Water-Quality Trends in the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, California

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CONVERSION FACTORS, DEFINITIONS, ACRONYMS AND ADDITIONAL ABBREVIATIONS

Multiply	By	To obtain
foot (ft)	0.3048	meter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
inch (in.)	25.4	millimeter
mile (mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer
acre-foot (acre-ft)	1233.5	cubic meter

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

ABBREVIATIONS

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

DEFINITIONS

Confidence criteria: The chance rejection of a hypothesis when the hypothesis is true. Usually represented by the Greek letter α (Neter and Wasserman, 1974). For the purposes of this report, if the 'p-value' (probability that the null hypothesis is true) was less than a confidence criterion of $\alpha=0.01$ the result was reported as highly significant. If the 'p-value' was greater than $\alpha=0.01$ but less than 0.1 the result was reported as significant.
Residuals: A residual is the difference between an observed value and the corresponding value estimated from a regression equation.
Water year: The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1995, is called the "1995 water year."

ACRONYMS AND ADDITIONAL ABBREVIATIONS

ESTREND	EStimated TREND.
LOWESS	LOcally WEighted Scatterplot Smoothing
MCL	Maximum Contaminant Level
MWD	Metropolitan Water District
NAWQA	National Water Quality Assessment
OCWD	Orange County Water District
SARWQHS	Santa Ana River Water Quality and Health Study
SMCL	Secondary Maximum Contaminant Level
U.S. EPA	United States Environmental Protection Agency

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ABSTRACT

The Santa Ana River, located in an extensively urbanized basin, drains about 2,670 square miles near Los Angeles, California. Almost all flow in the river, about 200,000 acre-feet annually, is diverted to ponds where it infiltrates and recharges underlying aquifers. About 2 million people are dependent on these aquifers for water supply. In recent years, base flow in the river has increased as a result of increased discharge of treated municipal wastewater, and high flows have increased as a result of increased precipitation and urbanization. Trends in water quality were calculated for two sites—at the Metropolitan Water District (MWD) Crossing (an upstream site) and below Prado Dam (a downstream site)—using the computer program ESTREND. Water-quality data for these sites were collected by the U.S. Geological Survey from 1969 to 1995. At MWD Crossing, flow-adjusted downward trends of -1.1 microsiemens per centimeter (μS/cm) per year and -1.6 milligrams per liter (mg/L) per year were calculated for specific conductance and dissolved solids, respectively. In contrast, a flow-adjusted upward trend of 2.2 μS/cm per year for dissolved solids was calculated for the Santa Ana River below Prado Dam. Specific conductance and dissolved solids in the Santa Ana River below Prado Dam had downward unadjusted trends (not adjusted for streamflow) of -8.3 μS/cm per year and -6.0 mg/L per year, respectively. For the Santa Ana River below Prado Dam, downward unadjusted trends were calculated for ammonia (-0.04 mg/L per year) and total organic carbon (-0.19 mg/L per year); flow-adjusted upward trends were calculated for nitrite plus nitrate (0.15 mg/L per year), total dissolved nitrogen (0.39 mg/L per year), and orthophosphate (0.03 mg/L per year). Statistically significant unadjusted and flow-adjusted trends were not obtained for organic nitrogen, ammonia plus organic nitrogen, phosphorus, and dissolved organic carbon. Data for selected trace elements and organic compounds collected between 1970-94 also are summarized in this report.

INTRODUCTION

The Santa Ana River drains about 2,670 mi^2 of the densely populated coastal area of southern California near Los Angeles (fig. 1). Almost all flow in the Santa Ana River, more than 200,000 acre-ft of water annually, is diverted to ponds where it is allowed to infiltrate and recharge underlying aquifers (Orange County Water District, 1996a). Pumpage from these aquifers is the primary source of supply for about 2 million people in Orange County, California (Orange County Water District, 1996a). In recent years, only water from the largest storms discharges to the Pacific Ocean.

Base flow in the Santa Ana River is maintained almost entirely by discharges of treated municipal wastewater. Large quantities of water recharged during stormflows in the winter improve the overall quality of water recharged from the Santa Ana River. However, because these stormflows include runoff from urban and agricultural areas, they may contain high concentrations of inorganic and organic constituents and bio-

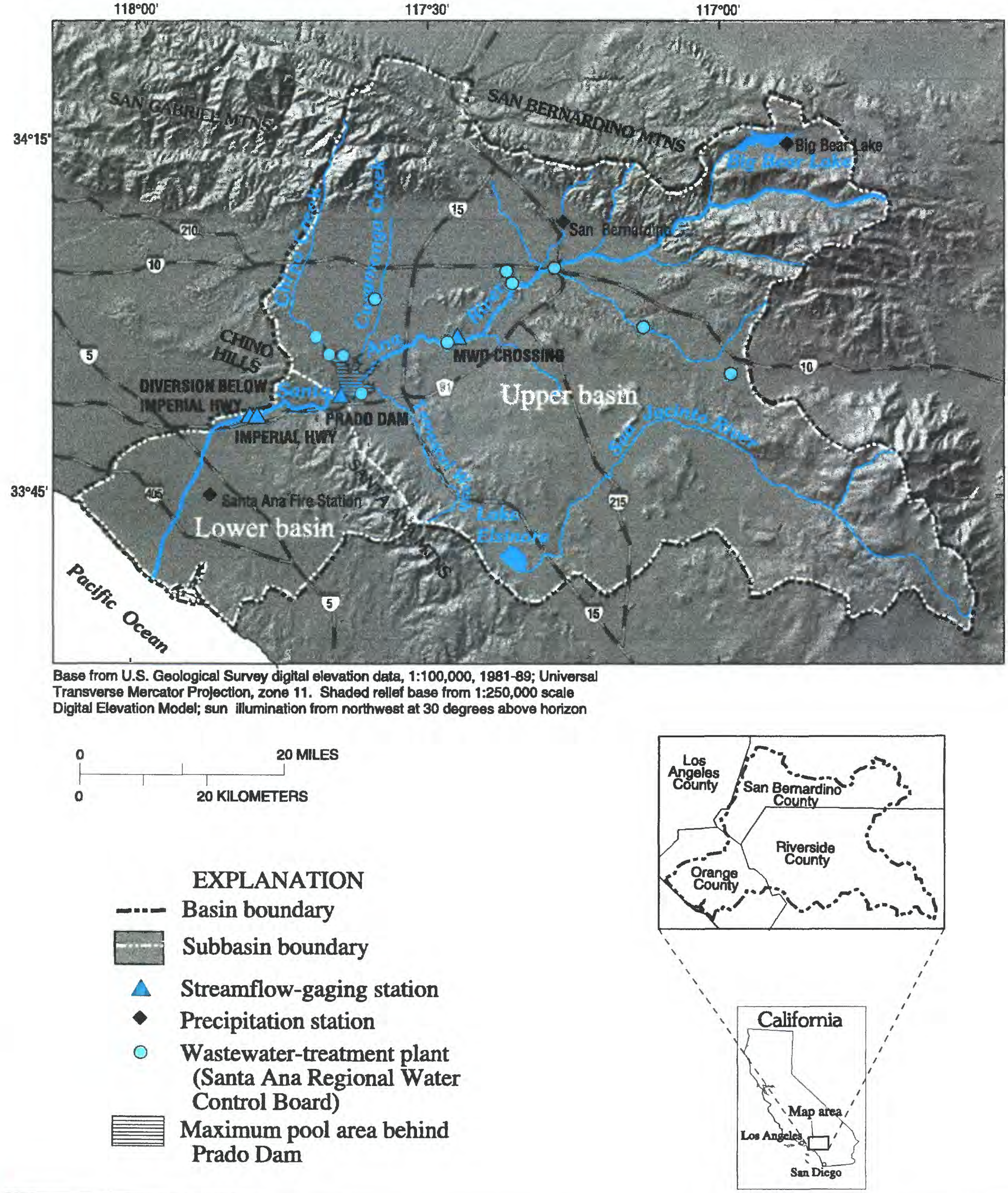


Figure 1. Santa Ana River basin and location of wastewater-treatment plants and water-quality and precipitation stations, southern California.

logical contaminants (such as viruses) that can degrade the water quality. The quality of stormflows may be especially degraded during the first storm of the winter season if soluble, colloidal, or particulate material that has accumulated in the drainage basin during the dry season is washed into the Santa Ana River or its tributaries.

Recently (1995), the Orange County Water District (OCWD) began a series of studies to characterize the quality of the Santa Ana River water, the effects of recharge from the river on ground-water quality, and the potential health effects associated with using water from the Santa Ana River to recharge aquifers that are pumped for water supply. These studies are collectively known as the Santa Ana River Water Quality and Health Study (SARWQHS) (Orange County Water District, 1996b). Much of the work to be done as part of the SARWQHS focuses on the characterization of the dissolved organic carbon composition of water recharged from the Santa Ana River—especially that part of the dissolved organic carbon believed to be of wastewater origin (Reinhard and others, 1995; Orange County Water District, 1996b). This report is based on preliminary results of the SARWQHS and was funded by the Orange County Water District in cooperation with the U.S. Geological Survey and the Santa Ana Basin National Water-Quality Assessment Program (NAWQA).

Purpose and Scope

The purpose of this report is to evaluate changes in the concentrations of selected water-quality constituents in the Santa Ana River at MWD Crossing and below Prado Dam from 1969 to 1995. (The period tested for trend for constituents having fewer data was shorter.) In addition, this report summarizes selected trace-element and organic-compound data collected from the Santa Ana River below Prado Dam between 1970 and 1994. These data serve as a baseline from which water-quality data collected as part of the SARWQHS can be evaluated.

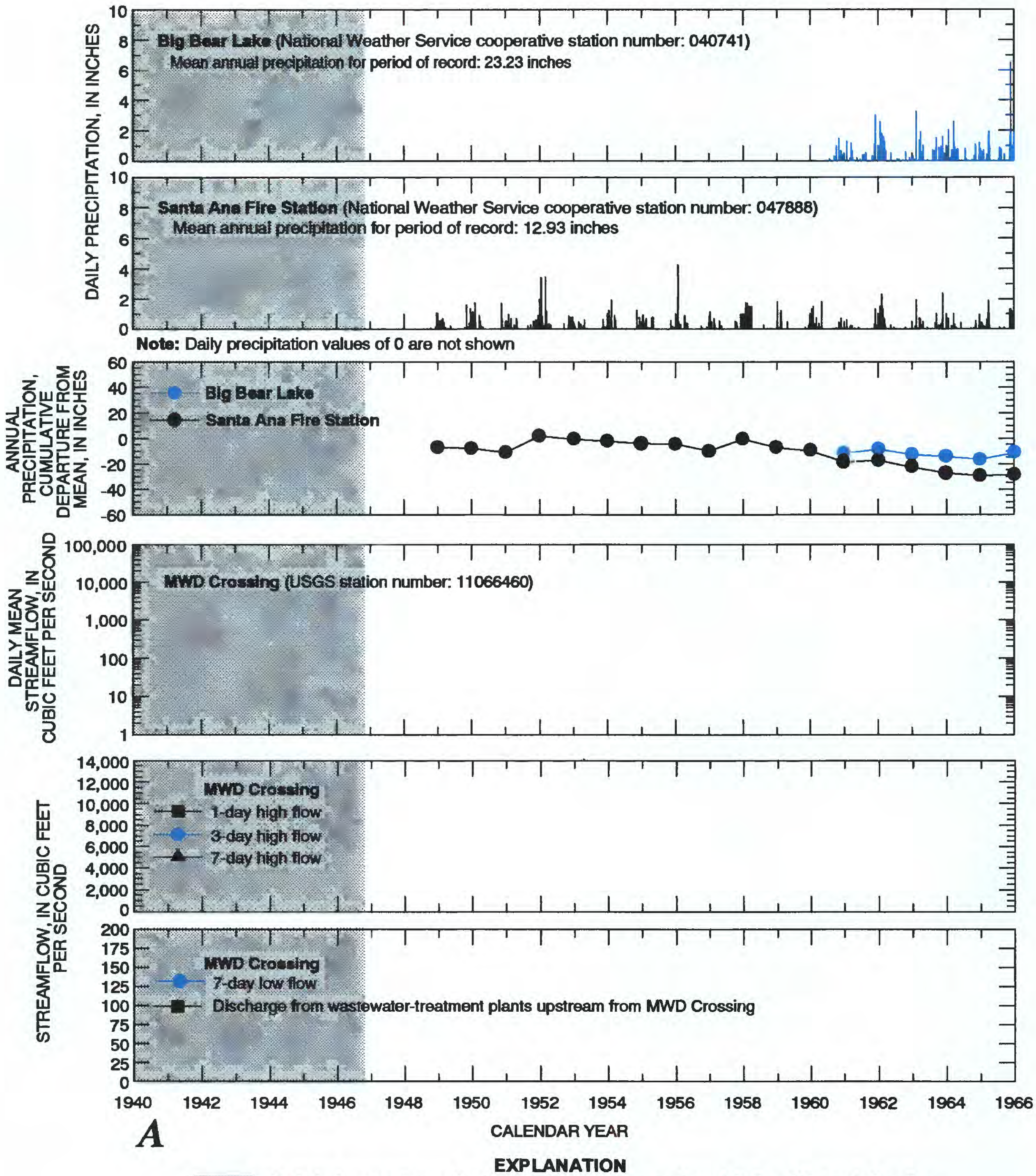
The scope of the study included analysis of historical streamflow data and selected water-quality data collected from the Santa Ana River by the U.S. Geological Survey at Metropolitan Water District (MWD) Crossing and below Prado Dam. Although other agencies have collected water-quality data at these sites (and at other sites along the Santa Ana River), it was not possible, within the scope of this report, to include those data in this report. Statistical analysis of water-quality data presented in this report was done using techniques developed by the U.S. Geological Survey for trend analysis.

Results presented in this report describe changes in water quality with changes in streamflow and during different "seasons" for the period of record evaluated for each constituent. In general, it is beyond the scope of this report to interpret observed trends in water quality relative to changes in water use, wastewater treatment, or other management practices within the Santa Ana River basin. Users of this report are cautioned that statistical significance does not imply environmental importance and that trends calculated for different periods may yield different results. In addition, trends presented in this report were calculated on the basis of historical data and are not predictive of future conditions in the Santa Ana River.

Acknowledgments

The authors thank Terry Schertz and Dane Ohe, of the U.S. Geological Survey, for their assistance with the computer program ESTREND; Greg Peacock and Dan Downing, of the U.S. Army Corps of Engineers, for their assistance in obtaining historical stage data for Prado Dam; and Alan Flowers, Chris McConaghy, and John Vandenburgh of the Orange County Water District for information about regulation of the Santa Ana River by Prado Dam and the diversion of water by the Orange County Water District at Imperial Highway. The authors also thank the staff of the Santa Ana Regional Water Quality Control Board, the Santa Ana Watershed Project Authority, and the South Coast Association of Governments for data and technical information provided in support of this study.

Colleague review was done by Terry Schertz, U.S. Geological Survey, Denver, Colo.; Charles Kratzer, U.S. Geological Survey, Sacramento, Calif.; and Susan Bradford, Orange County Water District, Fountain Valley, Calif. The report was greatly improved by their constructive comments and criticisms. The authors thank the reviewers for sharing their expertise and knowledge of the topic and study area.



EXPLANATION

Period when most years had greater than mean annual precipitation. (Wet period ending in 1946 established on the basis of precipitation data from San Bernardino (National Weather Service cooperative Station number: 047723).)

Figure 2. Precipitation at Big Bear Lake and Santa Ana Fire Station. (*A*) Wastewater discharge and streamflow in the Santa Ana River at MWD Crossing for period of record to September 30, 1995, Riverside County, California. (Cumulative departure from mean precipitation, high flow, and low flow were calculated on the basis of the water year.)

