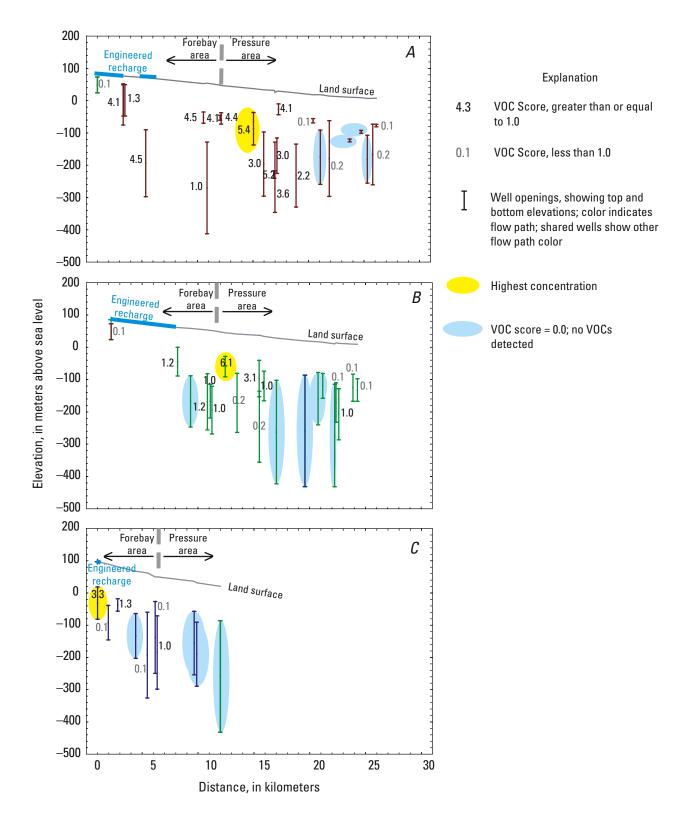


Figure 21. VOC scores in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

The spatial distribution of VOC scores on the SAR west flow path shows three groups of relatively high numbers of VOCs: group I shallow wells and a deep well in the proximal forebay, group II shallow wells that tap the upper aquifer in the distal forebayproximal pressure area, and group III deeper wells that tap the lower aquifer in the pressure area (fig. 21A). The high VOC score in each group is about the same. This pattern suggests that that the number of VOCs reaching ground water has remained about the same for a period of time. Farther along the flow path in the pressure area, VOC scores are all below 1.0, indicating older water that probably recharged before the 1940s. In contrast to the Central Basin flow paths, the most distal wells on the SAR west and east flow paths contain VOCs at low concentrations, with nondetections located just upgradient of these low VOC scores. These low VOC scores at the distal end of the flow paths may be showing the influence of injection wells near the coast.

VOC scores on the SAR east flow path have a different distribution than VOC scores on the SAR west flow path. On the SAR east flow path, only one group of high VOC scores was found in the shallow wells in the distal forebay-proximal pressure area (fig. 21B). This area corresponds to group II on the SAR west flow path in shallow wells between 9 and 15 km (fig. 21A). Group I on the SAR west flow path may not have been sampled on the SAR east flow path because no wells are at the same distance (between 2 and 5 km). There is no corresponding group III on the SAR east flow path; deeper wells at that distance (15 to 19 km) have low or no VOC scores (fig. 21B). The group of VOC scores of 0.0 in the pressure area (16 to 21 km) on the SAR east flow path includes the well at the end of the Santiago flow path. This 0.0 group may be showing the influence of the Santiago flow system on the SAR ground water chemistry.

The pattern of VOC scores along the Santiago flow path is different from the SAR flow paths. On the Santiago flow path, the highest number of VOCs was detected in the well closest to the engineered recharge facilities, and the most distal wells contained no VOCs detectable (fig. 21*C*). This pattern suggests that more VOCs are currently reaching ground water along the Santiago flow path than in the past, which may reflect the shorter operation time of the Santiago Creek recharge facilities compared to the Santa Ana River recharge facilities.

Chloroform

Chloroform was detected in 65 percent of the wells (<u>table 10</u>). It was the most frequently detected compound on all three flow paths, for all detections, and for detections above LRL. Chloroform concentrations were statistically higher on the SAR west flow path than on the SAR east and Santiago flow paths (<u>figs. 22</u> and <u>23</u>). There was no statistical difference in chloroform concentrations between the Santiago flow path and the SAR west or east flow paths (<u>table 7</u>).

There were inverse correlations between chloroform concentration and distance along the SAR west and Santiago flow paths, with more nondetections and lower concentrations in the distal wells. No correlation was found along the SAR east flow path (table 8 and fig. 22B). The highest chloroform concentrations on the SAR West flow path occurred at a distance of about 16 km in the pressure area, and no detections above LRL occurred more than 18 km downgradient (fig. 22A). On the Santiago flow path, chloroform concentrations decreased monotonically with distance, and no chloroform was detected at more than 6 km (fig. 22C). Chloroform concentrations at concentrations below LRL were all along the SAR east flow path, with the exception of wells between 15 and 21 km, which had no detectable chloroform (figs. 22B and 23*B*).

There was no correlation between chloroform concentration and depth on the SAR west or east flow paths (<u>table 8</u>). However, along the SAR west flow path, the highest concentrations were in deeper wells in the pressure area (<u>fig. 23A</u>). There was a slight decrease in chloroform concentration with increasing depth along the Santiago flow path, which may be due to the correlation between distance and well depth along the Santiago flow path (<u>table 8</u>).

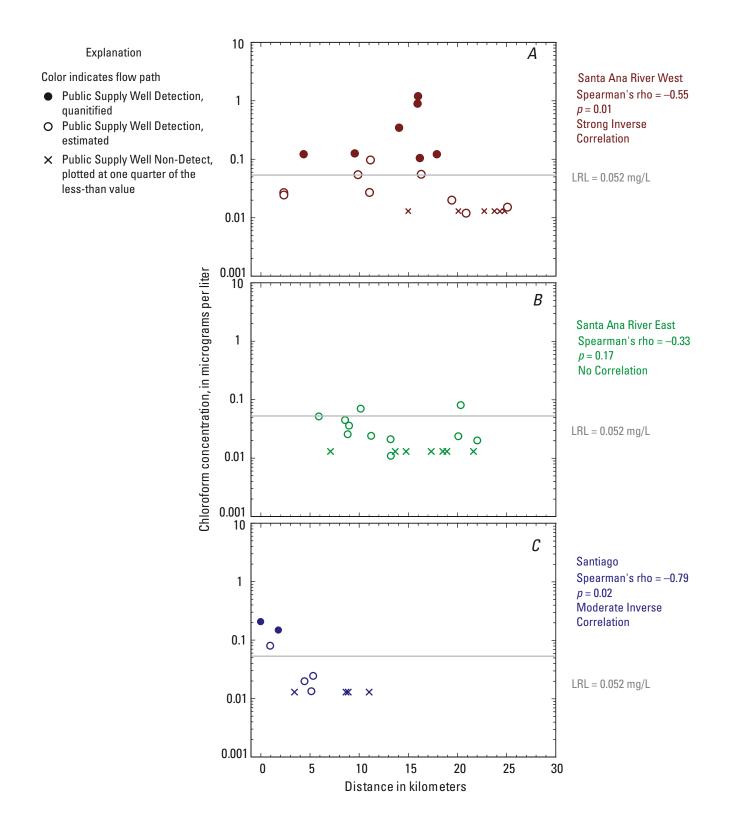


Figure 22. Trichloromethane (chloroform) concentration versus distance along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

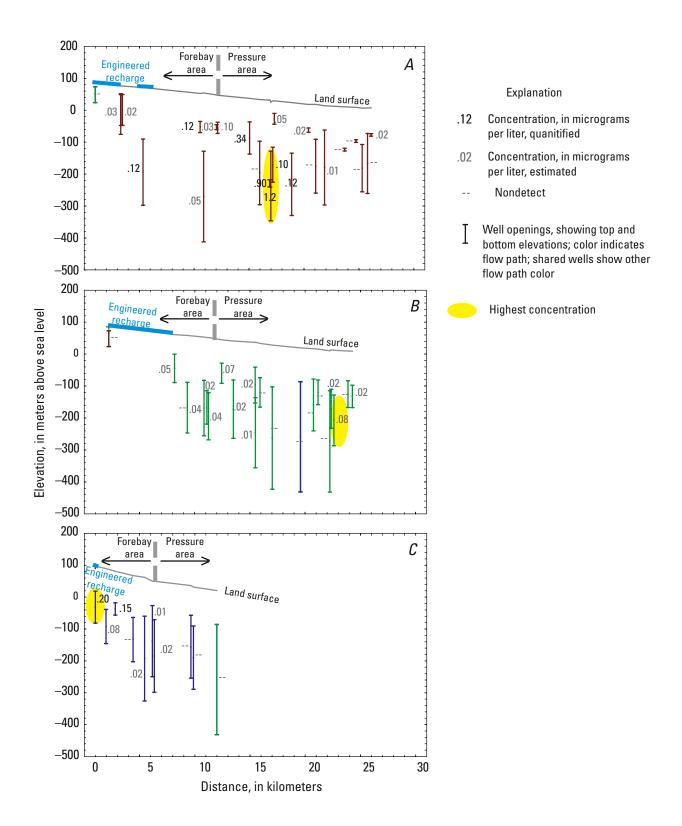


Figure 23. Trichloromethane (chloroform) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

The distribution of chloroform concentrations on the SAR west flow path (fig. 23A) shows one group of high concentrations in deeper wells in the pressure area, suggesting that current concentrations of chloroform reaching the ground water are lower than in the past. Low concentrations were in the forebay and pressure areas. Most nondetections were in the pressure area, mixed with low concentrations.

Chloroform concentrations in wells on the SAR east flow path are all below 0.08 and most are below the LRL (fig. 22*B*). At the same distance and depth that high concentrations were on the SAR west flow path, nondetections were on the SAR east flow path (figs. 22*A* and *B*). As with VOC score, this may be showing the diluting influence of the Santiago flow system. The most distal wells on both SAR flow paths contain low concentrations, and wells upgradient, had nondetections, perhaps showing an influence from the coastal injection wells (figs. 23*A* and *B*).