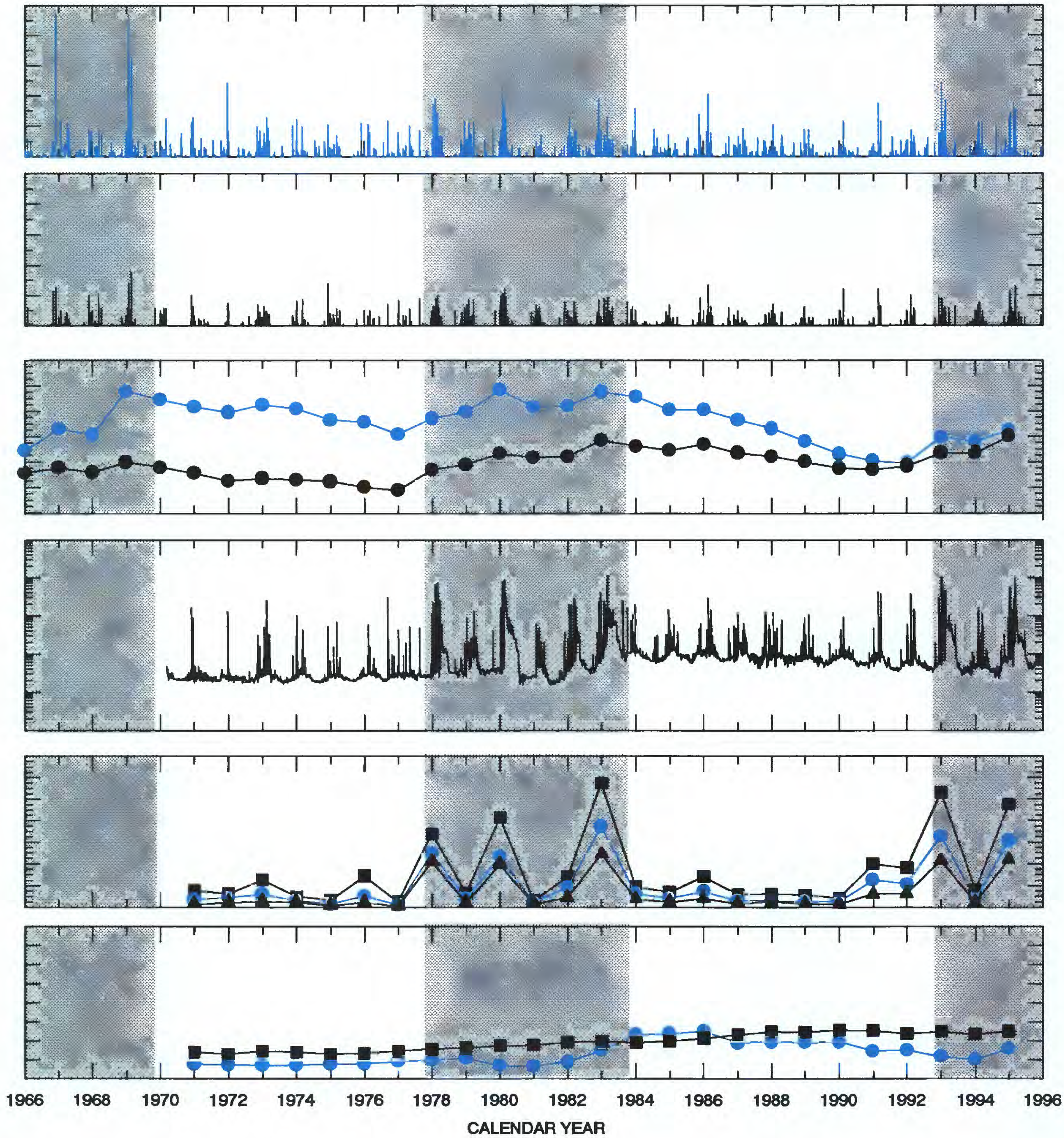


Figure 2—Continued.

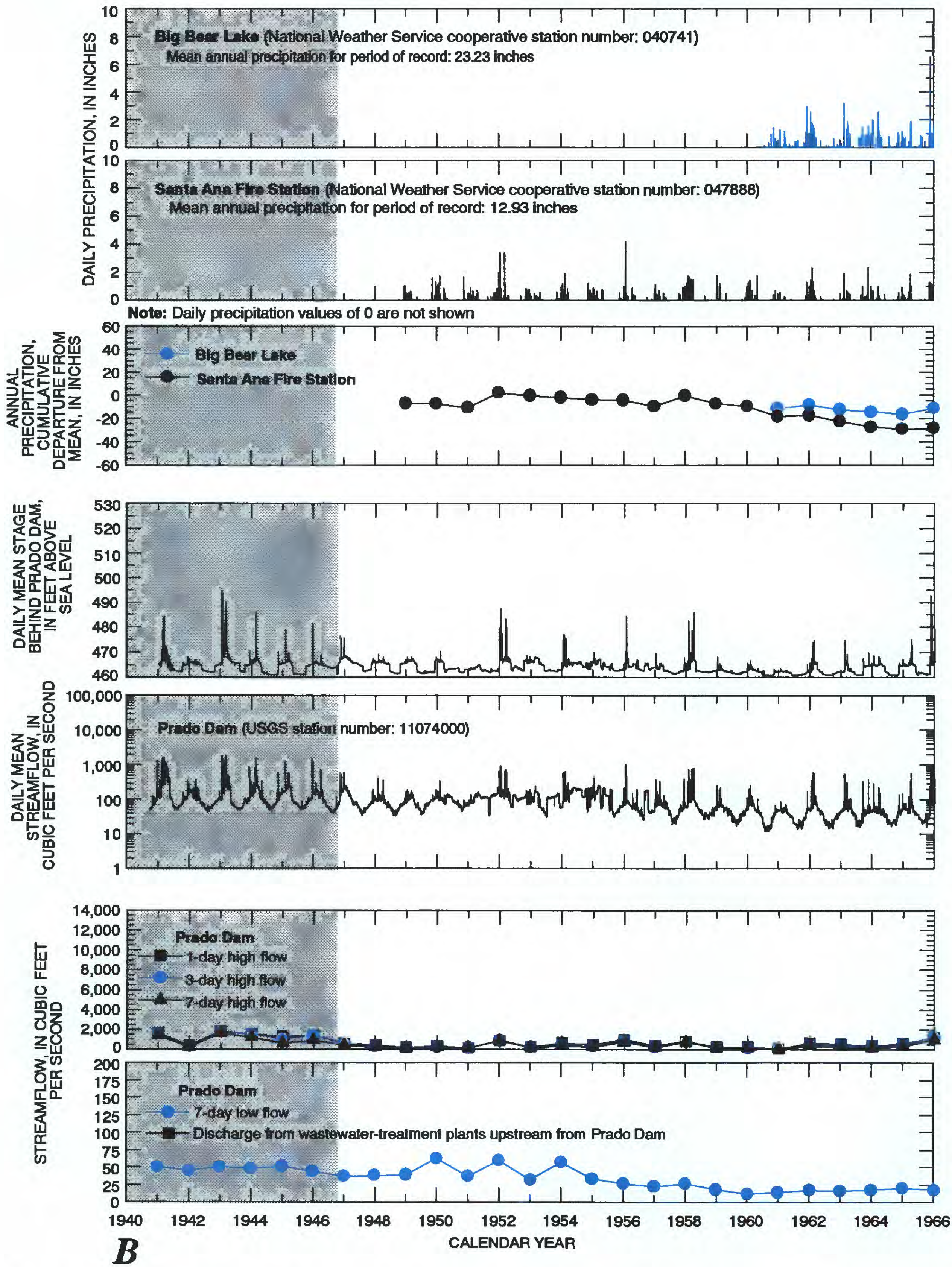


Figure 2. Precipitation at Big Bear Lake and Santa Ana Fire Station. (*B*) Stage behind Prado Dam and wastewater discharge and streamflow below Prado Dam for October 1, 1940, to September 30, 1995, Riverside County, California. (Cumulative departure from mean precipitation, high flow, and low flow were calculated on the basis of the water year.)

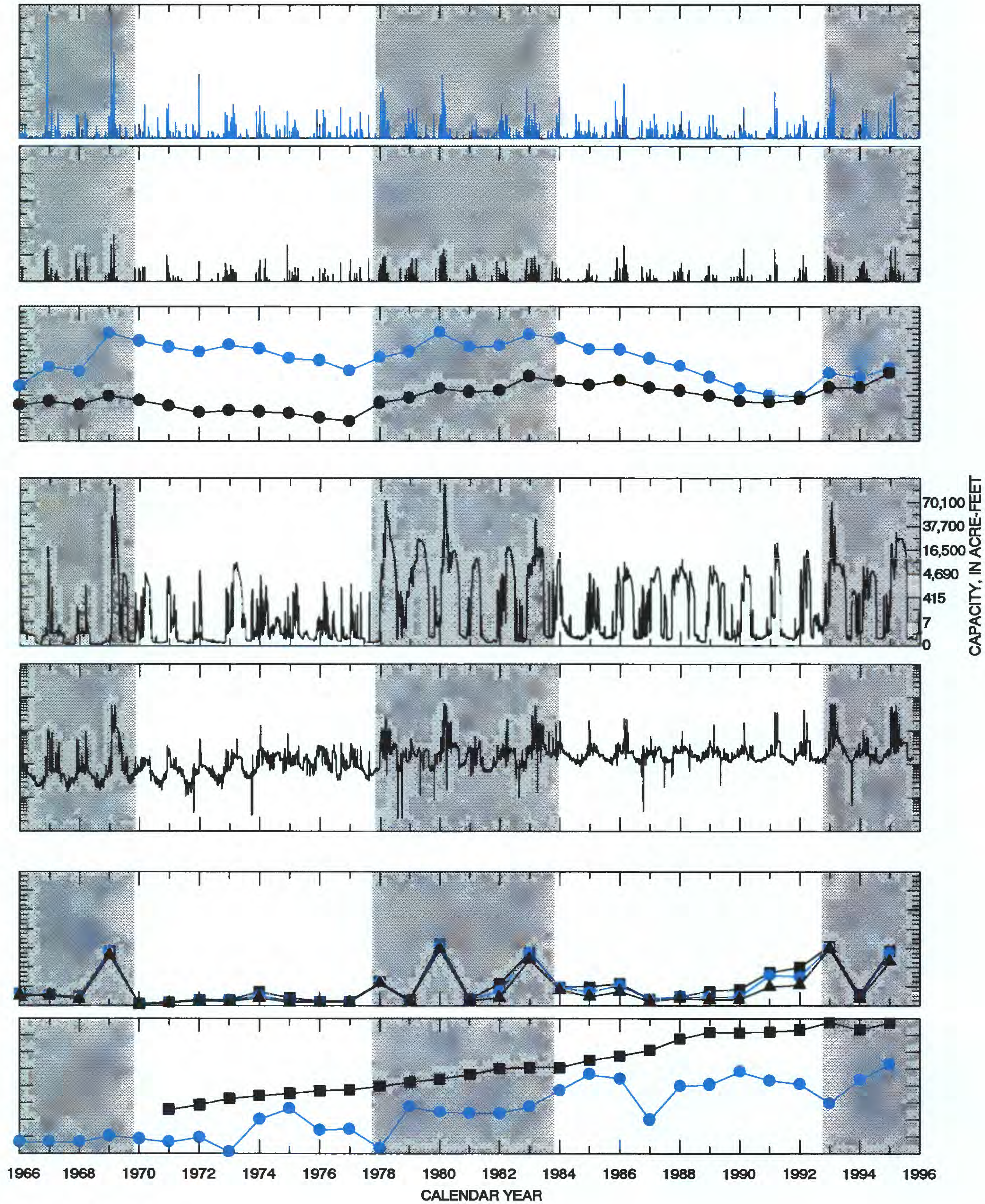


Figure 2—Continued.

DESCRIPTION OF THE SANTA ANA RIVER BASIN

The study area is the Santa Ana River hydrologic unit which includes the Santa Ana River drainage basin and a few small streams near the coast that discharge into the ocean. The Santa Ana River hydrologic unit is about 2,670 mi^2 and includes parts of San Bernardino, Riverside, Los Angeles, and Orange Counties (fig. 1). The river flows to the west and discharges into the Pacific Ocean. The topography of the study area ranges from steep, rugged mountains, with peaks as high as 11,500 ft above sea level, to broad alluvial valleys and a coastal plain to the west. The Mediterranean climate is characterized by warm, dry summers and cool, moist winters. Average annual precipitation ranges from about 12 in. near the coast to about 18 in. in the inland valleys. In the higher mountains, cool summers and cold winters prevail. Average annual precipitation can exceed 40 in. in some of the higher mountains. Throughout the study area, most precipitation falls during the winter (U.S. Army Corps of Engineers, 1994).

Daily precipitation data collected at Big Bear Lake (in the San Bernardino Mountains) and at the Santa Ana Fire Station (near the coast) are shown in figure 2. For two large storms in 1967 and 1969, daily precipitation exceeded 9 in. in the mountains. Cumulative departure of annual precipitation from the mean annual precipitation was calculated to show wet and dry periods. Upward-sloping line segments indicate periods during which the annual precipitation for most years was greater than average. Downward-sloping line segments indicate years during which annual precipitation was less than average. Comparison of the daily precipitation data and the cumulative-departure data at Big Bear Lake and at the Santa Ana Fire Station shows that the timing and the duration of wet and dry periods are similar in the higher altitudes of the mountains and in the lower altitudes near the coast.

Population and Land Use

Since the 1940's, the population in the Santa Ana River basin has increased rapidly, and agricultural and vacant land uses have decreased while urban land uses have increased. In 1990, the population in the Santa Ana River basin was more than 4.5 million people (Santa Ana Regional Water Quality Control Board, 1994), and land use ranged from dense urban development in the coastal plain and inland valleys to undeveloped wilderness in the high mountains. In 1990, urban land use composed about 32 percent of the study area; agricultural land use, which was largely cropland and pastures but also included orchards and dairies, composed about 11 percent of the study area; and vacant land, which included forests, composed about 57 percent of the study area. In 1995, about 340 animal confinement facilities managed more than 340,000 animals (primarily dairy cows) within the Santa Ana River basin (Santa Ana Regional Water Quality Control Board, 1996). Most of these facilities, about 300, and most of the animals, about 300,000, are in the area drained by Chino and Cucamonga Creeks to the northwest of Prado Dam (figs. 1 and 3).

To support the existing population, local water is extensively managed and additional water is imported into the basin from northern California and the Colorado River through aqueducts. Most of the water used for public supply is eventually discharged to the Santa Ana River and its larger tributaries (or to adjacent shallow ground water) as treated municipal wastewater. Much of this treated municipal wastewater is used to recharge aquifers underlying Orange County that are pumped for public water supply. To meet water-quality objectives established for the basin by the Santa Ana Regional Water Quality Control Board (1995), almost all municipal wastewater discharged to the river in 1995 was tertiary treated. Storm and sanitary sewers are separate in all communities within the Santa Ana River basin. As a result, combined sewer overflows to the river resulting from precipitation and subsequent runoff are not a common problem. In addition to the tertiary treatment of municipal wastewater, about half of the base flow of the Santa Ana River is treated to remove nitrate from a series of artificial wetlands upstream from Prado Dam (O'Connor, 1995; Brian Baharie, Orange County Water District, oral commun., 1996). Gray and others (1996) have shown that treatment within the artificial wetlands also increased the concentration of dissolved organic carbon and changed the composition of dissolved organic carbon in the Santa Ana River. Almost all flow in the Santa Ana River, about 200,000 acre-ft annually, is diverted by the Orange County Water District (1996a) for ground-water recharge downstream from Imperial Highway (fig. 1). Only water from the larger stormflows is not diverted for ground-water recharge.

Water rights to the Santa Ana River have been the subject of much litigation. The April 17, 1969, Stipulation for Judgement in Orange County Water District versus City of Chino, et. al. provides for a regional allocation of water supply among the major public water districts in the Santa Ana River basin; this decision included both the quantity and the quality of streamflow in the Santa Ana River below Prado Dam (Santa Ana River Watermaster, 1996).

Streamflow Characteristics

For the purposes of this report, the Santa Ana River basin was divided into an upper basin and a lower basin. The upper basin is that part of the basin upstream from the Chino Hills and the Santa Ana Mountains (fig. 1). The upper basin drains the headwater areas in the mountains in the eastern part of the basin and the inland alluvial valleys; the upper basin is about 2,470 mi^2, including 768 mi^2 in the San Jacinto River/Lake Elsinore drainage. The San Jacinto River/Lake Elsinore drainage does not normally contribute flow to the Santa Ana River, and in most years, Lake Elsinore (a naturally occurring graben lake) is the terminus for flow in the San Jacinto River. However, flow from the San Jacinto River/Lake Elsinore drainage into Temescal Wash and the Santa Ana River did occur in 1917, 1980, and 1995 (O'Connor, 1995; California Department of Water Resources, 1982; Santa Ana River Watermaster, 1996). Also during 1980 and 1983, water was pumped from Lake Elsinore into Temescal Wash to reduce flooding near Lake Elsinore (U.S. Army Corps of Engineers, 1994). The lower basin is that part of the Santa Ana River basin downstream from the Chino Hills and the Santa Ana Mountains—an area of about 200 mi^2.

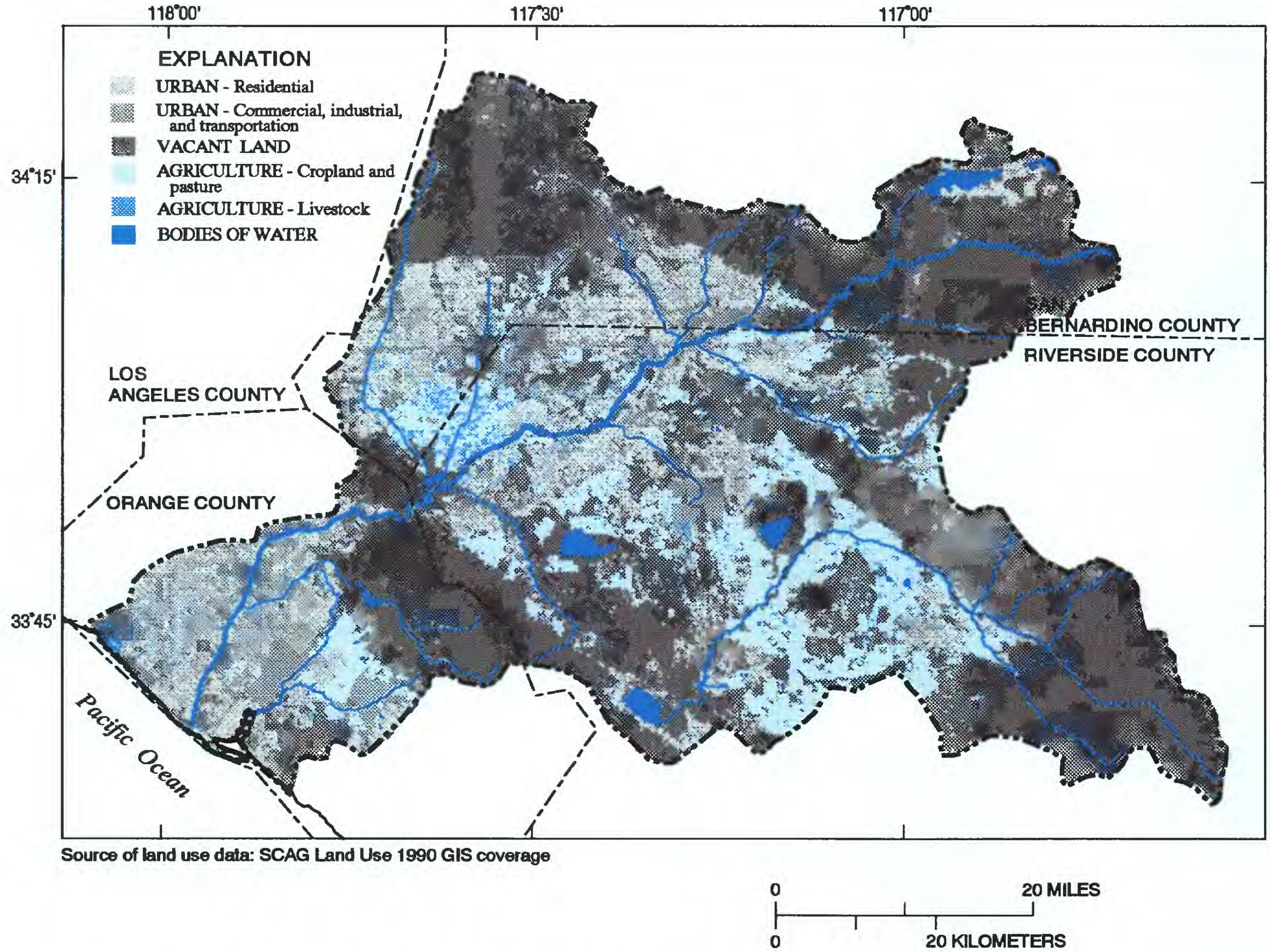


Figure 3. Land use in the Santa Ana River basin, southern California, 1990.

The lower basin drains the western slopes of the Chino Hills and Santa Ana Mountains and the coastal plain.

Predevelopment streamflow characteristics in the Santa Ana River have changed greatly as a result of water-resource development, flood-control projects, and changing land use in the basin. As early as 1900, streamflow in some reaches of the Santa Ana River and its larger tributaries was intermittent because of ground-water pumping. In contrast, streamflow in other reaches of the Santa Ana River and its tributaries increased because of irrigation returns at that time (Lippencott, 1903; U.S. Geological Survey, 1901). As a result of ground-water pumping, by the 1900's the areal extent of large natural wetlands along the river was reduced by about half (Mendenhall, 1905), and by the 1940's, many of the wetlands were dry (Miller and Singer, 1971).

Streamflow data were collected for four sites (fig. 1) along the Santa Ana River. Data for three of the sites (sites at MWD Crossing, below Prado Dam, and at Imperial Highway) are summarized in table 1. Available streamflow data were limited for the fourth site (the diversion downstream from the Imperial Highway site) and therefore were not included in table 1. Photographs of the Santa Ana River at MWD Crossing, below Prado Dam, and below the diversion below Imperial Highway are shown in figure 4. The gaging station at MWD Crossing is located in the upper part of the basin, about 16 mi upstream from Prado Dam. Two large tributaries, Chino Creek (and its tributary Cucamonga Creek) and Temescal Wash, enter the Santa Ana River between MWD Crossing and Prado Dam. The combined drainage area for Chino Creek and Cucamonga Creek is about 125 mi^2; many of the dairies in the study area are in the Chino Creek and Cucamonga Creek drainages (figs. 1 and 3). The drainage area for Temescal Wash is 224 mi^2-excluding the San Jacinto River/Lake Elsinore drainage.

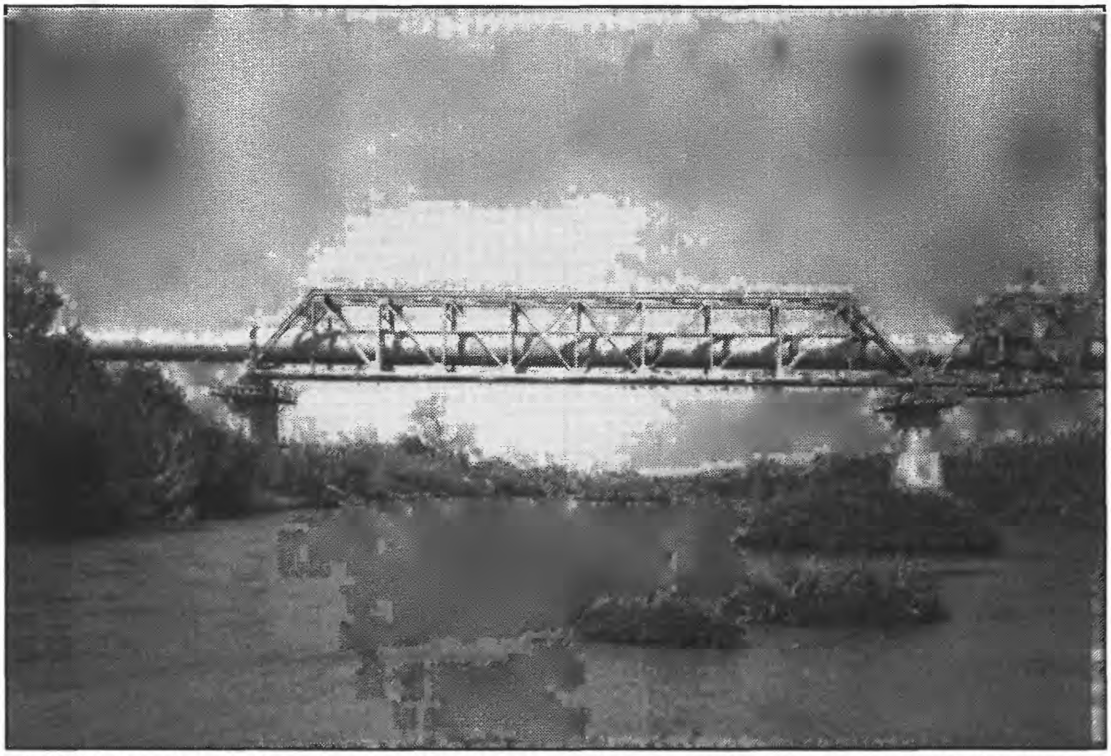
Since 1940, streamflow between the upper and lower parts of the Santa Ana River basin has been regulated by Prado Dam. Regulation of streamflow by Prado Dam has reduced peak flows during the winter by releasing stormwater gradually over a period of several days, weeks, or months. Prado Dam is operated according to a complex set of procedures intended to minimize flood damage in the lower part of the Santa Ana River basin, maximize availability of surface water for ground-water recharge by Orange County Water District, and minimize adverse effects on endangered species in wetland areas behind Prado Dam (U.S Army Corps of Engineers, 1994). To help minimize flood damage, the channel of the Santa Ana River

Table 1. Summary of streamflow data for the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, and at Imperial Highway, Orange County, California

[mi^2, square miles; ft^3/s, cubic feet per second]

Station name	Station No.	Period of record (month/year)	Drainage area (mi^2)	Mean annual streamflow for period of record (ft^3/s)	Maximum instantaneous streamflow for period of record (ft^3/s)
Santa Ana River at MWD Crossing, near Arlington	11066460	[1]3/70–9/96	852	129	[2]30,700
Santa Ana River below Prado Dam	11074000	[3]5/30–11/39 [4]3/40–9/96	[5]1,490	187	7,440
Santa Ana River at Imperial Highway near Anaheim	11075600	10/72–9/81	1,544	244	10,600

[1]Streamflow partly regulated by Big Bear Lake.
[2]Extremes outside the period of record includes 320,000 ft^3/s during the flood of January 22, 1862, measured at a site 8.2 miles upstream.
[3]Irrigation season only.
[4]Flow regulated by Prado Dam since 1940.
[5]Does not include San Jacinto River/Lake Elsinore drainage, 768 mi^2.



A. MWD Crossing, looking upstream. Structure is pipeline carrying imported water across the Santa Ana River (September 5, 1996, streamflow is approximately 72 cubic feet per second).

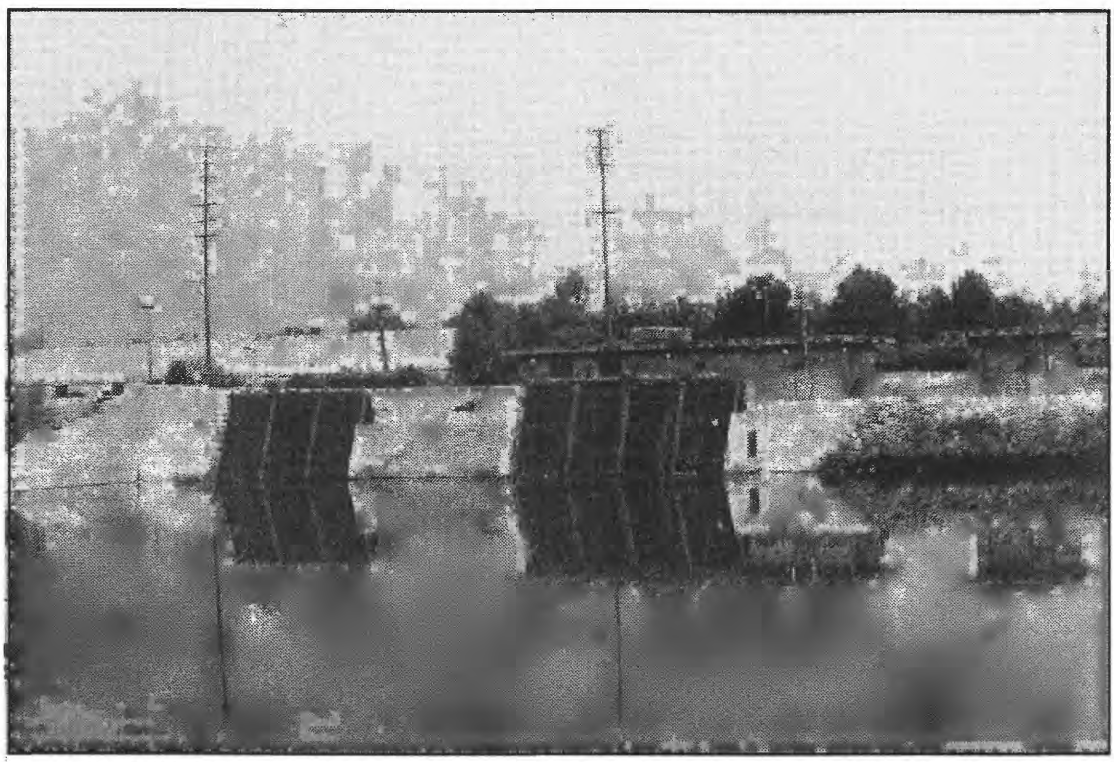
B. Below Prado Dam, looking upstream (September 5, 1996, streamflow is approximately 173 cubic feet per second).

Figure 4. The Santa Ana River (*A*) at MWD Crossing, Riverside County, (*B*) below Prado Dam, Riverside County, and (*C*) at the diversion downstream from Imperial Highway, Orange County, California.

downstream from Prado Dam has been extensively modified to serve as an urban floodway. Water is not stored behind Prado Dam during the dry season—and in some dry years, water is not stored behind Prado Dam throughout much of the rainy season.

Daily mean streamflow data for the Santa Ana River at MWD Crossing and below Prado Dam are shown in figure 2. Streamflow in the Santa Ana River varies greatly in response to precipitation. High-flow and low-flow statistics shown in figure 2 reduce some of this variation and allow for easier interpretation of the data. These statistics were calculated to show streamflow response (or lack of response) to wet and dry periods determined from precipitation data. High-flow statistics shown in figure 2 include 1-day, 3-day, and 7-day high flows. These statistics show the highest average flow for 1, 3, and 7 days duration each water year. Similarly, the 7-day low flow shows the lowest average flow of 7 days duration. For the Santa Ana River below Prado Dam, 1-day and 3-day low-flow statistics were greatly affected by artificially low flows resulting from regulation of streamflow at Prado Dam (these data are not shown in figure 2).

High flows in the Santa Ana River occur during the winter as a result of precipitation and subsequent runoff. The largest flow measured at MWD Crossing during the period of record (1970–96) was 30,700 ft^3/s (table 1). The largest historical flow in the Santa Ana River occurred in January 1862 and was estimated to be about 320,000 ft^3/s at Riverside Narrows near MWD Crossing (U.S. Army Corps of Engineers, 1994). Since 1940, peak flows below Prado Dam and at Imperial Highway have been smaller in magnitude than flows at MWD Crossing because of the regulation of streamflow. Peak flows have not exceeded 7,500 and 10,600 ft^3/s below Prado Dam and at Imperial Highway, respectively (table 1). However, on the basis of the 1-day, 3-day, and 7-day high-flow statistics, high flows downstream from Prado Dam are longer in duration than high flows at MWD Crossing because of the storage and the subsequent release of water by Prado Dam (fig. 2). Peak flows greater than 1,000 ft^3/s can occur at



C. Diversion below Imperial Highway, facing downstream and looking across from left bank (November 7, 1996, streamflow is approximately 190 cubic feet per second).

Figure 4—Continued.

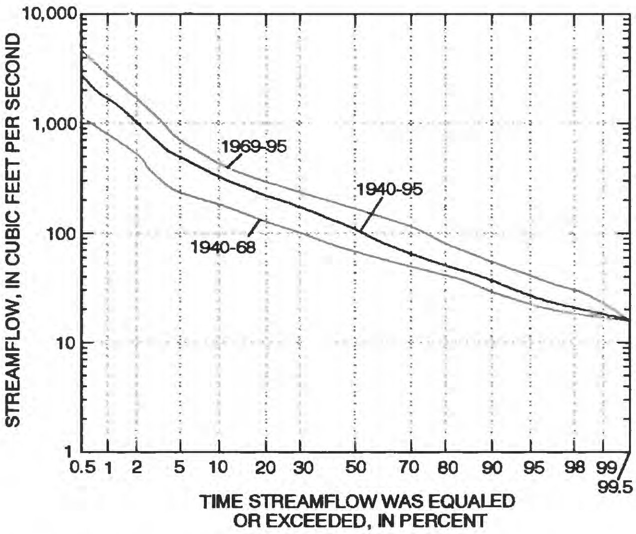


Figure 5. Flow-duration curves for the Santa Ana River below Prado Dam, Riverside County, California (for indicated years).