On the Santiago flow path (<u>fig. 23C</u>), the highest chloroform concentration was in the most upgradient well in the forebay area of the Santiago flow path. As with the VOC scores, this suggests that chloroform is currently reaching ground water in the proximal part of the flow path.

MTBE

MTBE was detected in 25 percent of the wells (<u>table 10</u>). It was detected most frequently on the SAR west flow path, and was only detected below LRL on the Santiago and SAR east flow paths. MTBE concentrations were not significantly different between any Main Basin flow path (<u>table 7</u>).

MTBE concentrations were inversely correlated with distance along the SAR west and Santiago flow paths, with the highest MTBE concentrations found proximal to the recharge facilities (figs. 24 and 25). On the SAR east flow path, MTBE was detected at low concentrations in three wells in the proximal part of the flow path. No MTBE was detected in wells more than 17 km along the SAR west flow path, more than 11 km along the SAR east flow path, or more than 2 km along the Santiago flow path (fig. 25). No correlation was found on either Santa Ana River flow path between MTBE concentration and depth. MTBE concentration did decrease with depth to the midpoint of well openings along the Santiago flow path; as with chloroform, this correlation may be due to the correlation between distance and well depth on the Santiago flow path (<u>table 8</u>).

The spatial distribution of MTBE on the SAR flow paths is similar to VOC score on each flow path. However, the highest concentration on the SAR west flow path was in the proximal forebay area, and the distal wells on both flow paths contained no MTBE (fig. 25A). The highest concentration on the SAR east flow path was in a shallow well in the proximal pressure area (fig. 25B). On the Santiago flow path, the two detections of MTBE were in shallow wells in the forebay (fig. 25C). Detections are mixed with nondetections on all three flow paths. The inverse correlations with distance and the predominance of detections in the forebay areas of all the flow paths indicate that MTBE is currently reaching ground water in the Main Basin.

TCE

TCE was detected in 22 percent of the wells (table 10). TCE was detected most frequently on the SAR west flow path, and only detected once on the SAR east and Santiago flow paths (figs. 26 and 27). There is an inverse correlation between TCE concentration and distance along the SAR west flow path, with the highest concentrations between 9 and 11 km, and no detections more than 17 km (figs. 26A and 27A). The two highest concentrations were detected in shallow wells associated with mapped TCE plumes (fig. 27A). Low concentrations were detected in wells near the Santa Ana River recharge facilities. TCE concentration decreased significantly with depth along the SAR west flow path (table 8). The one detection of TCE on the SAR east flow path occurred at about 10 km, just outside of a mapped TCE plume (fig. 27B) (Orange County Water District, 1991a, fig. 9; Orange County Water District, 1991b, fig. 7). The one detection on the Santiago flow path was in the most upgradient well, near the Santiago Creek recharge facility (fig. 27C).

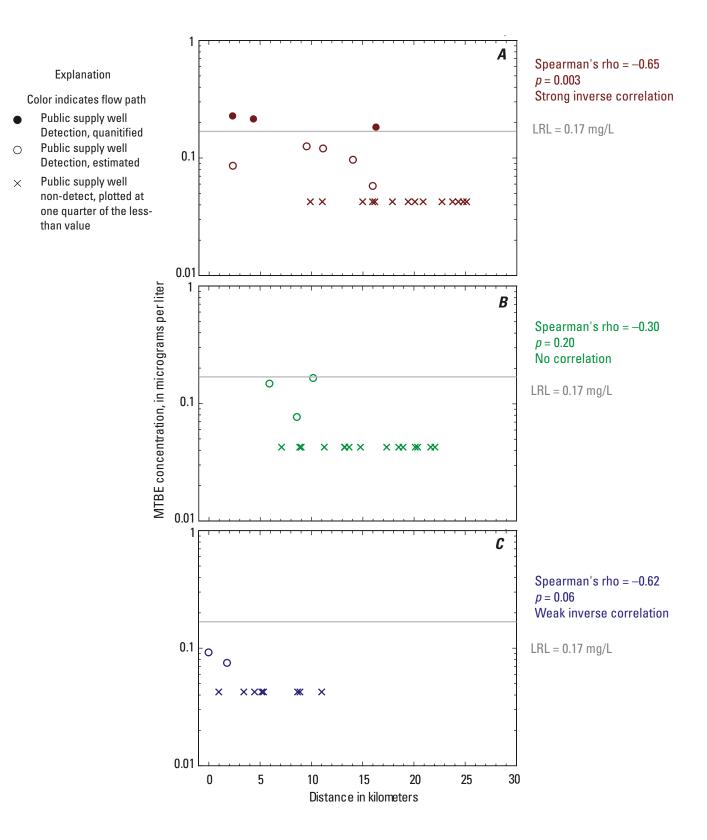


Figure 24. Methyl tert-butyl ether (MTBE) concentration versus distance along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

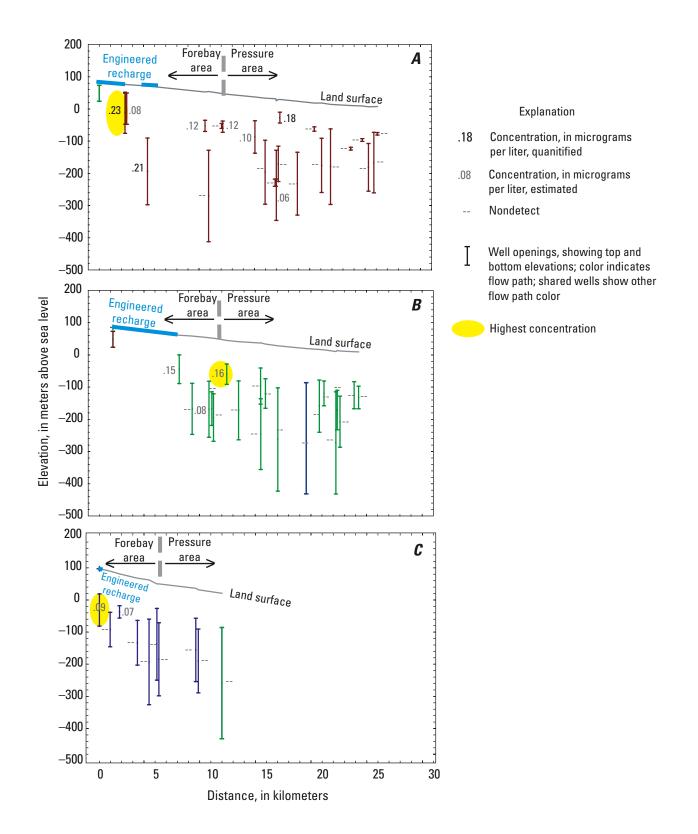


Figure 25. Methyl tert-butyl ether (MTBE) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

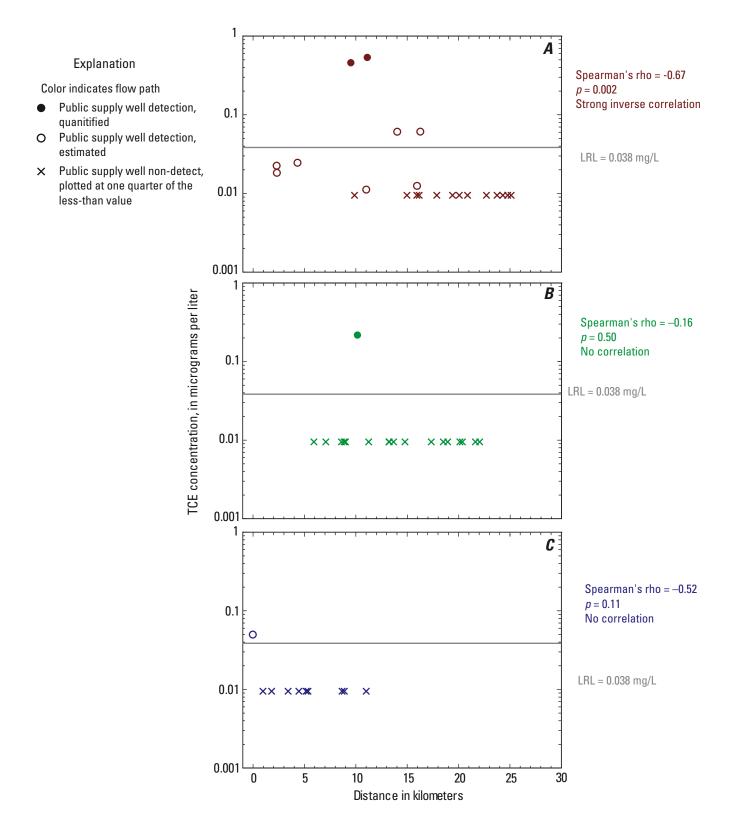


Figure 26. Trichloroethene (TCE) concentration versus distance along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

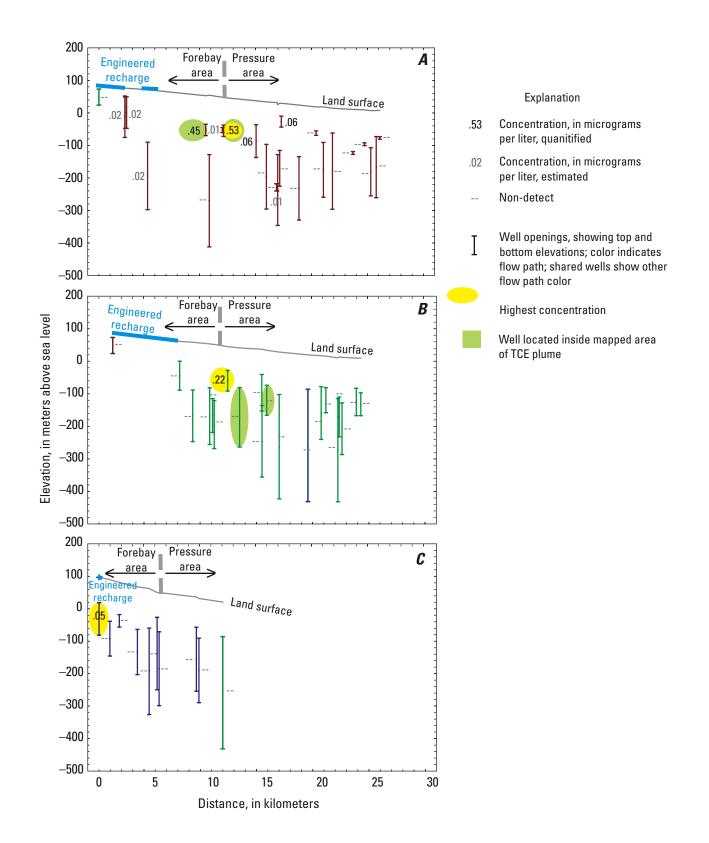


Figure 27. Trichloroethene (TCE) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

The patterns of TCE occurrence along the Main Basin flow paths suggest that higher TCE concentrations in ground water are associated with contaminant plumes. However, low concentrations were detected upgradient of the mapped TCE plumes and in deeper wells, suggesting another source of TCE to ground water in the Main Basin. Despite the presence of a TCE plume along the SAR east flow path, there was only one detection. No TCE was detected in distal wells on the SAR west, SAR east, or Santiago flow paths (fig. 27).