Imperial Highway, even when only small quantities of water are being released by Prado Dam, as a result of runoff in downstream parts of the basin (Alan Flowers, Orange County Water District, oral commun., 1996).

Streamflow data for the Santa Ana River below Prado Dam from 1940 to 1995 show that peak flows and volumes of water stored behind Prado Dam generally were greater between water years 1969 and 1995 than between water years 1940 and 1968 (fig. 2*B*). This difference probably is due, in part, to greater precipitation between water years 1969 and 1995, but it also may be due to increased urbanization of the basin and subsequent increased runoff (U.S. Army Corps of Engineers, 1994). Differences in streamflow for the Santa Ana River below Prado Dam between water years 1940 and 1968 and 1969 and 1995 are shown as flow-duration curves in figure 5. Flow-duration curves show the percentage of time that streamflow of a given magnitude is equaled or exceeded.

Low flows in the Santa Ana River at MWD Crossing respond similarly to the cumulative departure from annual precipitation during wet and dry periods—generally increasing during wet periods and decreasing during dry periods. In contrast, between 1972 and 1995, low flows in the Santa Ana River below Prado Dam increased independent of wet and dry periods. This increase is the result of increasing discharges of treated municipal wastewater to the Santa Ana River. Much of this wastewater discharge occurs downstream from MWD Crossing, and as a result, streamflow at MWD Crossing is not affected to the same extent as streamflow below Prado Dam (fig. 2). The location of wastewater-treatment plants that discharge to the Santa Ana River are shown in figure 1.

Streamflow in the Santa Ana River also is supplemented by releases of imported water from northern California and from the Colorado River. Unlike wastewater discharges, these releases are intermittent and are intended to supplement local water supply by increasing the amount of streamflow available for groundwater recharge. In addition, ground water pumped from aquifers underlying the Santa Ana River and its larger tributaries is discharged to the river to facilitate the distribution of water among agencies dependent on the river as a source of supply. A detailed analysis of these and other sources of streamflow to the Santa Ana River is provided annually by the Santa Ana River Watermaster (Santa Ana River Watermaster, 1996).

TREND ANALYSIS OF WATER-QUALITY DATA

Concentrations of many constituents in streams and rivers change with time as a result of changes within the basin, such as variation in climate, changes in land use, or changes in water use. Long-term changes in water quality resulting from these or other changes are known as water-quality trends. Schertz and others (1991) define "long term" as time frames greater than 5 years. Changes also can occur over shorter time periods, such as seasonally, diurnally, or during a stormflow. When water-quality trends are superimposed on short-term changes for constituent concentrations, trends can be difficult to identify.

In addition, trends in water-quality data may be even more difficult to detect because streamflow and water-quality data may not be normally distributed and may vary seasonally; water-quality data may have missing values, "less-than" values (often referred to as censored data), or outliers; and changes in water-quality may not be monotonic (for example, concentrations may increase and then decrease). Because of these problems, the results of conventional parametric trend tests, originally developed for normally distributed data, may not be accurate when applied to water-quality data (Hirsch and others, 1982). As a result, nonparametric statistical tests are needed to test for water-quality trends in streams and rivers.

Methods for Trend Analysis

In this study, the nonparametric Seasonal Kendall's Tau test (Kendall, 1975) was used to analyze data for trends in water quality. This test is incorporated into the computer program ESTREND (EStimated TREND) (Schertz and others, 1991) and is specifically designed for non-normal, seasonally varying data. In this report, the results of the seasonal Kendall's Tau test (and other statistical tests) are reported as significant or highly significant. Results are reported as significant if the p-value (the probability that the null hypothesis is true) was less than the confidence criterion of $\alpha=0.1$ but greater than 0.01. Results are reported as highly significant if the p-value was less than $\alpha=0.01$.

Prior to trend analysis, the annual cycle is divided (discretized) into smaller time steps designated as "seasons." For the purposes of trend analyses for this study, seasons do not necessarily correspond to calendar seasons. Instead, seasonal discretization for each constituent is determined on the basis of the amount and the distribution of the available data and on the basis of hydrologic factors believed to influence the concentrations of selected constituents within the basin. Comparisons are then made between a constituent value for a given year and season with the value for the same constituent in the next year and same season for which data are available. If the succeeding value is greater, +1 is recorded; if the succeeding value is smaller, -1 is recorded. Summing all the positive values and dividing by the number of entries yield a test statistic that represents the trend with time. This statistic (Kendall's Tau or τ) is then compared to the standard normal distribution function to establish the level of statistical significance. The median of the actual values, rather than the +1 or the -1, is the slope of the trend (Peters and others, 1982). Hirsch and others (1982) showed that the nonparametric Seasonal Kendall's Tau test is relatively insensitive to outliers and performed better than its parametric counterparts in the detection of trends in test data sets.

Individual seasons may have trends that are smaller or larger in magnitude than the median trend calculated by ESTREND. Identification of seasons having trends different in magnitude than the overall trend can aid in understanding the processes that control changes in constituent concentrations through time. For example, downward trends in constituent concentrations at the beginning of the rainy season that are greater in magnitude than the overall trend may suggest that land-management practices designed to prevent soluble, colloidal, or particulate material from washing into the river are at least partly effective.

As part of a trend analysis, ESTREND, using the method of least squares, calculates the relation between streamflow and the concentration of study constituents from several possible statistical models, including linear, log, inverse, and hyperbolic models. The form of the relation is automatically selected on the basis of best-fit by ESTREND. However, a specific relation can be selected by the user. For most constituents in this study, the hyperbolic model produced a better fit to the data than any other model tested. The Seasonal Kendall's Tau statistic (τ) is then calculated for the residuals about the best-fit model. This procedure, called flow adjustment, is intended to remove variation in constituent concentration caused by variation in streamflow. Flow adjustment can aid in the identification of trends in water quality from sources other than changes in streamflow (Schertz, 1990).

ESTREND incorporates a smoothing technique known as LOWESS (LOcally WEighted Scatterplot Smoothing) (Cleveland, 1979). LOWESS allows the user to visually evaluate short-duration, nonmonotonic changes in water-quality data that may be different than the overall trend.

Water-Quality Constituents Tested for Trend

Schertz and others (1991) defined the minimum criteria for use of the Seasonal Kendall's Tau test for trend within ESTREND as follows: there must be at least 5 years of data, the minimum number of observations must be at least three times the number of seasons, and missing values must not exceed 50 percent of the available data for the first fifth and last fifth of the study period.

The water-quality constituents used for trend analysis during this study were selected from more than 250 constituents collected and analyzed by the U.S. Geological Survey from water in the Santa Ana River at MWD Crossing and below Prado Dam. Constituents selected for trend analysis at MWD Crossing include specific conductance and dissolved solids (residue on evaporation at 180°C). Constituents selected for trend analysis below Prado Dam include specific conductance, dissolved solids, selected nutrients (including several different nitrogen and phosphate compounds), dissolved and total organic carbon, and chemical oxygen demand (table 2). The concentrations of many of the constituents tested for trend are influenced by the discharge of treated municipal wastewater or agricultural runoff (Smith and others, 1987; Iwatsubo and Woodward, 1993); there may be public health implications for recharge of this water into aquifers used as a source of public supply. For nutrients and chemical oxygen demand, there were not enough data available at MWD Crossing to calculate trends using ESTREND.

Major-ion data were not included in trend analysis. The aggregate trends in major-ion data are reflected in specific-conductance values and dissolved-solids concentrations. Trace elements and organic compounds were not included in trend analysis because, for some constituents, there were not enough data for use in ESTREND; for other constituents, the results of many of the analyses were less than analytical detection limits; and in other cases, there have been changes in the sample collection, handling, and laboratory methods that could affect the comparability of the data. However, trace-element and organic-compound data collected below Prado Dam are summarized later in this report.

Data used in the trend analysis were collected and analyzed using standard methods approved by the U.S. Geological Survey (Fishman and Friedman, 1989;

Table 2. Summary of water-quality data for selected constituents for the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, California

[All concentrations in milligrams per liter, except specific conductance in microseimens per centimeter. All constituents filtered through a 0.45 micron pore-sized membrane filter, except specific conductance, total organic carbon, and chemical oxygen demand. Dissolved solids is residue on evaporation at 180°C. N, nitrogen; P, phosphorous; <, actual value is less than value shown]

Property or constituent	Period of record	Number of samples analyzed	Mean	Minimum	25th percentile	50th percentile (median)	75th percentile	Maximum
MWD Crossing								
Specific conductance	8/69–9/95	529	965	165	934	1,030	1,100	1,220
Dissolved solids	8/69–9/95	525	609	111	578	654	698	946
Nitrite plus nitrate as N	10/71–2/75	18	6.9	1.0	3.4	7.9	9.7	11
Organic nitrogen as N	10/71–2/75	19	1.6	<.01	.3	.5	3.8	5.4
Orthophosphate as P	10/71–2/75	19	.5	.1	.4	.5	.7	.8
Total organic carbon	10/71–2/75	18	18	<.1	3.1	4.9	37	92
Below Prado Dam								
Specific conductance	10/66–9/95	563	1,010	308	895	1,070	1,160	1,510
Dissolved solids	10/66–9/95	559	629	156	546	660	722	956
Nitrite plus nitrate as N	10/71–10/94	201	5.3	<.1	3.2	4.9	7.3	12
Ammonia as N	10/79–10/94	119	1.3	.1	.4	1.0	1.9	5.0
Organic nitrogen as N	8/70–10/94	233	1.5	<.1	.9	1.3	1.8	7.8
Ammonia plus organic nitrogen as N	10/75–9/86	101	2.7	.2	1.8	2.4	3.2	7.9
Total dissolved nitrogen as N	10/75–7/91	74	7.7	2.7	5.3	7.6	9.7	14
Phosphorous as P	9/73–10/94	145	2.1	<.01	1.3	2.2	2.9	5.3
Orthophosphate as P	10/71–10/94	212	1.9	<.01	1.1	2.0	2.5	4.5
Total organic carbon	10/71–9/86	152	11	3.9	7.5	9.8	13	54
Dissolved organic carbon	10/77–9/86	35	9.7	3.7	5.7	9.0	11	31
Chemical oxygen demand	7/73–8/82	110	40	10	28	37	50	86

Ward and Harr, 1990). If a method of sample collection, handling, or analysis changed over time, the sample results were included in the trend analysis, but only if the change did not affect the comparability of the data. This approach minimized the variability associated with changes in sample collection, handling, and laboratory methods over time. The data are available in the U.S. Geological Survey's computer data base. Although other agencies have collected water-quality data at MWD Crossing and below Prado Dam (and at other sites along the Santa Ana River), it was not possible, within the scope of this report, to include those data in the trend analyses.

WATER-QUALITY TRENDS IN THE SANTA ANA RIVER

Water-quality trends during water years 1970–95 were calculated from specific-conductance and dissolved-solids data from the Santa Ana River at MWD Crossing and below Prado Dam. This 26-year period began in October 1969 which was the start of a dry period and includes several dry and wet periods (fig. 2). This period also includes the period during which low flow below Prado Dam increased in response to increased discharge of treated municipal wastewater to the river. This is the same period of record used for the flow-duration curves in figure 5. For other constituents analyzed from the Santa Ana River below Prado Dam, the available data limited the length of the period that could be tested for trend or the seasonal discretization that could be used within that period. The authors recognize the potential problems associated with comparisons between trends for constituents having different periods of record and different seasonal discretization.

We believe that some data are not representative of water quality in the Santa Ana River and therefore excluded that data from the trend analysis. Most of the excluded data were data from samples collected below Prado Dam during low flows that resulted solely from short-term regulation at the dam. The effect of the short-term regulation on streamflow can be seen in figure 2*B*. Low flows (generally less than 20 ft^3/s) at the beginning of the period tested for trend (before 1975) were not the result of regulation of the dam and are believed to be representative of water-quality conditions in the Santa Ana River at that time. The data for these samples were not excluded from the trend analysis, even though such low flows do not presently occur on the Santa Ana River, because removing these data would have effectively shortened the period tested for trend. Examination of the data in figures 8 and 9 (presented later in this report) shows that these data affect the relations between constituent concentration and streamflow, and as a result, these relations (and the discussion of seasonality) are valid only for the period tested for trend and may not accurately reflect present-day conditions in the Santa Ana River.

Seasonality

The concentrations of many constituents in the Santa Ana River, and most other rivers and streams, may change seasonally. Part of this seasonal variation in concentration may be related to seasonal variations in streamflow. As a result, the seasonal variations in concentration are accounted for when the relation with streamflow is determined. Seasonal variation also may be related to seasonal changes in land use, such as cropping patterns or fertilizer applications, or to less obvious factors, such as seasonal changes in the efficiency of wastewater-treatment plants that discharge to the river.

Twelve month-long seasons were used for trend calculation for constituents with enough available data. When 12 seasons are used to calculate trend, some seasons within the annual cycle may behave in a similar manner. However, when 12 seasons are used in a calculation, more available data can be used than when fewer seasons are used in the calculation. This approach results in a better estimate of trend than seasonal discretizations that use fewer seasons and, consequently, less available data. For this study, a hydrologic-based seasonal discretization was used for constituents with fewer data. The hydrologic-based discretization included a minimum of two seasons—seasons that approximate the wet and dry seasons that occur in the Santa Ana River basin. If enough data were available, six seasons representing the wet and dry seasons and the transitions between the wet and dry seasons were used. Because seasonal discretization may affect the results of trend analyses, several iterations using different seasonal discretizations were done before the final seasons were selected for trend calculations. The seasonal discretization used for each constituent is shown in table 3.