PCE

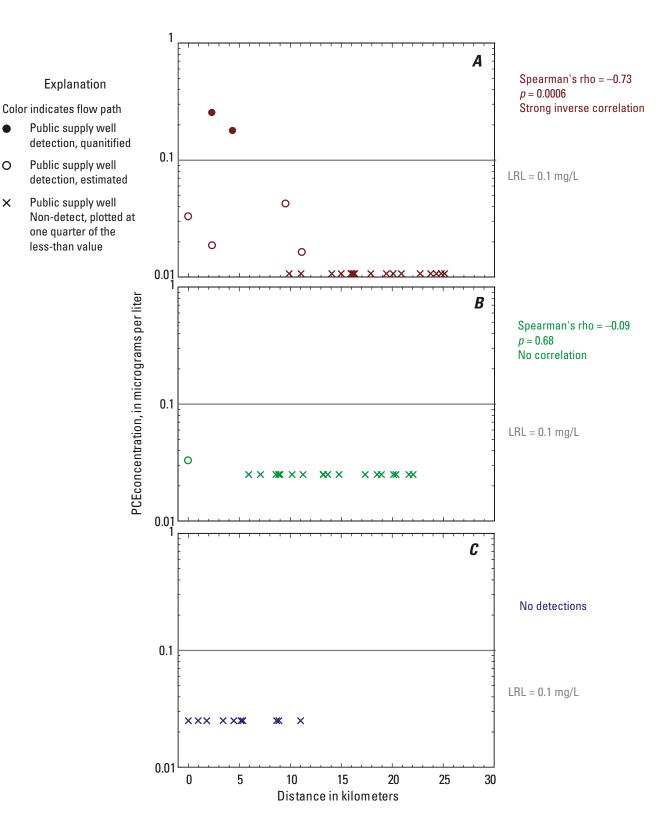
PCE was detected in 12 percent of the wells (table 10). It was detected most frequently on the SAR west flow path, with the highest concentrations in wells near the Santa Ana River recharge facilities. On the SAR east flow path, PCE was detected at a low concentration in the most upgradient well, and in no wells on the Santiago flow path (figs. 28 and 29). An inverse correlation was found between PCE concentration and distance along the SAR west flow path; all detections occurred at less than 12 km, with the highest concentrations at less than 5 km (fig. 29A). No correlation between PCE concentration and depth was found on the SAR west flow path (table 8).

PCE concentrations in the Main Basin have similar distributions to MTBE. The highest measured concentrations on the SAR west flow path were in proximal wells, and the only detection on the SAR east flow path was in the most proximal well. No detections were in the pressure area or on the Santiago flow path. This pattern suggests that a recent source of PCE is currently reaching ground water on the SAR flow paths in the forebay, but not on the Santiago flow path.

CFC-11

CFC-11 was detected in 24 percent of the wells (table 10). Detection frequency was higher on the SAR west flow path than on the SAR east flow path; CFC-11 was not detected on the Santiago flow path (table 10 and figs. 30 and 31). There was an inverse correlation between CFC-11 concentration and distance along the SAR west flow path (table 8), with the highest concentration occurring at 11 km (fig. 30A). No correlation was found between concentration and distance on the SAR east flow path, although the highest concentration also occurred near 11 km in a deeper well (fig. 30B). CFC-11 concentrations did decrease significantly with depth on the SAR east flow path, but showed no correlation with depth on the SAR west flow path (table 8).

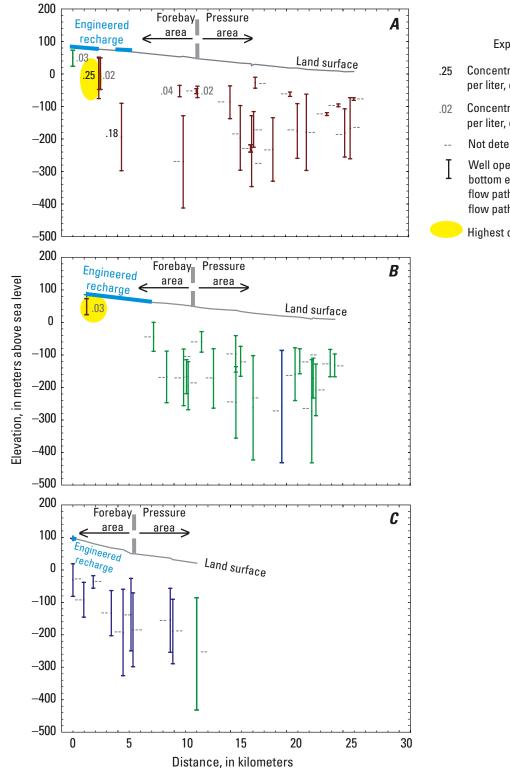
The pattern of CFC-11 detections on both SAR flow paths is similar to that of the VOC score. Detections occur in middle distance wells (figs. 31A and B), suggesting that higher concentrations of CFC-11 were reaching ground water at some time in the past. The nondetections in most of the proximal wells on all three flow paths suggests that CFC-11 is not currently reaching ground water at detectable concentrations.



0

×

Figure 28. Tetrachloroethene (PCE) concentration versus distance along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

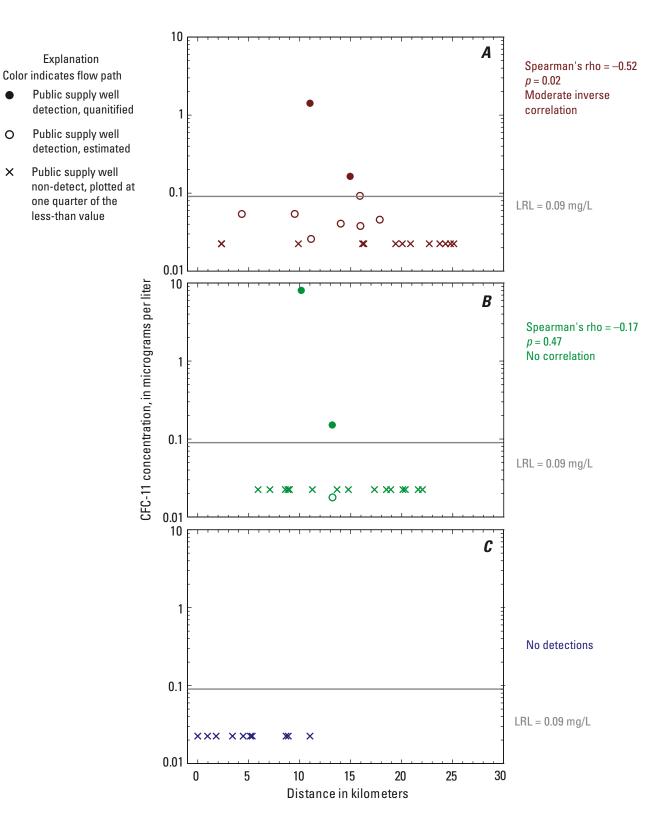


Explanation

- Concentration, in micrograms per liter, quanitified
- Concentration, in micrograms per liter, estimated
- Not detected
- Well openings, showing top and bottom elevations; color indicates flow path; shared wells show other flow path color

Highest concentration

Figure 29. Tetrachloroethene (PCE) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.



0

X

Figure 30. Trichlorofluoromethane (CFC-11) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

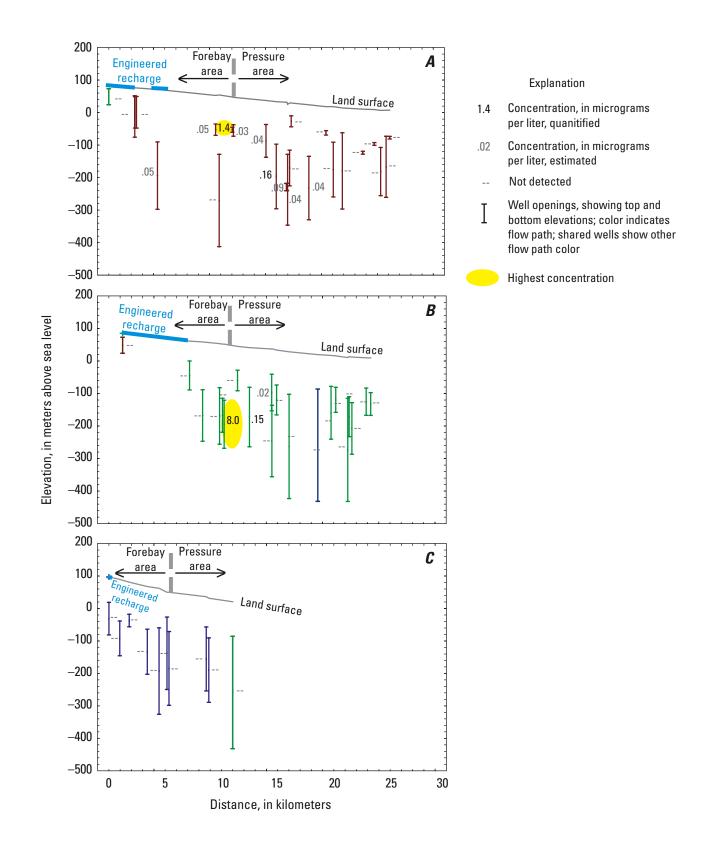


Figure 31. Trichlorofluoromethane (CFC-11) concentrations in wells along the (A) Santa Ana River west, (B) Santa Ana River east, and (C) Santiago flow paths, Main Basin, Orange County, California, 2000.

BUNKER HILL BASIN, SAN BERNARDINO COUNTY

Hydrogeology

Two ground-water flow paths were selected in the Bunker Hill Basin of the inland Santa Ana groundwater basin (fig. 32). Both paths begin near engineered recharge facilities located along the San Bernardino Mountain front, and end near the San Jacinto Fault. The SAR flow path is located along of the Santa Ana River, and the Newmark flow path is located along the Warm and the East Twin creeks. The ground-water flow system in the Bunker Hill Basin is radially convergent. Ground water recharges at several points along the upgradient edges of the basin (proximal area) and moves to a focused area of discharge near the San Jacinto Fault (distal area). The distal parts of the flow paths are confined (fig. 32). However, Dutcher and Garrett (1963, p. 28 and 63) describe the uppermost confining unit near land surface as discontinuous and ranging from semiconfining to confining. Duell and Schroeder (1989, p. 9) describe the confining units at depth in the aquifer system as poorly permeable and leaky.

Recharge to the flow system varies seasonally and is largely from infiltration of runoff from streams exiting the San Gabriel and San Bernardino Mountains (fig. 32). Much of the runoff is diverted to engineered recharge facilities along the mountain front, in or adjacent to stream channels. These facilities have been in operation since the early 1900s using runoff from the San Bernardino Mountains to the north and the San Gabriel Mountains to the west (Moreland, 1972), and imported water from northern California in the 1970s and 1980s (Hardt and Freckleton, 1987). The flow paths are influenced by recharge facilities on the East Twin Creek, Santa Ana River, Mill Creek, and, to a lesser extent, Warm Creek and City Creek. Groundwater discharge is primarily by pumping.

The Bunker Hill Basin flow paths were selected to approximately follow ground-water gradients based on water-level contours (<u>fig. 33</u>) (Wildermuth Environmental, Inc., 2000). Depths to water range from tens of meters near the flanks of mountains to near land surface along rivers and in wetland areas in the distal area of the flow paths. Well information for wells sampled in the Bunker Hill Basin is given in <u>table 11</u>. Wells on two different flow paths were selected in the Bunker Hill Basin. The Newmark flow path (6 km long) follows the radial flow that originates near the East Twin Creek recharge facilities (<u>fig. 32</u>). Ten monitoring wells and 1 public supply well were sampled on the Newmark flow path. The SAR flow path (16 km long) follows the radial flow that originates near the Santa Ana River and Mill Creek recharge facilities. Ten monitoring wells and 5 public supply wells were sampled on the SAR flow path.

Distance downgradient along the Bunker Hill flow paths was measured relative to a point of convergence on the San Jacinto Fault (fig. 34). The convergence point is roughly 16 km from the recharge area on the SAR flow path, but is only about 11 km from the recharge area on the Newmark flow path. For consistency with distance measurements in the coastal plain flow paths, well distances increase in the downgradient direction. Consequently, in Bunker Hill, a well at a distance of 10 km on the SAR flow path is 10 km from the recharge area, but on the Newmark flow path a well at 10 km is only about 5 km from the recharge area.

The Newmark path has flow lines running north to south, and the Santa Ana River path has flow lines running east to west. The distributions of wells on the Bunker Hill flow paths differ. Wells on the Newmark path are located in the middle and downgradient parts of that flow path, with no wells in the upgradient area. Wells on the SAR flow path are located upgradient and downgradient, with no wells in the middle part of that flow path. For this investigation, these two flow paths were analyzed as one, increasing the coverage of wells along the flow paths and the number of wells available for analysis. To justify the combining of the two flow paths, statistical comparisons were made along the lower parts of both flow paths (distances greater than 11 km) where the distribution of wells was the same. No statistical difference was found between the flow paths, except in stable isotopes and benzene occurrence (table 12). Depths to the tops and midpoints of the wells are similar between both flow paths; the bottoms of well openings are significantly deeper on the SAR flow path (table 12). There was no correlation between well depths and distance downgradient along the Bunker Hill flow paths (table 13).

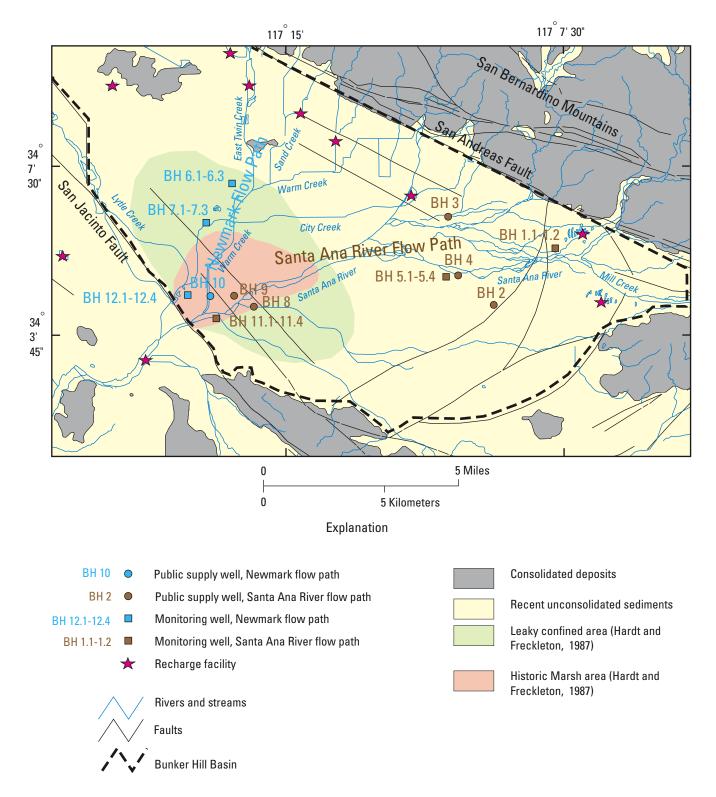


Figure 32. Locations of wells sampled and major hydrologic features of the Bunker Hill Basin, San Bernardino County, California.

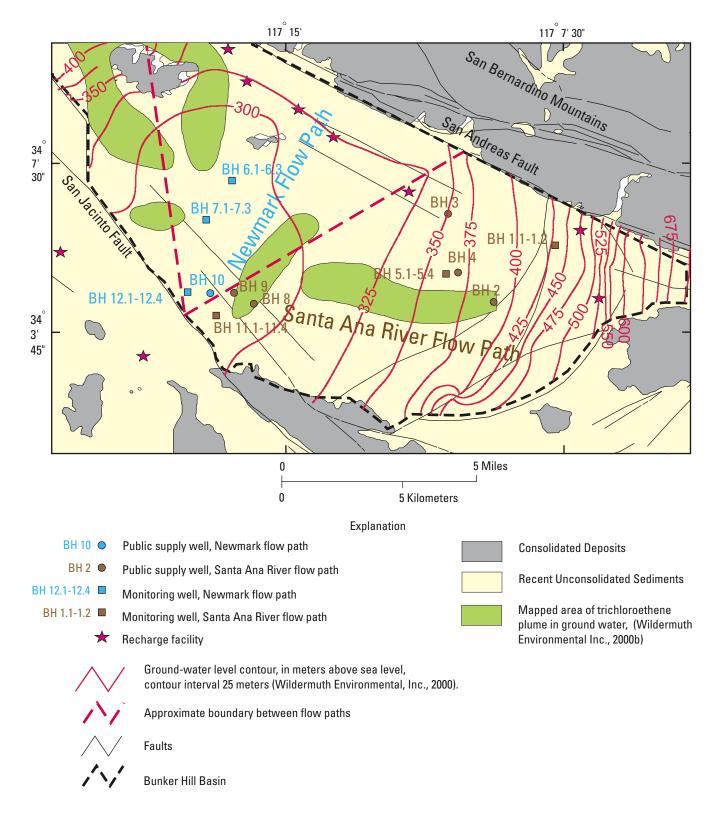


Figure 33. Ground-water level contours and well locations in the Bunker Hill Basin, San Bernardino County, California.

Site Num- ber	USGS Site ID	State well number	Distance down gradient, in kilo- meters	Depth to middle of open- ings, in meters below land surface
BH 1.1	340541117074402	001S002W07Q002S	0.4	155
BH 1.2	340541117074401	001S002W07Q001S	0.4	238
BH 2	340426117092701	001S003W23A005S	3.0	119
BH 3	340623117104001	001S003W03Q003S	4.4	244
BH 4	340505117101901	001S003W14E001S	4.6	70
BH 5.1	340503117104105	001S003W15K005S	5.1	152
BH 5.2	340503117104104	001S003W15K004S	5.1	232
BH 5.3	340503117104103	001S003W15K003S	5.1	287
BH 5.4	340503117104102	001S003W15K002S	5.1	120
BH 6.1	340707117162708	001S004W02D008S	10.0	55
BH 6.2	340707117162707	001S004W02D007S	10.0	113
BH 6.3	340707117162706	001S004W02D006S	10.0	160
BH 7.1	340615117170904	001S004W10B004S	11.9	34
BH 7.2	340615117170903	001S004W10B003S	11.9	94
BH 7.3	340615117170902	001S004W10B002S	11.9	210
BH 8	340423117155201	001S004W23H001S	13.2	48
BH 9	340438117162301	001S004W23C003S	14.3	191
BH 10	340437117170301	001S004W22B006S	14.5	107
BH 11.1	340408117165304	001S004W22J004S	14.7	11
BH 11.2	340408117165303	001S004W22J003S	14.7	76
BH 11.3	340408117165302	001S004W22J002S	14.7	162
BH 11.4	340408117165301	001S004W22J001S	14.7	259
BH 12.1	340439117173907	001S004W22D007S	15.0	8
BH 12.2	340439117173902	001S004W22D002S	15.0	55
BH 12.3	340439117173905	001S004W22D005S	15.0	172
BH 12.4	340439117173904	001S004W22D004S	15.0	199

Table 11	Wells sampled in the Bunker Hill Basin.	San Bernardino County	California 2000
			, Gamonna, 2000.