Seasonal (monthly) variations in specific-conductance values and dissolved-solids concentra-

Table 3. Trends for selected constituents in the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, California

[All constituents filtered except specific conductance, total organic carbon, and chemical oxygen demand. Dissolved solids is residue on evaporation at 180°C. Trends in milligrams per liter per year, except specific conductance in microseimens per centimeter per year. Positive trends indicate increasing concentrations, or values, with time; negative trends indicate decreasing concentrations, or values, with time. Significant trends, confidence criterion α=0.1, are in bold. Highly significant trends, confidence criterion α=0.01, are shown in bold italics. Seasons having trends that are statistically different in magnitude from the overall trend are shown as follows: ⇓, highly significant smaller trend; ↓, significant smaller trend; ↑, significant greater trend; ⇑, highly significant greater trend. —, flow-adjusted trends were not calculated because there was not a statistically significant relation between concentration and streamflow]

Property or constituent	Period tested for trend	Number of analyses	Trend (not adjusted for streamflow)	Trend (adjusted for streamflow)	Number of seasons	Seasonal discretization and seasons having trends that were statistically different from the overall trend											
						Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	June	July	Aug	Sept
At MWD Crossing																	
Specific conductance	10/69–9/95	303	***-7.9***	***-1.1***	12		⇓										
Dissolved solids	10/69–9/95	315	***-5.9***	***-1.6***	12	↓	⇓						↓				
Below Prado Dam																	
Dissolved sollids	10/69–9/95	310	***-8.3***	***2.2***	12						↑				↑		
Residue on evaporation	10/69–9/95	340	**-6.0**	1.0	12												
Nitrite plus nitrate as N	10/71–9/94	122	***.11***	***.15***	6				⇑		↑		↑		↑		
Ammonia as N	10/79–9/94	88	**-.04**	—	6						↓						
Organic nitrogen as N	10/71–9/94	134	0	—	6												
Ammonia plus organic nitrogen as N	10/77–9/86	54	-.10	—	6												
Total dissolved nitrogen as N	10/79–9/86	41	.40	***.39***	6												
Phosphorous	10/77–9/94	101	.02	.03	6												
Orthophosphate	10/71–9/94	128	.01	***.03***	6		↑		↑								
Total organic carbon	10/71–9/86	85	**-.19**	—	6												
Dissolved organic carbon	10/77–9/86	19	-.47	—	[1]2												
Chemical oxygen demand	10/73–9/81	41	**3.3**	—	6												

[1]The beginning and end of these seasons do not coincide with the beginning and end of the water year. Seasonal discretization is December 15 to March 15 and March 16 to December 14.

tions for the Santa Ana River at MWD Crossing and below Prado Dam are shown in figure 6. At MWD Crossing, lower values and greater variation in specific-conductance values and dissolved-solids concentrations occurred during the wet season. It is possible that the lower value and greater variation resulted from dilution of base flow during and after storms. Specific-conductance values and dissolved-solids concentrations were higher and the variation was smaller during August, September, and October when only base flow was present. Specific-conductance values and dissolved-solids concentrations are more variable throughout the year below Prado Dam, but not necessarily always higher. Lower specific-conductance values and dissolved-solids concentrations occurred near the end of the wet season (February and March). During these months, the mean and median specific-conductance values and dissolved-solids concentrations

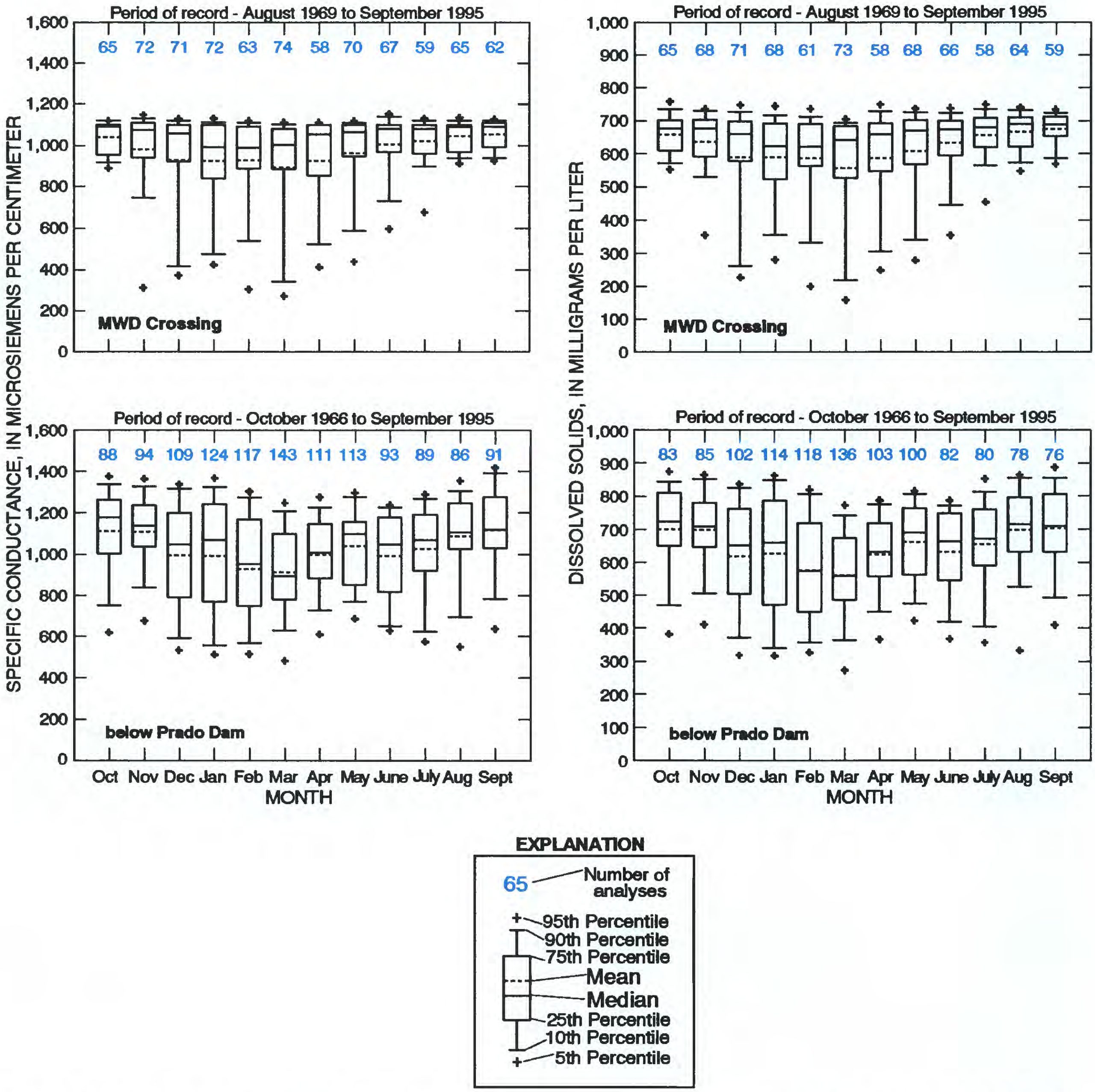


Figure 6. Specific-conductance values and dissolved-solids concentrations, by month, in the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, California.

were lower below Prado Dam than at MWD Crossing. Near the end of the wet season, there often is stormflow runoff water stored behind Prado Dam. This water may be released gradually during a period of weeks or months and can dilute base flow (which is largely discharges from wastewater-treatment plants) in the Santa Ana River.

Seasonal variations in the concentrations of selected constituents in the Santa Ana River below Prado Dam are shown in figure 7. In general, concentrations of nitrite plus nitrate, total dissolved nitrogen, phosphorus, and orthophosphate were lower during the wet seasons and higher during the dry seasons. Concentrations of these constituents may have been diluted by stormflow runoff during the wet season. In contrast, concentrations of ammonia, organic nitrogen, ammonia plus organic nitrogen, total organic carbon, and chemical oxygen demand were higher during the wet seasons. Concentrations of these constituents may have increased during the wet season because soluble, colloidal, or particulate material that accumulated in the drainage basin during the dry season was washed into the Santa Ana River and its tributaries. In addition, reactions that converted these constituents to other forms may have been less efficient during the cooler, wetter months.

Concentrations of dissolved organic carbon did not show large seasonal changes (fig. 7). Seasonal changes in dissolved organic carbon concentrations were difficult to identify for this study because of the small amount of data that limited the seasonal discretization. Gray and others (1996) identified seasonal changes in the concentration and the composition of dissolved organic carbon in the artificial wetlands used to remove nitrate from water in the Santa Ana River. However, at least some of the changes in dissolved organic carbon concentration and composition may have been related to seasonal changes in streamflow.

Relation to Streamflow

In the Santa Ana River, and in most other rivers and streams, the concentrations of many constituents are related to streamflow. This relation is complex and depends on many factors including the number and the types of sources for a given constituent (both natural and manmade); the type, the distribution, and the magnitude of storms and subsequent runoff within a drainage basin; and the physical and the chemical behavior of the constituent in the environment—including reactions that occur within a stream that change, remove, or add individual constituents. Before an analysis of trends can be done, it is necessary to determine how selected constituents vary with streamflow.

Highly significant (confidence criterion of α=0.01) hyperbolic relations were obtained for streamflow and specific conductance and dissolved solids for the Santa Ana River at MWD Crossing and below Prado Dam (fig. 8). At both sites, specific-conductance values and dissolved-solids concentrations decreased with increasing streamflow. At a given streamflow, specific-conductance values and dissolved-solids concentrations were higher below Prado Dam than at MWD Crossing. However, because streamflow is greater below Prado Dam than at MWD Crossing (fig. 2), specific-conductance values and dissolved-solids concentrations may sometimes be less below Prado Dam than at MWD Crossing. At both sites, relatively high R^2 values were obtained (R^2 is a statistic describing the "goodness-of-fit" of data about a regression line; R^2 can range from 0 for no relation to 1 for a perfect fit.) However, the regression equations estimated from data collected at MWD Crossing tend to underpredict specific-conductance values and dissolved-solids concentrations during high flows (greater than 1,000 ft^3/s). In contrast, although the regression equations estimated from data collected below Prado Dam predict well throughout the entire range of data, there is a large amount of variability in the data during midflows (about 200 ft^3/s). It is likely that this increased variation is related to the regulation of streamflow by Prado Dam.

Examination of the residuals about the regression lines (fig. 8) as a function of time shows that, for both the Santa Ana River at MWD Crossing and below Prado Dam, the regression equations tend to overestimate specific-conductance values and dissolved-solids concentrations during wet periods and underestimate during dry periods. For MWD Crossing, the bias may be as much as 10 percent. For the Santa Ana River below Prado Dam, these biases are greater and may be as much as 20 percent.

Highly significant relations were obtained for streamflow and the concentrations of nitrate plus nitrite, total dissolved nitrogen, phosphorus, and orthophosphate in the Santa Ana River below Prado Dam (fig. 9). For these constituents, concentrations decreased with increasing streamflow. The R^2 values for these constituents are much lower than the R^2 values for the relation between streamflow and specific-conductance values or dissolved-solids concentrations (fig. 8). Comparatively low R^2 values are typical of relations for streamflow and the concentrations of nitrate plus nitrite, total dissolved nitrogen, phosphorus, and orthophosphate (Hirsch and others, 1982; Smith and others, 1982, 1987; Hay and Campbell, 1990). The lower R^2 values indicate that the concentrations of these constituents may be controlled by factors

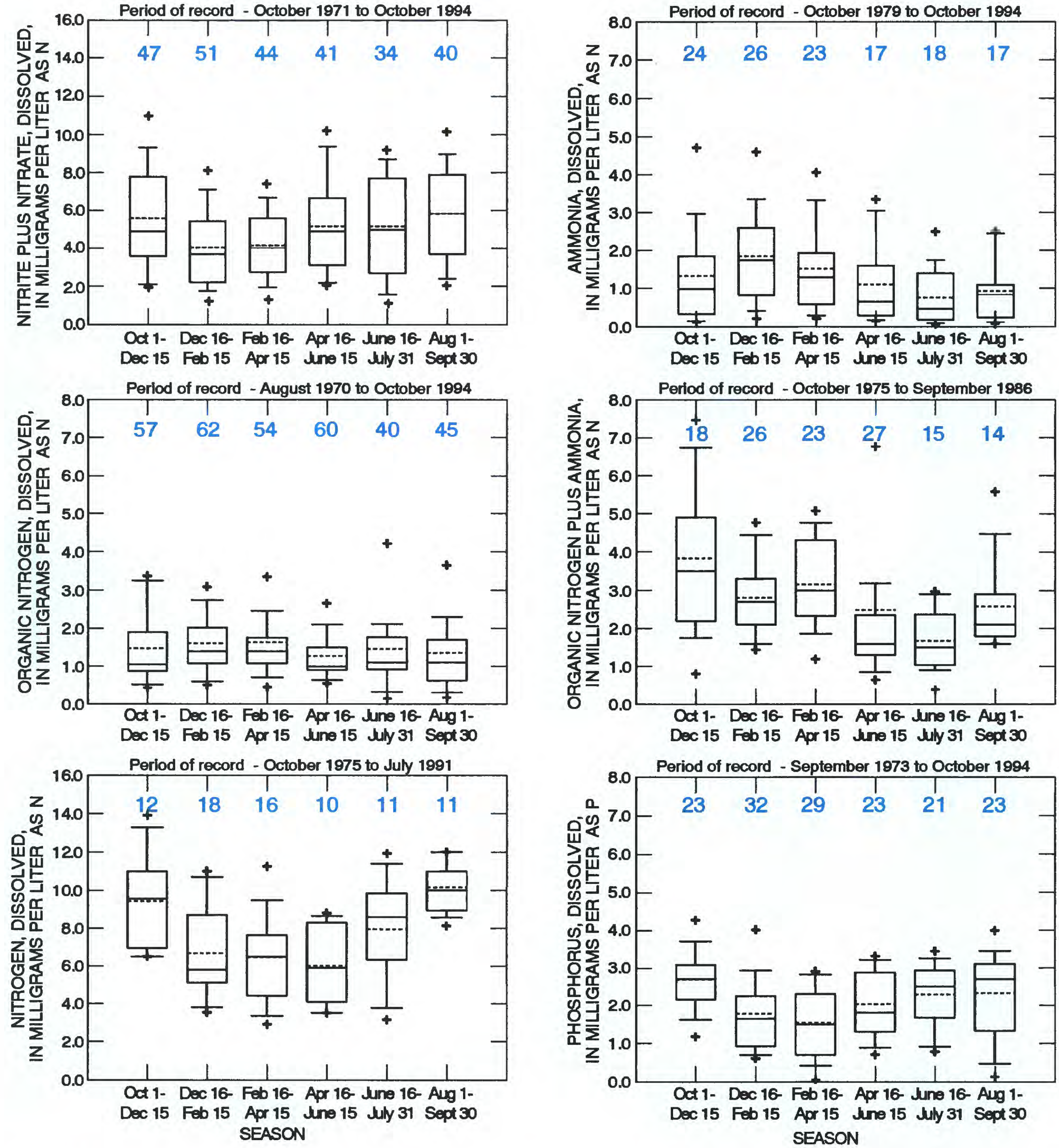
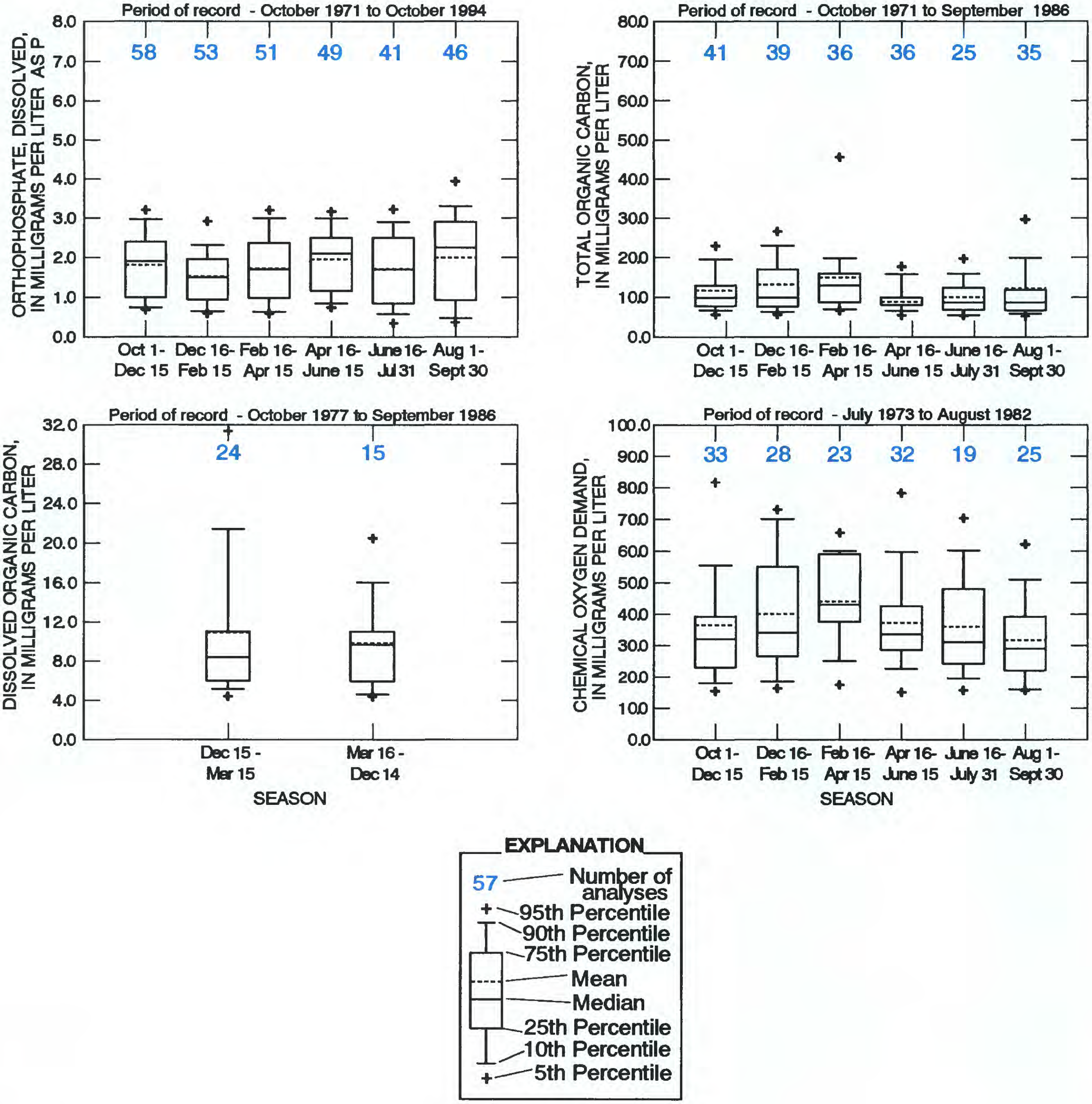


Figure 7. Selected constituents, by season, in the Santa Ana River below Prado Dam, Riverside County, California.

other than streamflow, such as chemical reactions and biological processes that occur within the stream. Regulation of streamflow by Prado Dam also has increased the variation in the data and decreased the R^2 values for constituents sampled in the Santa Ana River below the dam.