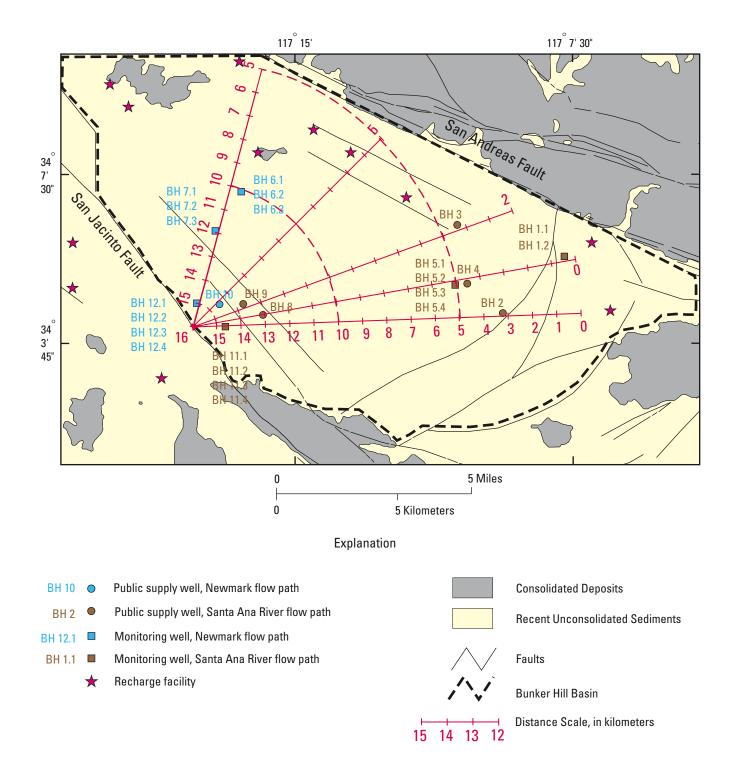


Figure 34. Well locations and distance measurement along flow paths in the Bunker Hill Basin, San Bernardino County, California.

Table 12. Statistical differences between the Newmark and Santa Ana River ground-water flow paths, Bunker Hill Basin, San Bernardino County, California, 2000.

LRL, laboratory reporting limit; VOC, Vol	All Wells	Wells from 11 to 16 kilometers
Variable	Rank-sum <i>p</i> -value	Rank-sum p-value
Distance	² 0.03	0.84
Depth to top of openings	0.30	1.00
Depth to mid-point of openings	0.15	0.95
Depth to bottom of openings	¹ 0.09	0.70
δ Oxygen-18	³ 0.0005	² 0.05
δ Deuterium	³ 0.0004	² 0.03
VOC Score	0.12	0.70
Number of detections above LRL	0.10	0.69
Total number of VOCs detected	0.19	1.00
Trichlorofluoromethane (CFC-11)	0.74	0.89
Tetrachloroethene (PCE)	0.87	0.69
Trichloromethane (Chloroform)	0.53	0.30
Trichloroethene (TCE)	0.90	0.33
Methyl tert-butyl ether (MTBE)	² 0.02	0.15
Benzene	² 0.03	¹ 0.08
1,2-Dimethylbenzene	³ 0.01	0.24
1,4-Dimethylbenzene	³ 0.01	0.24
cis-1,2-Dichloroethene	0.77	0.81
Bromodichloromethane	0.77	0.24
1,1-Dichloroethene	0.90	0.93
Ethylbenzene	² 0.04	0.24
1,2-Dichloropropane	0.14	0.53
Carbon Disulfide	0.84	0.42
Tribromomethane	0.40	0.24
Chlorodibromomethane	0.35	0.24
Dichlorodifluoromethane	0.40	0.79
2-Ethyltoluene	¹ 0.10	0.24
1,2,4-Trimethylbenzene	² 0.04	0.24
Isopropylbenzene	0.10	0.24
n-Propylbenzene	0.10	0.24
Chloromethane	0.36	0.37
1,1-Dichloroethane	0.64	0.71
1,1,1-Trichloroethane	0.78	1.00
1,2-Dichlorobenzene	¹ 0.02	0.13
Dibromomethane	0.10	0.24
Napthalene	0.28	0.47
1,2,3,4-Tetramethylbenzene	0.28	0.47
sec-Butylbenzene	0.28	0.47
1,1,1,2-Tetrachloroethane	0.91	0.47
Chlorobenzene	1.00	1.00
1,4-Dichlorobenzene	0.18	0.20
1,2,3-Trimethylbenzene	0.28	0.47
1,3,5-Trimethylbenzene	0.10	0.24
Bromochloromethane	0.10	0.24
<i>n</i> -Butylbenzene	1.00	1.00
<i>p</i> -Isopropyltoluene	0.18	0.20

[LRL, laboratory reporting limit; VOC, Volatile Organic Compounds]

¹ blue, p = 0.10 to 0.06 ² green, p = 0.05 to 0.02 ³ yellow, p = 0.01 to < 0.0001

Table 13. Statistical correlations along ground-water flow paths in the Bunker Hill Basin, San Bernardino County, California, 2000.

[VOC, Volatile Organic Compounds]

Variable	Spearman <i>p</i> -value	Spearman's rho	Statistical Correlation				
Correlations with distance down grad	dient:						
Depth to top of openings	0.19	0.26	No				
Depth to mid-point of openings	0.13	0.30	No				
Depth to bottom of openings	0.12	0.32	No				
δ Oxygen-18	³ 0.01	³ 0.54	Positive ³				
δ Deuterium	³ 0.01	³ 0.53	Positive ³				
VOC Score	¹ 0.06	¹ 0.37	Positive ¹				
Number of detections above LRL	¹ 0.06	¹ 0.37	Positive ¹				
Total number of VOCs detected	0.12	0.31	No				
Trichloromethane (Chloroform)	0.81	-0.05	No				
Methyl tert-butyl ether (MTBE)	² 0.04	² 0.40	Positive ²				
Trichloroethene (TCE)	0.40	0.17	No				
Tetrachloroethene (PCE)	0.19	0.26	No				
Trichlorofluoromethane (CFC-11)	³ 0.008	³ 0.53	Positive ³				
Correlations with depth to the mid-point of openings:							
Distance down gradient	0.13	0.30	No				
δ Oxygen-18	¹ 0.10	¹ -0.35	Inverse ¹				
δ Deuterium	¹ 0.07	¹ -0.39	Inverse ¹				
VOC Score	¹ 0.09	¹ -0.34	Inverse ¹				
Number of detections above LRL	² 0.05	² -0.40	Inverse ²				
Total number of VOCs detected	0.36	-0.18	No				
Trichloromethane (Chloroform)	0.64	-0.09	No				
Methyl tert-butyl ether (MTBE)	0.34	-0.19	No				
Trichloroethene (TCE)	² 0.05	² -0.40	Inverse ²				
Tetrachloroethene (PCE)	0.69	-0.08	No				
Trichlorofluoromethane (CFC-11)	0.31	-0.20	No				

¹ blue, p = 0.10 to 0.06 ² green, p = 0.05 to 0.02 ³ yellow, p = 0.01 to < 0.0001

Stable Isotopes

A plot of δ^{18} O in relation to δ D measured in wells along the SAR and Newmark flow paths is shown in figure 35. Ground-water values from all wells plot along the Global Meteoric Water Line (Craig, 1961). Delta oxygen-18 and δ D are significantly lighter along the SAR flow path than along the Newmark flow path (fig. 35). This difference may be related to the elevation of the drainage basins of the creeks that recharge the aquifer system. Elevations of the San Bernardino Mountains increase from west to east, suggesting that recharge water to the SAR flow path may originate from a higher elevation than recharge water to the Newmark flow path, and would, therefore, have a lighter isotopic signature.

Volatile organic compounds

Twenty-seven VOCs were detected above LRL in ground water in the Bunker Hill Basin; an additional 11 VOCs were detected only below LRL (table 14). Sixty-five percent (17 of 26) of the wells sampled contained one or more VOCs above LRL; an additional 15 percent (4 of 26) of the wells had one or more VOCs only below LRL. Nineteen percent (5 of 26) of the wells sampled had no VOC detections. All but two of the VOC detections-trichloroethene and benzenealong Bunker Hill Basin flow paths were below federal or state MCLs (table 14) (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001). Of VOCs that had MCLs, 78 percent of all detections were less than 1 percent of their MCL concentrations. The 5 compounds discussed in this report (chloroform, MTBE, TCE, PCE, and CFC-11) were detected on both flow paths and are the most frequently detected VOCs in the Bunker Hill Basin (table 15).

VOC Score

VOC score showed a positive correlation with distance downgradient, increasing monotonically along the flow paths from proximal to distal areas (fig. 36A).

VOC scores were statistically higher in the shallower wells (<u>table 13</u>), although high numbers of VOCs were detected at all well depths (<u>fig. 36B</u>).

The spatial distribution of VOC scores on the Bunker Hill flow paths is the opposite of the general patterns found in the Central and Main Basins. The higher numbers of VOCs detected in more distal wells suggest that either (1) the number of VOCs currently reaching ground water in the proximal part of the flow paths is much lower than in the past, or (2) VOCs are being contributed to ground water all along the flow paths. If the VOCs detected in deep wells in the distal part of the flow path were introduced at land surface in the distal area, then the confining units are not insulating the ground water from compounds introduced at land surface in the Bunker Hill Basin. Therefore, as ground water flows downgradient, it is continually picking up VOCs. It is also possible that pumping wells are selectively removing cleaner ground water, thus increasing the amount of VOCs in the remaining ground water in the distal parts of the flow system.

Chloroform

Chloroform was detected in 27 percent of the wells (<u>table 15</u>). Unlike the coastal basins, chloroform was not the most frequently detected VOC. The lower detection frequency may reflect the mountain source of recharge to the Bunker Hill Basin; mountain recharge contains relatively little water that has previously been used, such as treated wastewater that could contain disinfection by-products such as chloroform. No correlation was found between chloroform concentration and distance, or between chloroform concentration and depth, on either flow path (<u>table 13</u>).

The spatial distribution of chloroform is similar to VOC score. Concentrations of chloroform were similar in the proximal and distal areas, with slightly more detections and higher concentrations detected in distal wells (<u>fig. 37A</u>). The highest concentration was detected in the distal part of the flow paths at mid-depth (<u>fig. 37B</u>), whereas the highest VOC score was detected in a shallow well. Nondetections were in the proximal and distal parts of the flow paths.

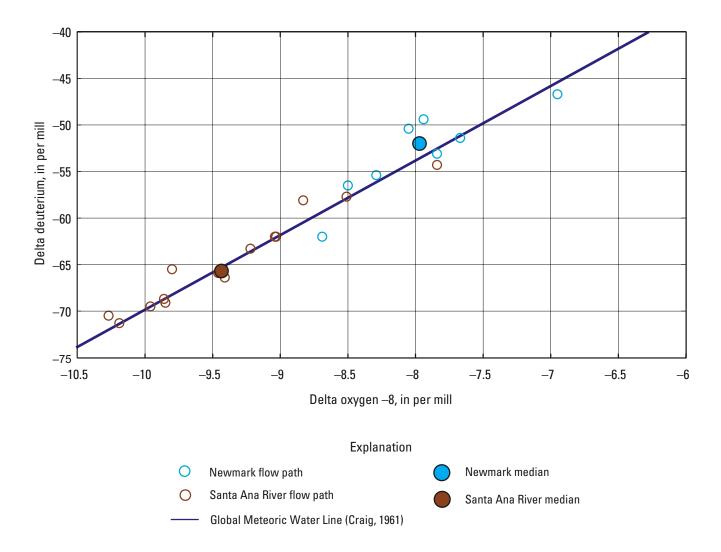


Figure 35. Relation between delta oxygen-18 and delta deuterium in ground water along flow paths, Bunker Hill Basin, San Bernardino County, California.

 Table 14.
 Volatile organic compounds detected in 26 ground-water samples from selected wells in the Bunker Hill Basin, San Bernardino County, California, 2000.

[LRL, laboratory reporting limit; MCL	, maximum contaminant level; -	, no value available or applicable; E, o	concentration estimated]

Constituent	LRL, in μ g/L	Number of detections at or above LRL	Number of detections below LRL	Minimum detection, in μg/L	Maximum detection, in μg/L	MCL, in μg/L	Number of wells exceed ing a MCL
Total number of VOCs detected	_	_		0	16	_	_
VOC Score	—	—	_	0.0	12.0	—	—
Trichlorofluoromethane (CFC-11)	0.09	7	3	0.02	2.53	² 150	0
Tetrachloroethene (PCE)	0.1	3	4	0.0163	0.532	¹ 5	0
Trichloromethane (Chloroform)	60.052, 0.024	5	2	0.021	0.543	^{1,3} 80	0
Trichloroethene (TCE)	0.038	5	2	0.009	10.6	¹ 5	1
Methyl <i>tert</i> -butyl ether (MTBE)	0.17	2	3	0.07	4.35	² 13	0
Benzene	0.021	3	1	0.007	25.8	² 1	1
1,2-Dimethylbenzene	0.038	3	1	0.032	0.133	⁴ 1,750	0
1,4-Dimethylbenzene	0.06	3	1	0.05	0.99	⁴ 1,750	0
cis-1,2-Dichloroethene	0.038	3	0	0.074	0.242	² 6	0
Bromodichloromethane	0.048	2	1	0.046	0.502	1,380	0
1,1-Dichloroethene	0.04	2	1	0.01	0.06	² 6	0
Ethylbenzene	0.03	2	1	0.01	0.44	¹ 700	0
1,2-Dichloropropane	0.029	1	2	0.014	0.059	¹ 5	0
Carbon Disulfide	0.07	1	2	0.02	0.73	_	_
Tribromomethane	0.06	2	0	0.09	0.72	^{1,3} 80	0
Chlorodibromomethane	0.18	1	1	0.08	0.67	^{1,3} 80	0
Dichlorodifluoromethane	0.27	1	1	0.15	0.28	_	_
2-Ethyltoluene	0.06	1	1	0.05	1.86	_	_
1,2,4-Trimethylbenzene	0.056	1	1	0.016	0.154	_	_
Isopropylbenzene	0.032	1	1	0.022	26.100	_	_
n-Propylbenzene	0.042	1	1	0.040	38.000	_	_
Chloromethane	⁶ 0.5, 0.25	0	2	0.04	0.04	_	_
1,1-Dichloroethane	⁶ 0.066, 0.035	0	2	0.020	0.029	² 5	0
1,1,1-Trichloroethane	0.032	0	2	0.009	0.020	¹ 200	0
1,2-Dichlorobenzene	0.048	0	2	0.024	0.036	¹ 600	0
Dibromomethane	0.05	1	0	0.05	0.05	_	
Napthalene	0.25	1	0	21.9	21.9	_	
1,2,3,4-Tetramethylbenzene	0.23	1	0	6.93	6.93	_	_
sec-Butylbenzene	0.032	1	0	5.5	5.5	_	_
1,1,1,2-Tetrachloroethane	0.06	1	0	0.19	0.19	² 1,200	0
Chlorobenzene	0.028	0	1	0.004	0.004	¹ 100	0
1,4-Dichlorobenzene	0.05	0	1	0.01	0.01	² 5	0
1,2,3-Trimethylbenzene	0.12	0	1	0.04	0.04		
1,3,5-Trimethylbenzene	0.044	0	1	0.038	0.038	_	_
Bromochloromethane	0.044	0	1	0.023	0.023	_	_
<i>n</i> -Butylbenzene	0.19	0	1	0.04	0.04	_	_
<i>p</i> -Isopropyltoluene	0.07	0	1	0.02	0.02	_	_
Methyl benzene ⁵	0.05	4	4	0.01	0.89	² 150	0

¹ U.S. Environmental Protection Agency, 2001.

² California Department of Water Resources, 2001.

³ Total Trihalomethanes, as of 01/01/02 ,U.S. Environmental Protection Agency, 2001.

⁴ Total Xylenes, California Department of Water Resources, 2001.

⁵ Methyl benzene concentrations may be due to sample contamination during collection and analysis.

⁶ 2 LRLs used during the sampling period.

Table 15.
 Detection frequencies of volatile organic compounds detected in 26 wells sampled in the Bunker Hill Basin, San Bernardino County, California, 2000.

[LRL, laboratory reporting limit]

Constituent	Detection Frequency, in percent					
	All Detections	Detections above LRL	Detections below LR			
Trichlorofluoromethane (CFC-11)	38	27	12			
Tetrachloroethene (PCE)	31	15	15			
Trichloromethane (Chloroform)	27	19	7.7			
Trichloroethene (TCE)	27	19	7.7			
Methyl <i>tert</i> -butyl ether (MTBE)	19	7.7	12			
Benzene	15	12	3.8			
1,2-Dimethylbenzene	15	12	3.8			
1,4-Dimethylbenzene	15	12	3.8			
cis-1,2-Dichloroethene	12	12	0.0			
Bromodichloromethane	12	7.7	3.8			
1,1-Dichloroethene	12	7.7	3.8			
Ethylbenzene	12	7.7	3.8			
1,2-Dichloropropane	12	3.8	7.7			
Carbon Disulfide	12	3.8	7.7			
Tribromomethane	7.7	7.7	0.0			
Chlorodibromomethane	7.7	3.8	3.8			
Dichlorodifluoromethane	7.7	3.8	3.8			
2-Ethyltoluene	7.7	3.8	3.8			
1,2,4-Trimethylbenzene	7.7	3.8	3.8			
Isopropylbenzene	7.7	3.8	3.8			
<i>n</i> -Propylbenzene	7.7	3.8	3.8			
Chloromethane	7.7	0.0	7.7			
1,1-Dichloroethane	7.7	0.0	7.7			
1,1,1-Trichloroethane	7.7	0.0	7.7			
1,2-Dichlorobenzene	7.7	0.0	7.7			
Dibromomethane	3.8	3.8	0.0			
Napthalene	3.8	3.8	0.0			
1,2,3,4-Tetramethylbenzene	3.8	3.8	0.0			
sec-Butylbenzene	3.8	3.8	0.0			
1,1,1,2-Tetrachloroethane	3.8	3.8	0.0			
Chlorobenzene	3.8	0.0	3.8			
1,4-Dichlorobenzene	3.8	0.0	3.8			
1,2,3-Trimethylbenzene	3.8	0.0	3.8			
1,3,5-Trimethylbenzene	3.8	0.0	3.8			
Bromochloromethane	3.8	0.0	3.8			
<i>n</i> -Butylbenzene	3.8	0.0	3.8			
<i>p</i> -Isopropyltoluene	3.8	0.0	3.8			

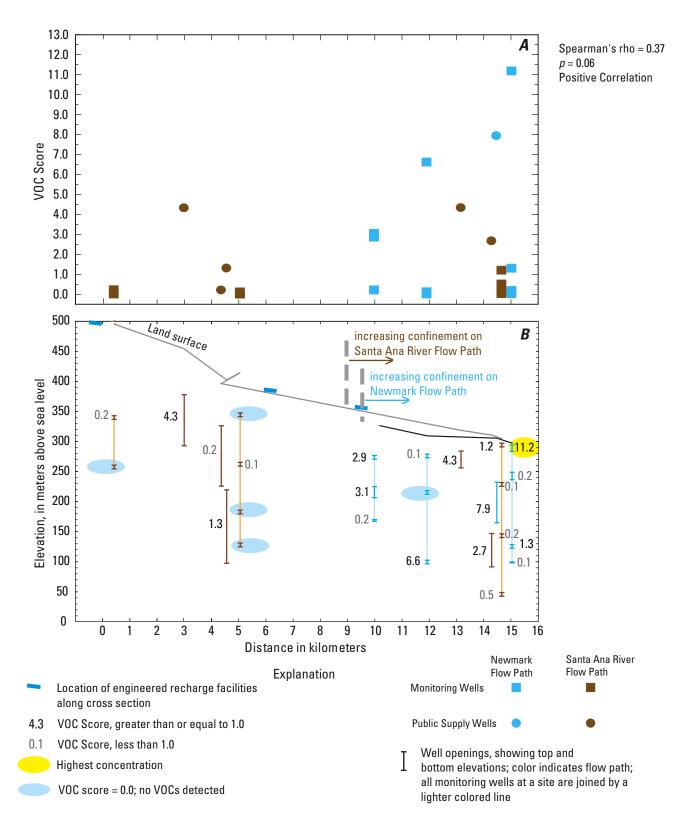


Figure 36. VOC score (A) versus distance and (B) in wells along flow paths, Bunker Hill Basin, San Bernardino County, California, 2000.