Significant relations for streamflow and concentrations of ammonia, organic nitrogen, ammonia plus organic nitrogen, total and dissolved organic carbon, and chemical oxygen demand in the Santa Ana River below Prado Dam were not present. With the exception of ammonia, the concentrations of each of these con-



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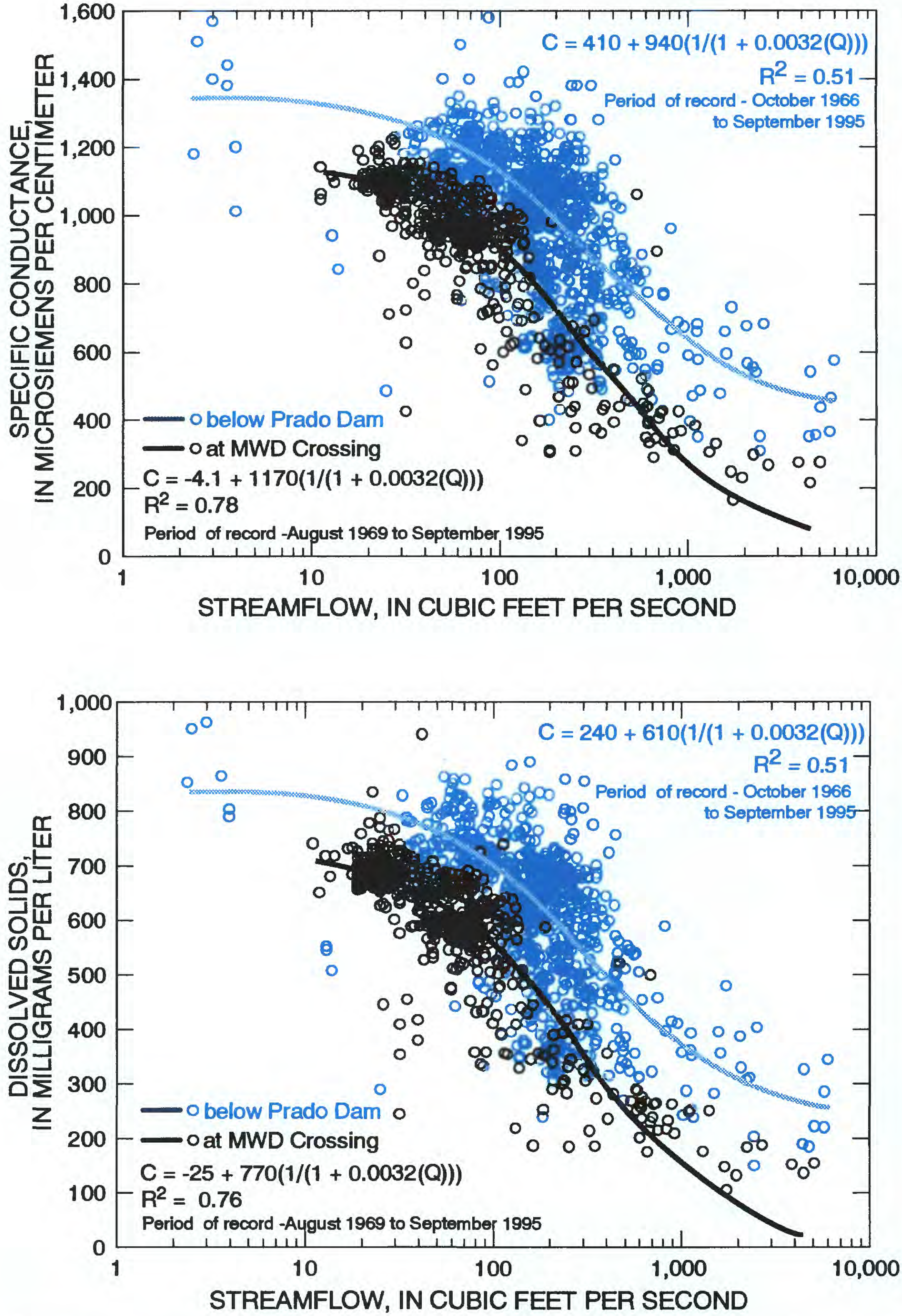


Figure 8. Specific-conductance values and dissolved-solids concentrations as a function of streamflow in the Santa Ana River at MWD Crossing and below Prado Dam, Riverside County, California. (Equation is shown if relation is statistically significant at a confidence criterion of α=0.01. C is the predicted concentration from streamflow; Q is streamflow; R^2 is a statistic describing the "goodness-of-fit" of data about a regression line. R^2 can range from 0 for no relation to 1 for a perfect fit.)

stituents are usually associated with the concentrations of organic carbon in the water. Organic carbon in the Santa Ana River can have a wide range of chemical compositions (Gray and others, 1996) and is derived from many different sources, both natural and man-made. Although the concentration of organic carbon (in both dissolved and suspended forms) is not statistically related to streamflow, the chemical composition of the organic carbon may change with increases or decreases in streamflow in the Santa Ana River.

Trends

Trends calculated using ESTREND describe the rate of increase or decrease in constituent concentrations (or values) for a selected period. For specific-conductance values and dissolved-solids concentrations trends were calculated for water years 1970–95. For other constituents, a shorter period of record was tested for trend. The length of the period tested depended on the available data. Trends calculated for one time period are not necessarily comparable with trends calculated for a different time period. Raw trends in constituent concentrations (unadjusted trends) and trends in flow-adjusted constituent concentrations (flow-adjusted trends) are presented in this report. Flow-adjusted trends remove changes in concentrations (or values) that can be explained by changes in streamflow during the period tested for trend and allow for the identification of trends caused by other processes, such as changes in land use, imported water use, or wastewater discharges. The data may show that concentrations (or values) change linearly, in steps, or change in a complex fashion (for example, increase and then decrease). LOWESS-smoothed curves presented in this report assist the reader in the examination of the data and in the interpretation of trends.

Interpretation of trends in water-quality data requires consideration of the magnitude of the trends, diurnal and seasonal changes in constituent concentration, and applicable water-quality standards—significant trends (or even highly significant trends) are not always environmentally important. Results of trend calculations that are not statistically significant are not trends as defined by this report. However, if the changes in concentrations (or values) are large in magnitude or the constituent is environmentally important, additional study may be necessary to characterize changes in these constituents. Trends presented in this report were calculated on the basis of historical data and are not predictive of future conditions in the Santa Ana River.

Highly significant downward unadjusted trends (confidence criterion α=0.01) of -7.9 µS/cm per year and -5.9 mg/L per year were calculated for specific-conductance values and dissolved-solids concentrations in the Santa Ana River at MWD Crossing, respectively (fig. 10A). Similarly, highly significant downward flow-adjusted trends of -1.1 µS/cm per year and -1.6 mg/L per year were detected for specific-conductance values and dissolved-solids concentrations, respectively. The flow-adjusted trends were smaller in magnitude than the unadjusted trends, suggesting that, although much of the decrease in specific-conductance values and dissolved-solids concentrations at MWD Crossing can be explained by changes in streamflow, at least some of the decrease is related to factors other than streamflow. Identification of these factors is beyond the scope of this report. The downward unadjusted and flow-adjusted trends in both specific-conductance values and dissolved-solids concentrations are larger in magnitude during November—the beginning of the wet season—than at other times of the year (table 3).

Highly significant downward unadjusted trends of -8.3 µS/cm per year and -6.0 mg/L per year were calculated for specific-conductance values and dissolved-solids concentrations in the Santa Ana River below Prado Dam, respectively (fig. 10*B*). In contrast to MWD Crossing, a highly significant, flow-adjusted upward trend in specific conductance of 2.2 µS/cm per year was detected. This suggests that most of the decrease in specific-conductance values below Prado Dam is the result of increased streamflow and that specific-conductance values may have actually increased if streamflow had not increased during the period tested for trend. A flow-adjusted trend was not detected in dissolved-solids concentrations in the Santa Ana River below Prado Dam suggesting that most of the decrease in dissolved-solids concentration below Prado Dam can be explained by increased streamflow.

LOWESS-smoothed curves superimposed on the data collected at both MWD Crossing and below Prado Dam show that the changes (estimated by both unadjusted and, where detected, flow-adjusted trends) in specific-conductance values and dissolved-solids concentrations were not uniform during the period tested for trend. This is especially true below Prado Dam.

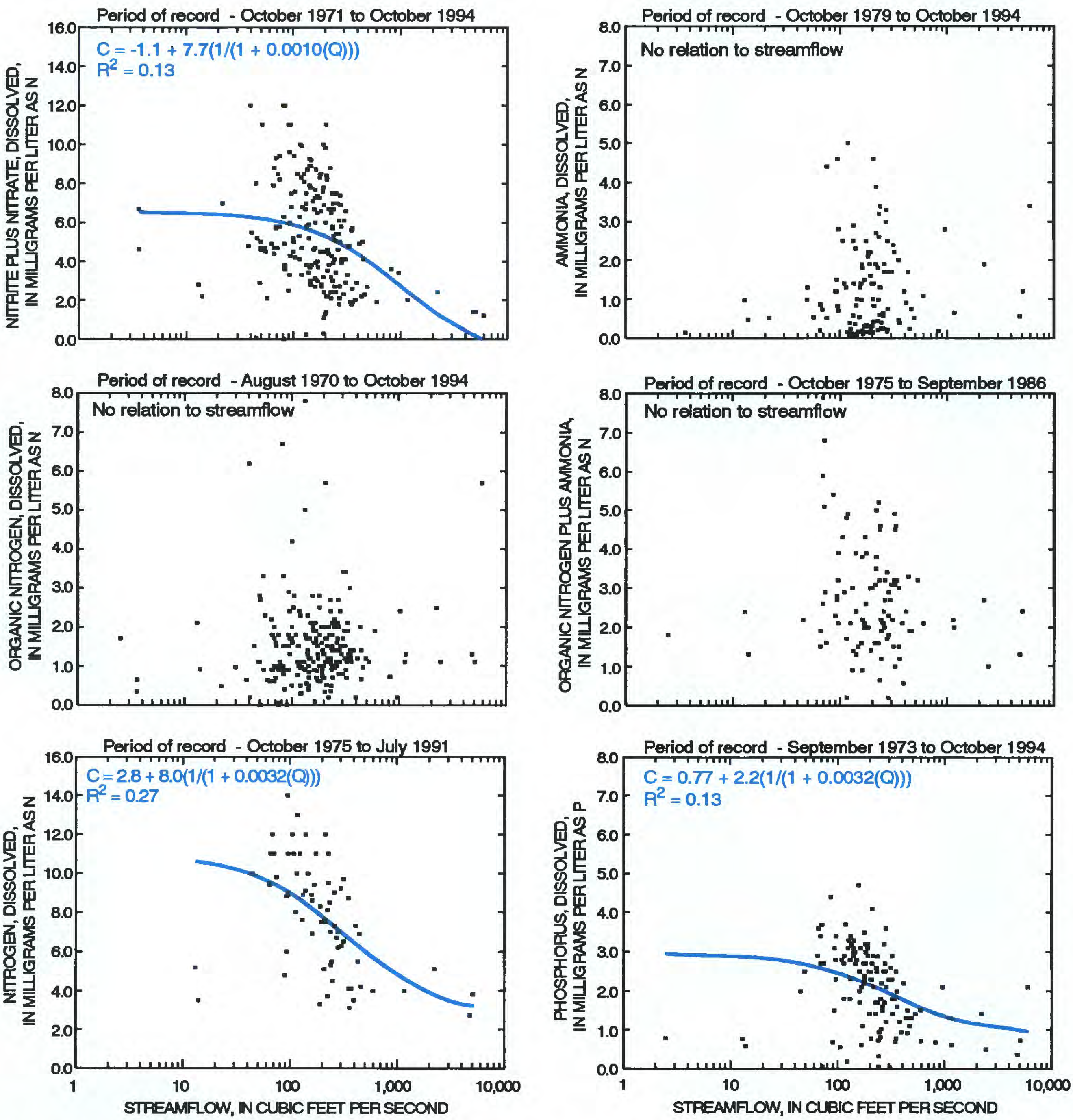
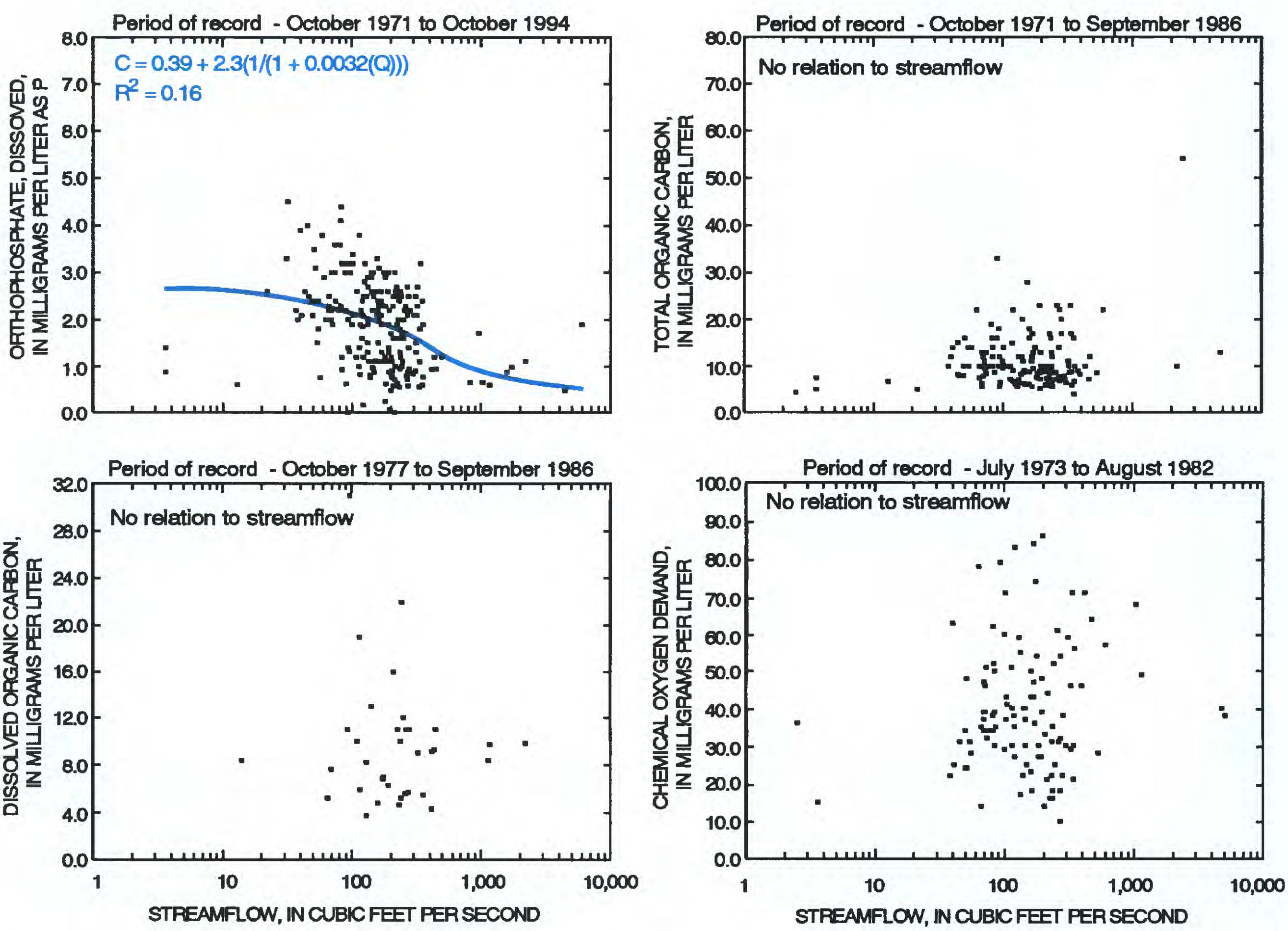


Figure 9. Selected constituents as a function of streamflow in the Santa Ana River below Prado Dam, Riverside County, California. (All constituents, with the exception of total organic carbon and chemical oxygen demand, were filtered in the field through a 0.45 micron pore-sized membrane. Equation is shown if relation is statistically significant at a confidence criterion of α=0.01. C is the predicted concentration from streamflow; Q is streamflow; R^2 is a statistic describing the "goodness-of-fit" of data about a regression line. R^2 can range from 0 for no relation to 1 for a perfect fit.)