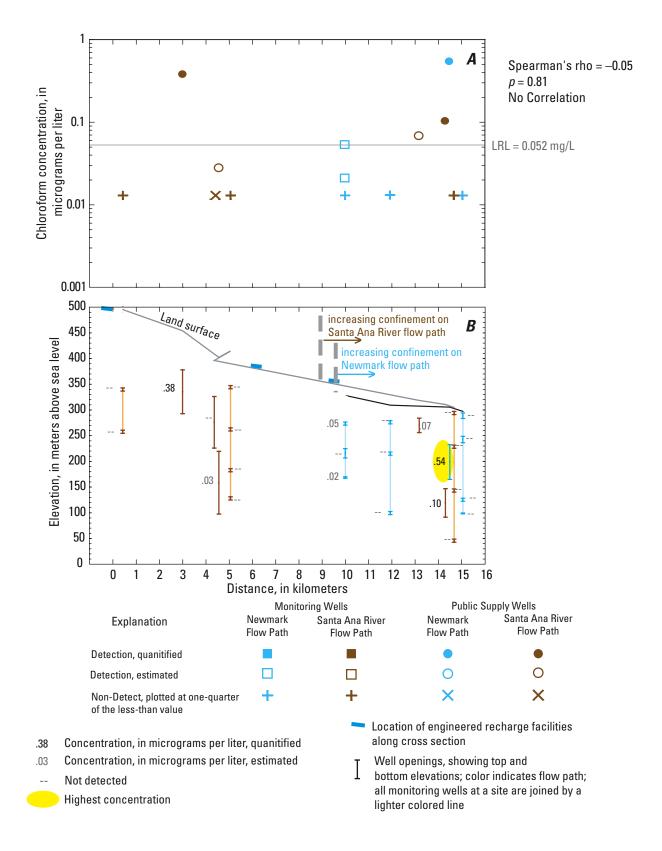


Figure 37. Trichloromethane (chloroform) concentration (A) versus distance and (B) in wells along flow paths in the Bunker Hill Basin, California, 2000.

MTBE

MTBE was detected in 19 percent of the wells (table 15). Only one low detection was on the SAR flow path in the deepest downgradient monitoring well. MTBE concentrations increased significantly downgradient, with the highest concentration detected in a deeper monitoring well at 15 km (fig. 38*B*). No MTBE was detected in wells less than 6 km downgradient. No correlation was found on either Bunker Hill flow path between MTBE concentration and depth (table 13).

The distribution of MTBE concentrations is similar to VOC score. MTBE was detected in the distal area of the ground-water flow paths, but not in the proximal areas (fig. 38B). The highest concentration was detected in a deep monitoring well at the distal end of the flow paths (fig. 38B). This suggests that MTBE, a recently introduced compound, is not currently reaching ground water in the proximal recharge areas, but is reaching ground water in the distal, confined part of the flow path. Because MTBE use in the recharge area would not have been higher in the past than it is now, it probably was not transported horizontally downgradient from the forebay areas, but reached ground water vertically from land surface in the distal, confined area of Bunker Hill flow paths. This suggests that the confining units present in the distal part of the Bunker Hill Basin do not prevent VOCs from reaching ground water.

TCE

TCE was detected in 27 percent of the wells (<u>table 15</u>). No correlation was found between TCE concentration and distance along either Bunker Hill flow path (<u>table 13</u>). The highest concentration over the federal and state MCL (California Department of Health Services, 2001; U.S. Environmental Protection Agency, 2001) was in the distal area at about 13 km in a shallow public supply well. Three of the highest concentrations were detected in the public supply wells associated with mapped TCE plumes (Wildermuth Environmental, Inc., 2000b, fig. 3); one high concentration was detected in a public supply well downgradient from mapped TCE plumes (<u>fig. 39</u>). There was a significant decrease in concentration with increasing depth (<u>table 13</u>).

As in the Main Basin, higher TCE concentrations are associated with mapped TCE plumes (figs. 33 and 39B). The distribution of TCE is similar to VOC score and MTBE. Higher concentrations were detected in distal wells or in wells associated with mapped plumes. Low concentrations and nondections were in the proximal and distal parts of the flow system in wells outside of mapped plumes. The presence of TCE in wells outside of mapped plumes suggests that there may be other sources of TCE, or that the known sources have contributed TCE to areas outside of the mapped plumes.

PCE

PCE was detected in 31 percent of the wells (<u>table 15</u>). There was a no statistical difference in PCE concentration between the two Bunker Hill flow paths (<u>table 12</u>). No correlation was found between PCE concentration and distance along the either flow path (<u>table 13</u> and <u>fig. 40A</u>). However, PCE concentrations increased downgradient, with the highest concentration detected at about 14 km in a relatively deep public supply well (<u>fig. 40B</u>). No correlation was found between PCE concentration and depth (<u>table 13</u>).

The spatial distribution of PCE concentration is similar to VOC score. High PCE concentrations were detected in distal wells on both flow paths (fig. 40*B*). Low concentrations and nondetections occurred at all depths in the proximal and distal areas. These patterns suggest that either high concentrations were recharged in the past in the proximal part of the flow paths and migrated downgradient to the distal area or PCE is currently reaching ground water all along the flow paths.

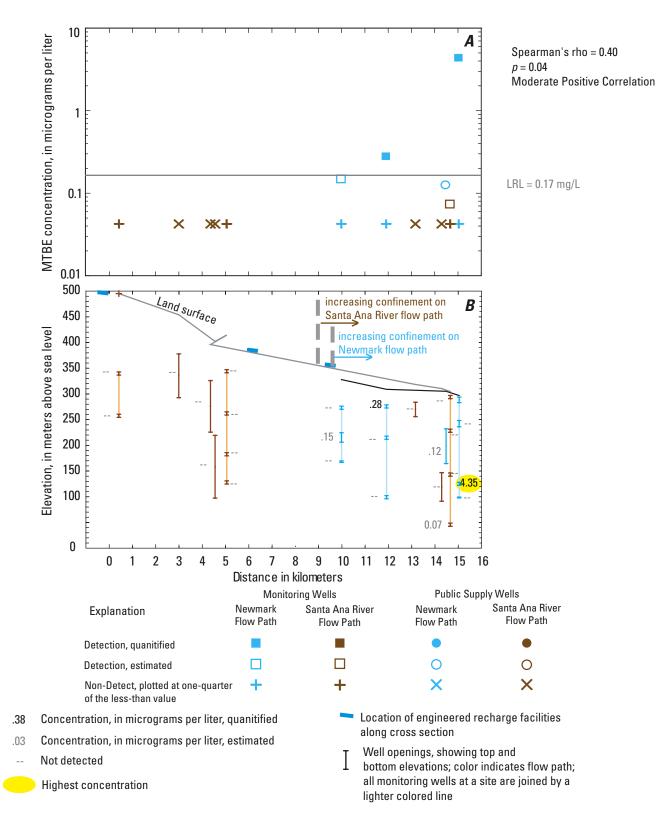


Figure 38. Methyl tert-butyl ether (MTBE) concentrations (A) versus distance and (B) in wells along flow paths, Bunker Hill Basin, San Bernardino County, California, 2000.

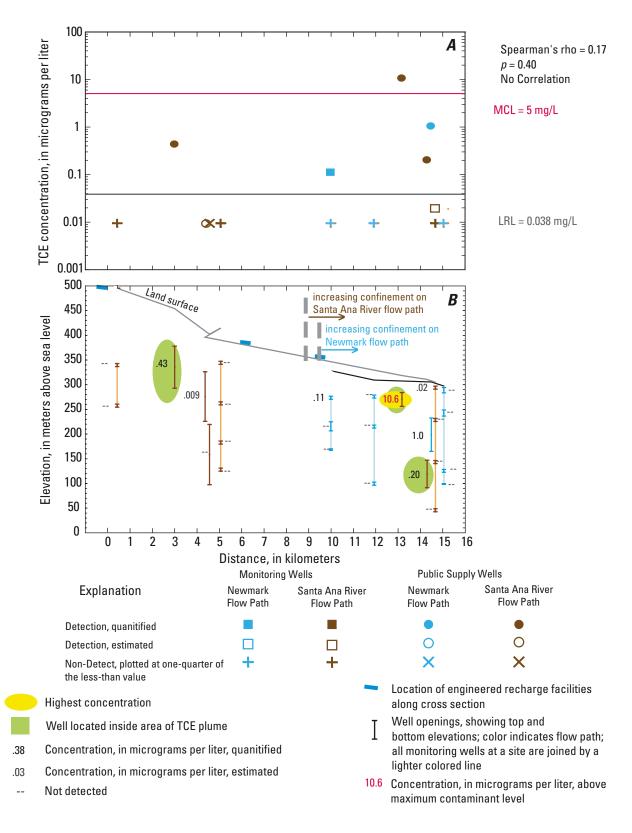


Figure 39. Trichloroethene (TCE) concentrations (A) versus distance and (B) in wells along flow paths, Bunker Hill Basin, San Bernardino County, California, 2000.

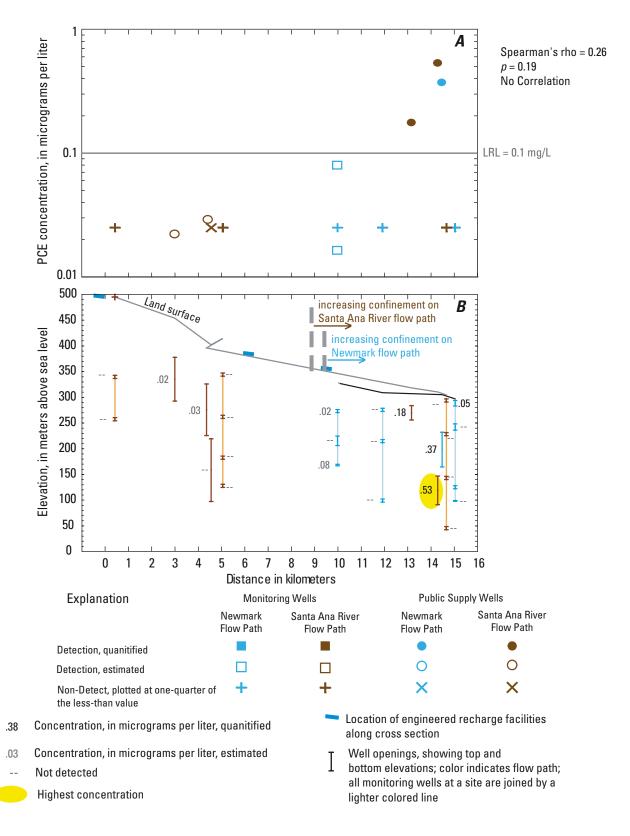


Figure 40. Tetrachloroethene (PCE) concentrations (A) versus distance and (B) in wells along flow paths, Bunker Hill Basin, San Bernardino County, California, 2000.

CFC-11

CFC-11, detected in 38 percent of the wells, was the most frequently detected VOC on the Bunker Hill flow paths (<u>table 15</u>). This is in contrast to the five coastal plain flow paths, where chloroform was the most frequently detected compound (<u>tables 5</u> and <u>10</u>). No statistical difference in CFC-11 concentration was found between the Bunker Hill flow paths (<u>table 12</u>). CFC-11 concentrations are significantly correlated with distance, with higher concentrations detected greater than 14 km downgradient (<u>fig. 41</u>); however, in contrast to the other VOCs, the highest concentration was detected in the upgradient well closest to the Santa Ana River recharge facilities (<u>fig. 41B</u>). There was no correlation between CFC-11 concentrations and well depths (<u>table 13</u>), with detections in shallow, middle, and deep wells.

The spatial distribution of CFC-11 is similar to VOC score, with one exception. Unlike the other VOCs analyzed in the Bunker Hill Basin, the highest concentration of CFC-11 was detected in the most upgradient well (fig. 41*B*). However, other high concentrations were detected in the most distal wells on the flow paths. In the distal wells, the highest concentration was detected in a shallow well. This pattern suggests that, in contrast to the coastal plain flow paths, CFC-11 is currently reaching ground water in more than one location along the Bunker Hill flow paths.

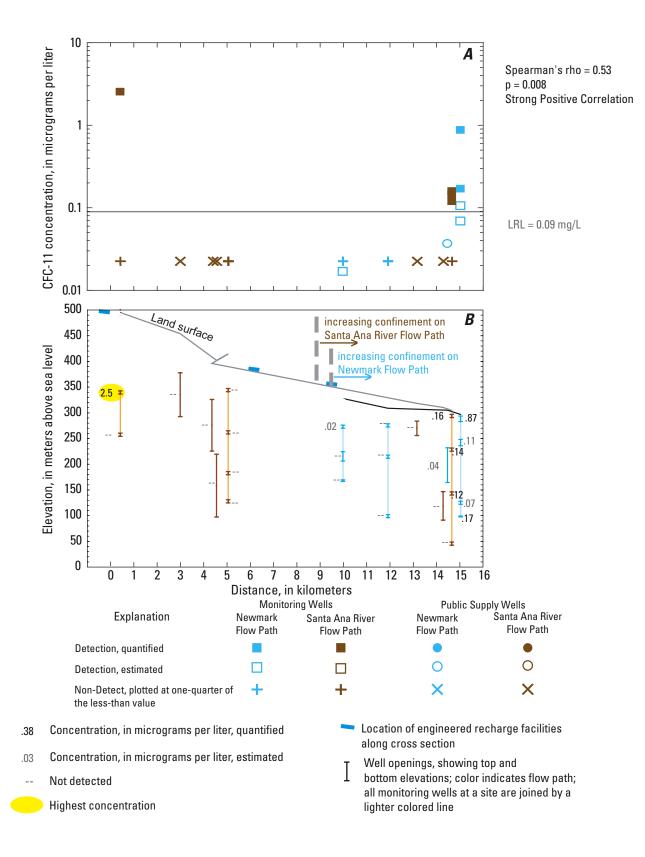


Figure 41. Trichlorofluoromethane (CFC-11) concentrations (A) versus distance and (B) in wells along flow paths, Bunker Hill Basin, California, 2000.

SUMMARY AND CONCLUSIONS

Stable isotopes and volatile organic compounds (VOC) were examined along ground-water flow paths in three southern California basins. Five flow paths are located in the southern California coastal plain. Ground-water flow systems in the Coastal Plain are characterized by areas of focused ground-water recharge; ground-water flows radially outward into the basins toward dispersed areas of ground-water pumping (discharge). Two flow paths are located in the Inland Santa Ana Basin, which is characterized by dispersed areas of ground-water recharge; groundwater flow converges radially toward an area of focused discharge.

As part of this study, a new way of counting VOC detections in a sample, the VOC score, was developed to include detections of VOCs below the laboratory reporting levels (LRL) in data analyses. About half of the VOC detections in this study were at concentrations below the LRL. The VOC score allows all the VOC detections to be used for graphical and statistical analyses, and takes into account the analytical certainty based on the LRL. The VOC score gives more weight to detections above LRL, which have less than 1 percent chance of false positive or false negative detections, and less weight (one tenth) to detections below the LRL, which may have a greater than 1 percent chance of false negative detections.

In the Central Basin, Los Angeles County, the two flow paths sampled originate at the San Gabriel and Rio Hondo recharge facilities in the Montebello forebay area. Stable isotopes indicate that ground water along both flow paths is from similar sources. The patterns of VOC score and concentrations indicate that a volume of water that contains VOCs and is presumably young (has recharged since the 1930s) extends about 20 km into the Central Basin from the Montebello forebay and to depths of at least 400 m below land surface. In this volume of water, VOC score and concentration are variable and may reflect the history of VOC inputs and fate in the subsurface environment. This water is mixing with presumably older ground water that contains no VOCs. The patterns also suggest that some VOCs were introduced to ground water at higher concentrations in the past than at present and that VOCs continue to enter the Central Basin through the Whittier Narrows. The pattern of MTBE concentrations is different from the

other VOCs, and suggests that MTBE is currently being introduced into ground water in the upgradient areas of the Central Basin at higher concentrations than in the past.

An important exception to the general pattern is the very high concentrations of TCE and PCE in shallow wells located in the pressure area. These wells are downgradient from wells with much lower concentrations. This indicates that even in the pressure area, ground-water is susceptible to contamination from VOC sources.

In the Main Basin, Orange County, three flow paths were sampled. The Santa Ana River (SAR) west flow path is located in the radial flow system that originates at the SAR recharge facilities. The Santiago flow path is located in the radial flow system from the Santiago Creek recharge facilities. The SAR east flow path originates in the SAR flow system, but also is along the convergence of the Santa Ana River and Santiago Creek flow systems. Ground water is isotopically the same on SAR flow paths, indicating similar sources of water. Ground water along the Santiago flow path is isotopically different from the other two flow paths, indicating a different source of ground water on the Santiago flow path.

Although stable isotopes show that the SAR west and east flow paths are similar and the Santiago flow path is different, the VOCs show a contrasting relation. VOC score and VOC concentrations on the SAR west flow path are different from both the SAR east and Santiago flow paths. VOC occurrences were statistically similar between the SAR east and Santiago flow paths, suggesting that recharge from Santiago Creek is affecting VOC occurrences on the SAR east flow path. The patterns of VOC scores, chloroform, and TCE along the Santiago flow path are different than on the SAR flow paths and suggest that more VOCs are currently reaching ground water than in the past. These patterns may reflect that the Santiago Creek recharge facilities have been operational for a shorter period of time than the SAR recharge facilities. VOC score and concentrations on the SAR west flow path show a pattern similar to the Central Basin flow paths. A volume of presumably young water containing VOCs extends to a distance around 18 km from the SAR recharge facilities and a depth of at least 300 m, and is mixing with presumably older water containing no VOCs.

In the Inland Bunker Hill Basin, two flow paths were sampled. In contrast to the Coastal Plain basins, ground-water recharge in the Bunker Hill Basin is dispersed along the mountain front, and ground-water flow converges radially to an area of focused discharge along the San Jacinto Fault. The two flow paths originate in different sections of the mountain front and converge near the San Jacinto Fault. The stable isotopes indicate different sources of water for the two flow paths; however, VOC occurrence is similar between them. In contrast to the patterns found in the Central and Main Basins, higher VOC scores and concentrations of MTBE, TCE, and PCE in the Bunker Hill Basin were detected at the distal end of the flow paths in the confined part of the flow system. This suggests that either (1) high concentrations of these VOCs reached ground water at some time in the past in the unconfined, upgradient area of the flow paths and have migrated downgradient or (2) VOCs are introduced all along the flow paths, even in the confined part of the aquifer. The absence of MTBE in the proximal part of the flow paths and presence in the distal part suggest that the confining units present in the distal part of the Bunker Hill Basin do not prevent VOCs from reaching ground water. The patterns of VOC score and concentration in the Bunker Hill Basin indicate a different situation than in the coastal plain. In Bunker Hill, a volume of presumably young water containing relatively few VOCs is moving outward from the recharge areas and mixing with a volume of possibly intermediate to older water that contains many VOCs.

The susceptibility of public supply wells to land surface contamination can be understood, in part, by developing an understanding of the regional groundwater flow system. In the southern California coastal plain, and perhaps other radially divergent confined flow systems, VOC score and concentrations tend to decrease with increasing distance. In the inland Santa Ana Basin, and perhaps other radially convergent, confined flow systems, VOC score and concentrations tend to increase with increasing distance. These results suggest that distal wells tapping older ground water are less susceptible to land surface contamination than proximal wells tapping younger ground water in radially divergent confined systems. Conversely, distal wells tapping older ground-water probably are more susceptible than proximal wells tapping younger

ground water in radially convergent, confined systems. These differences in susceptibility are partly controlled by the pattern of ground-water flow (radially divergent or radially convergent) and perhaps by the degree of confinement.

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