In a summary of stream water-quality trends in California for water years 1980–89, Iwatsubo and Woodward (1993) also concluded that there was no flow-adjusted trend in dissolved-solids concentrations in the Santa Ana River below Prado Dam. However, streamflow in the Santa Ana River had increased at both MWD Crossing and below Prado Dam during the period tested for trend by Iwatsubo and Woodward (1993). Much of this increase is the result of increased wastewater discharges. High specific-conductance values and dissolved-solids concentrations that occurred during low flows in the early part of the period tested for trend are not likely to recur under present-day conditions because of increased streamflow. As a result, decreases in specific-conductance values and dissolved-solids concentrations, indicated on the basis of unadjusted trends, are real even if flow-adjusted trends are not present. In complex, heavily managed river systems, such as the Santa Ana River, where streamflow characteristics have changed through time as a result of human activities, flow-adjusted trends alone may not correctly characterize the changes that have occurred within the basin. Similarly, large regional studies of surface water-quality trends that focus only on flow-adjusted trends and do not consider unadjusted trends may not correctly characterize changes that have occurred on the regional or national scale.

Flow-weighted, average-annual dissolved-solids concentrations in the Santa Ana River below Prado Dam were calculated by the Santa Ana River Watermaster (1996) for 1970–95. These data were calculated from continuous streamflow and hourly specific-conductance data using a relation between specific conductance and dissolved solids. The Watermaster data are another measure of the changes in dissolved-solids concentrations in the Santa Ana River below Prado



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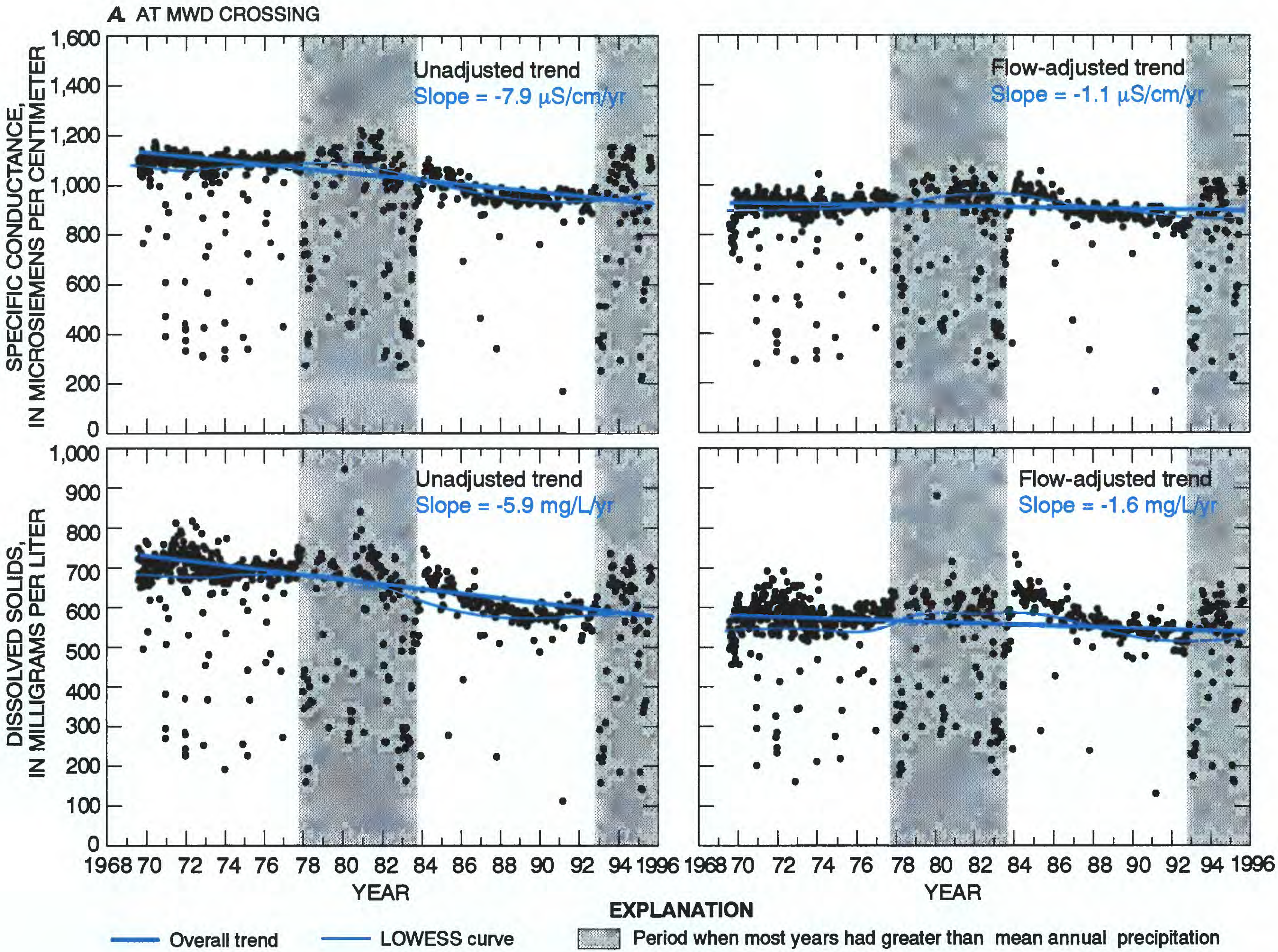
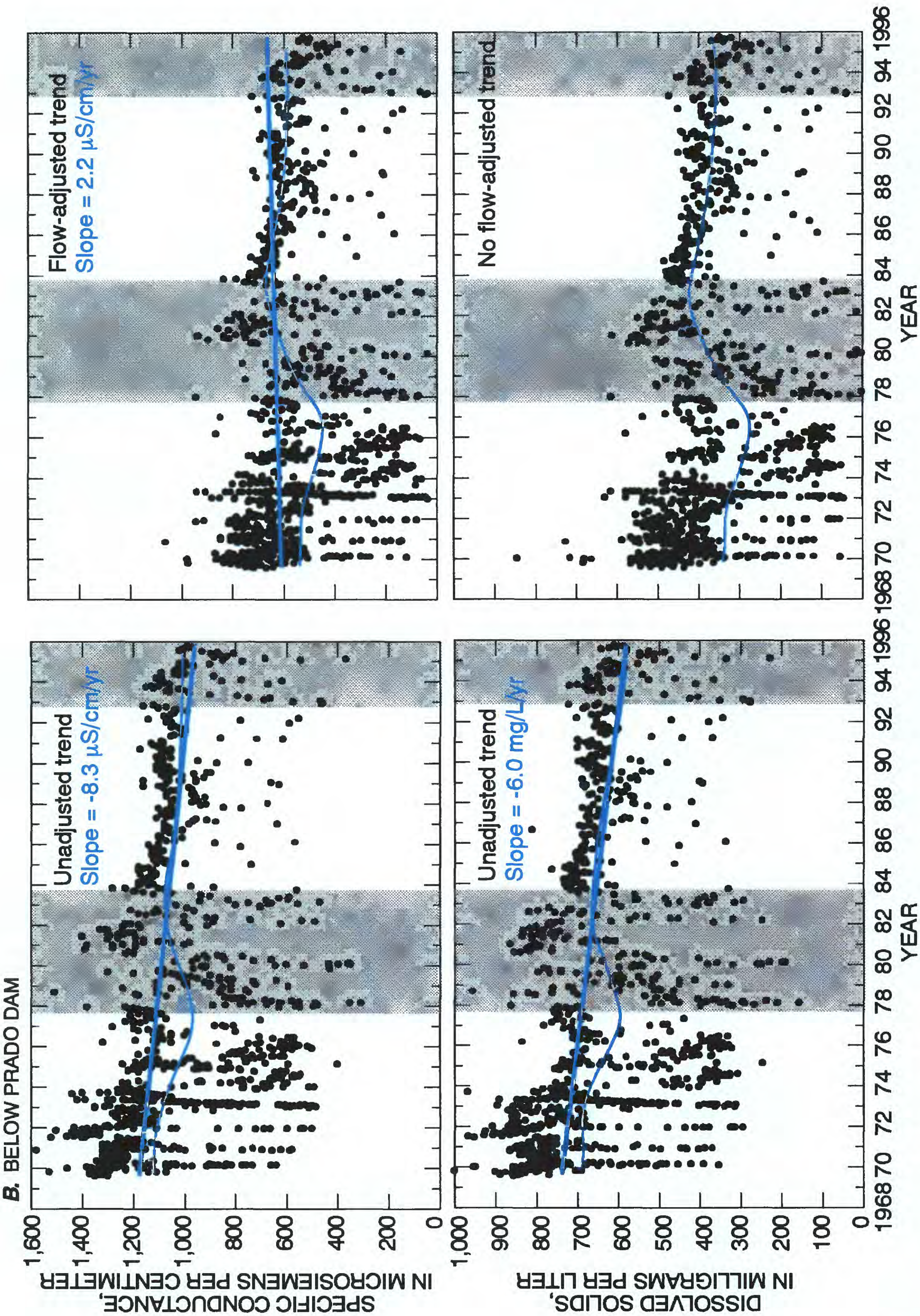


Figure 10. Trends in specific-conductance values and dissolved-solids concentrations in the Santa Ana River (*A*) at MWD Crossing and (*B*) below Prado Dam, Riverside County, California. (Overall trend is shown if trend is highly statistically significant at a confidence criterion of α=0.01. µS/cm/yr, microsiemens per centimeter per year; mg/L/yr, milligrams per liter per year)



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Dam through time. In contrast, ESTREND calculated trend from samples collected bimonthly. Unadjusted trends in dissolved-solids concentrations calculated using ESTREND compare favorably and yield results similar in direction and magnitude to unadjusted trends in flow-weighted, average-annual dissolved-solids concentrations calculated from the Watermaster data (fig. 11). This suggests that estimates of trend calculated from discrete water-quality samples can produce essentially the same results as estimates of trend that rely on more frequent, almost continuous, measurement of streamflow and water quality.

Significant downward unadjusted trends (confidence criterion α=0.1) were calculated for ammonia (-0.04 mg/L per year) and total organic carbon (-0.19 mg/L per year) in the Santa Ana River below Prado Dam (fig. 12 and table 3). These trends were not flow-adjusted because there is not a statistically significant relation between the concentrations of these constituents and streamflow. Because concentrations of these constituents are not related to streamflow, it is likely that these downward trends are the result of some factor other than changes in streamflow. Highly significant upward unadjusted trends were calculated for nitrite plus nitrate (0.11 mg/L per year) and significant upward unadjusted trends were calculated for chemical oxygen demand (3.3 mg/L per year).

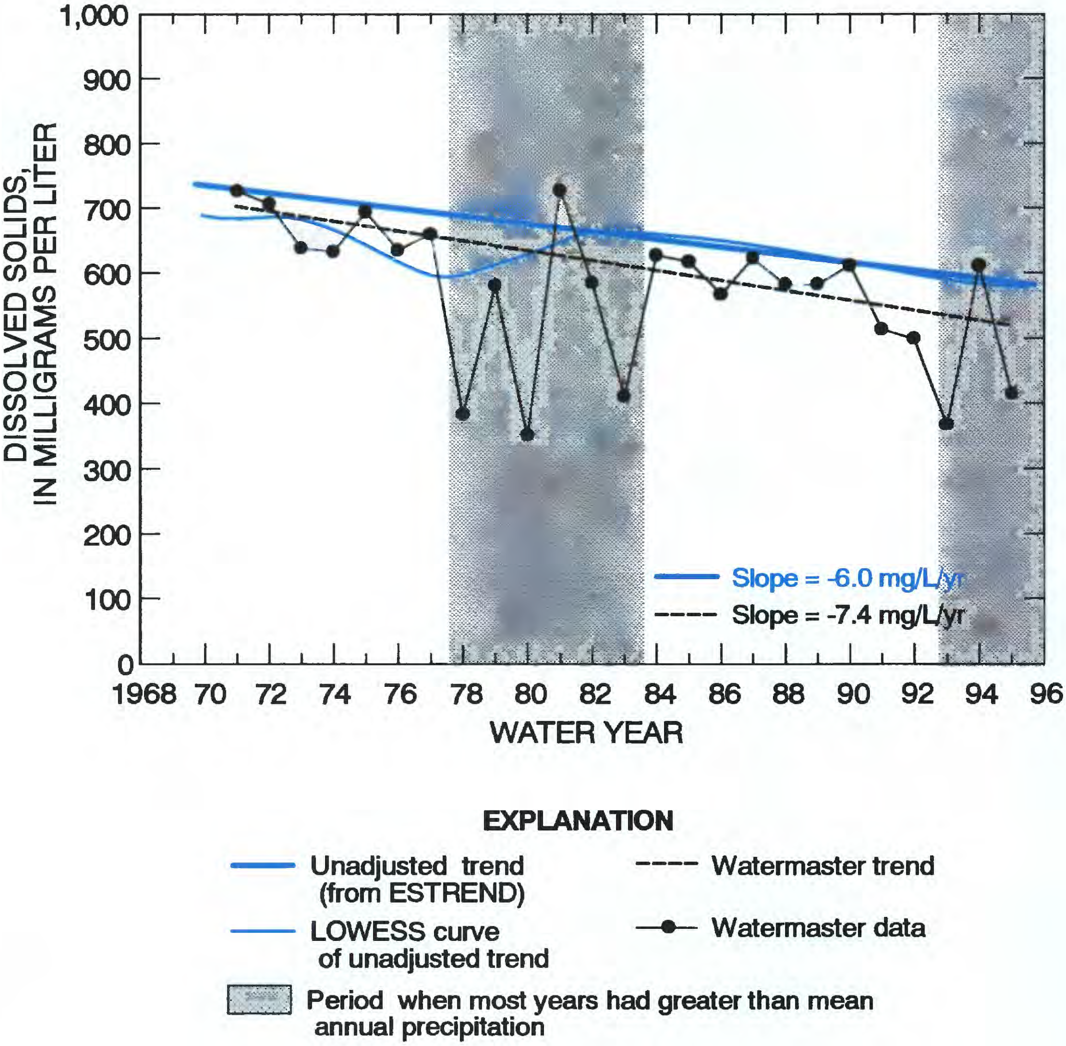

Figure 11. Unadjusted trends in dissolved-solids concentrations and flow-weighted dissolved-solids concentrations (Santa Ana River Watermaster, 1996) in the Santa Ana River below Prado Dam, Riverside County, California. (mg/L/yr, milligrams per liter year.)

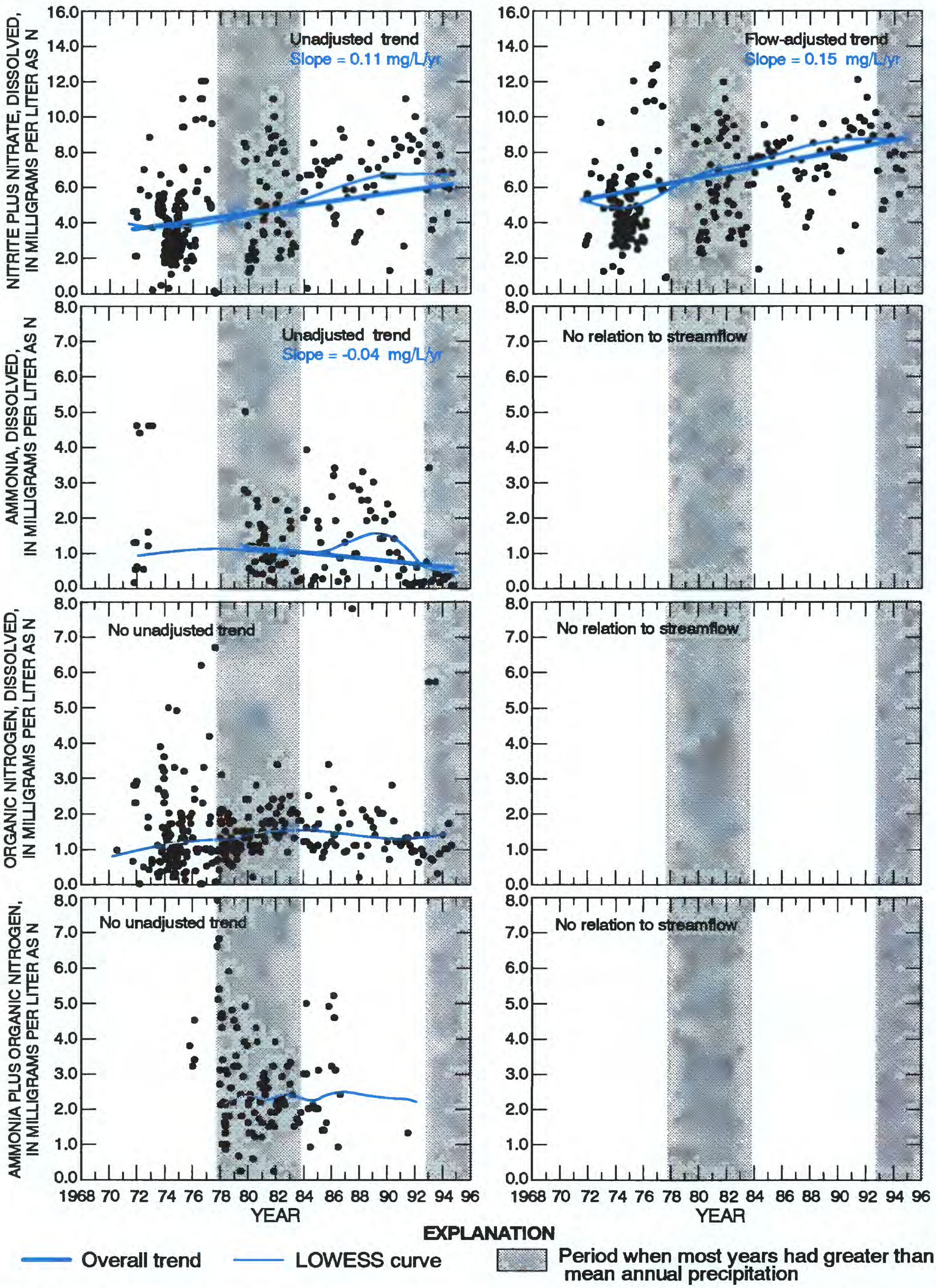

Figure 12. Trends of selected constituents in the Santa Ana River below Prado Dam, Riverside County, California. (Trend is shown if highly statistically significant at a confidence criterion of α=0.01, except for ammonia, total organic carbon, and chemical oxygen demand, which are significant at α=0.10. mg/L/yr, milligrams per liter per year.)

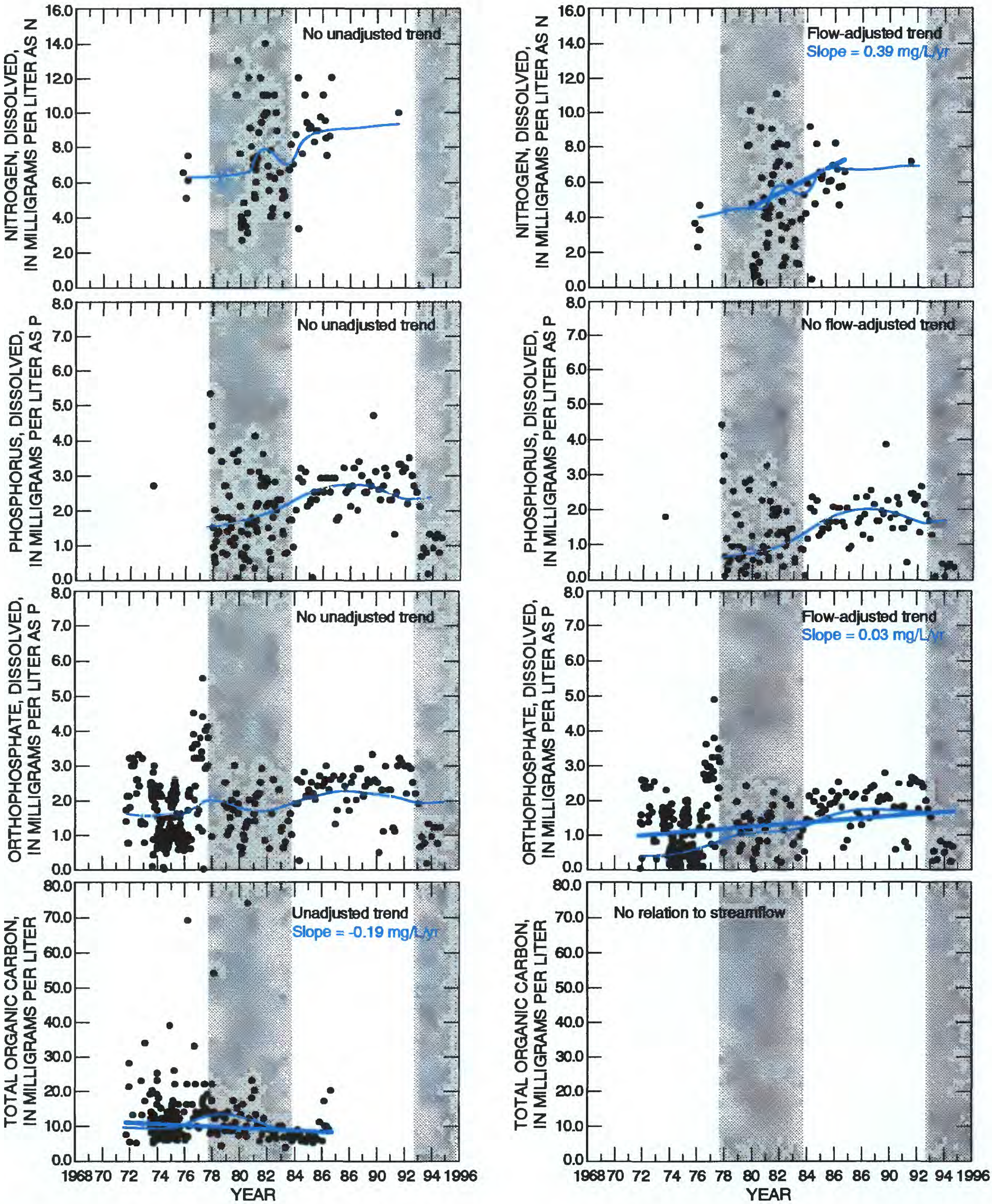

Figure 12—Continued.

Highly significant upward flow-adjusted trends were calculated for nitrite plus nitrate, (0.15 mg/L per year) and orthophosphate (0.3 mg/L per year) (fig. 12 and table 3). Because these trends were adjusted to remove the effects of changes in streamflow, it is likely that these upward trends are the result of some factor other than changes in streamflow. The upward flow-adjusted trends (and unadjusted trends) in nitrite plus nitrate concentrations were largest in magnitude during January, the middle of the wet season. Smith and others (1987) also calculated statistically significant upward, flow-adjusted trends for nitrate in the Santa Ana River below Prado Dam in their study of water-quality trends in major rivers of the United States for the period 1974 to 1981. Smith and others (1987) showed that increases in nitrate (and total phosphorus) concentrations in the Nation's rivers were strongly associated with agricultural activity such as livestock density. The results of their national study, however, may not apply directly to the Santa Ana River basin,

Statistically significant trends were not obtained for organic nitrogen, ammonia plus organic nitrogen, phosphorus, and dissolved organic carbon. Although not a trend as defined in this report, the decrease in dissolved organic carbon between October 1977 and September 1986 was large in magnitude—about 0.47 mg/L per year (table 3).

LOWESS-smoothed curves showed that, in general, constituent concentrations did not change uniformly through time (figs. 10 and 12). Factors, other

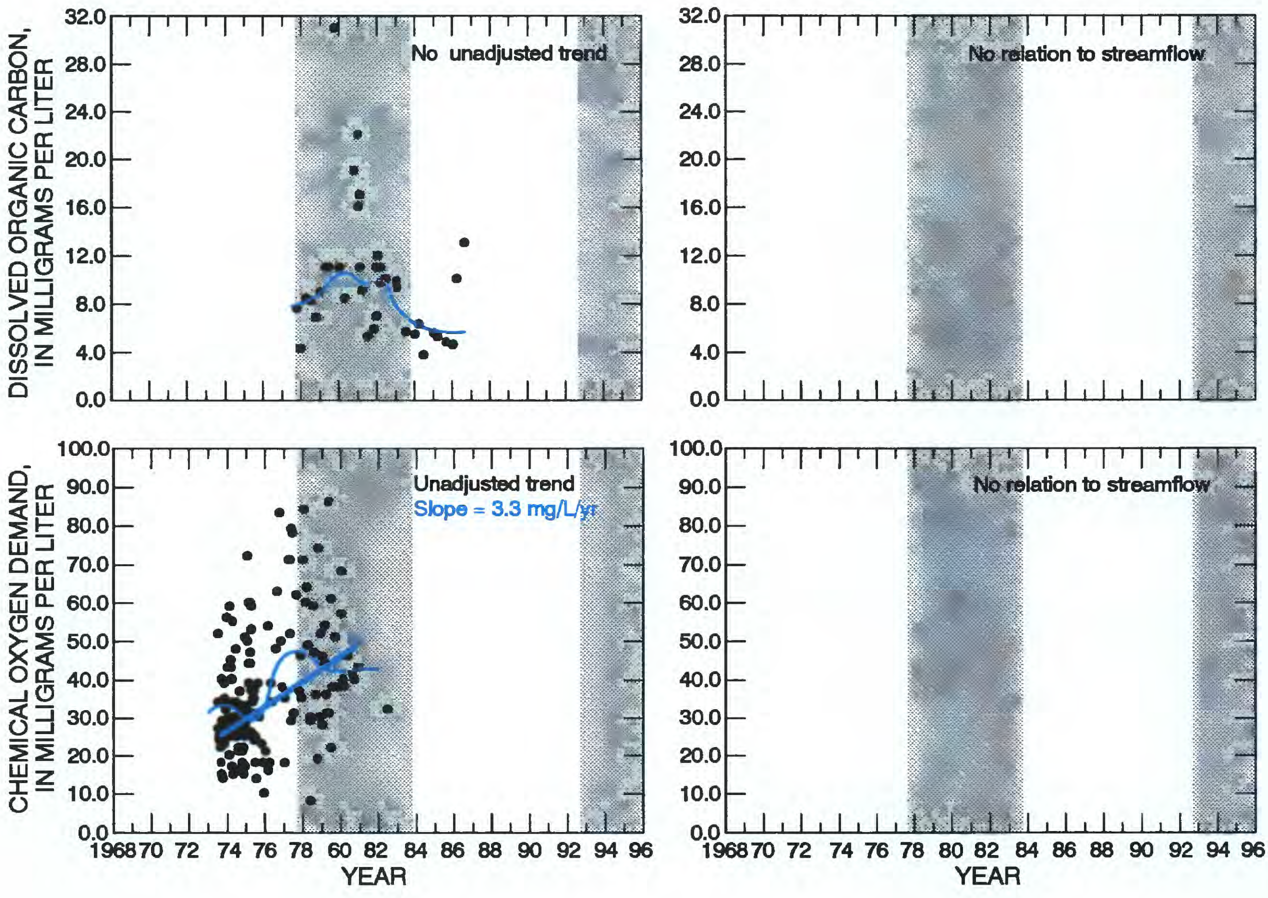

Figure 12—Continued.

than seasonality or changes in streamflow, which were not addressed in the trend analysis, such as the length of time since the last storm or the storage of water behind Prado Dam, also may affect constituent concentrations and create nonmonotonic trends.

EFFECT OF ANTECEDENT CONDITIONS ON WATER QUALITY

Trend calculations indicate generalized changes in water quality with time, with changes in streamflow, and during different seasons. Because the Santa Ana River is highly developed and intensively managed for flood control, water supply, and water quality, actual changes in the water quality (especially short-term changes during stormflows) are often complex and difficult to predict. The changes are difficult to predict because they may depend on antecedent conditions, such as time since the last storm or the presence or absence of water stored behind Prado Dam. These conditions cannot be directly incorporated into the trend analyses. However, an increased understanding of how antecedent conditions increase variability in water quality may increase the understanding of trends presented earlier in this report.

Hourly specific-conductance data collected from the Santa Ana River below Prado Dam were evaluated for the rising limb of hydrographs of 58 storms that occurred during water years 1988 to 1995. Although changes in specific conductance for most of the 58 storms occurred on the falling limbs of the hydrographs, the rising limb was selected for analysis to simplify interpretation of the data. Eight first storms of the season, and several storms affected by the storage of water behind Prado Dam, were evaluated.

In this simplified, idealized response, specific-conductance values decreased as streamflow increased (fig. 8). However, other responses to changes in streamflow also are possible. For example, specific-conductance values may increase as streamflow increases because soluble, colloidal, or particulate material is washed from the basin. In some areas, this response occurs after extended dry periods and is referred to as the "first flush." However, it also is possible that there may be no change in constituent concentrations during stormflow or that concentrations may change in a complex manner that cannot be readily explained by changes in streamflow.

Each of these responses (increases, decreases, no change, or a complex change) was observed during the 58 storms studied. Specific-conductance values decreased as streamflow increased during 24 of the 58 storms (about 40 percent). Specific-conductance values increased during 10 storms, showed no change during 16 storms, and during 8 storms showed a complex increase and (or) subsequent decrease on the rising limb of the hydrograph. The mix of responses to stormflow observed for all 58 storms was not greatly different from the mix of responses observed for the first storms of the season (8 storms) or for storms that occurred after a long period, more than 2 months between storms (11 storms). This suggests that the first storm of the season and storms that occur after extended dry periods, do not necessarily create a first flush with respect to specific-conductance values in the Santa Ana River below Prado Dam. In contrast, the response of specific conductance to stormflow was different for storms that occurred less than 1 week apart. Under these conditions, almost one-half of the storms showed no change in specific conductance with increases in streamflow—probably because most of the water released from Prado Dam during these stormflows was water already in storage behind the dam.

The single most important factor controlling changes in specific conductance during stormflows is the presence or the absence of water stored behind Prado Dam. If little or no water was stored behind Prado Dam (pool height less than 480 ft above sea level), specific-conductance values decreased during about 70 percent of the storms. Another factor is the size and duration of the storm. Streamflow and hourly specific-conductance data show that large storms are more likely to produce changes in specific conductance than are small storms—especially when large volumes of water are stored behind Prado Dam. These results are consistent with the increased variation between streamflow and specific conductance observed for the Santa Ana River below Prado Dam during trend analysis.

Although it is not possible to apply conclusions made on the basis of hourly specific-conductance values to other constituents, these data indicate that there may be considerable variation in water quality related to antecedent conditions (such as storage and subsequent release of water by Prado Dam). Additional data are necessary to determine how other constituents change in the Santa Ana River in response to antecedent conditions.

Table 4. Summary of selected trace-element and organic-compound data for the Santa Ana River below Prado Dam, Riverside County, California

[All concentrations in micrograms per liter. —, no data or not applicable. Selected trace elements filtered through a 0.45 micron pore-sized membrane filter. Selected organic compounds unfiltered. EPA, Environmental Protection Agency; <, actual value is less than the value shown]

Constituent	Period of record	Number of samples analyzed	Reporting limit	Number above detection limit[1]	U.S. EPA maximum contaminant level[2]	Number of samples above maximum contaminant level	Maximum concentration
			Selected trace elements				
Arsenic	10/71–5/91	112	1	100	50	0	35
Barium	5/73–9/94	83	100	0	2,000	0	<100
Beryllium	11/82–5/91	39	25	0	4	0	<25
Cadmium	10/71–5/91	110	1	39	5	6	34
Chromium	5/73–9/94	83	1	22	100	0	10
Cobalt	10/91–9/94	118	50	0	—	—	<50
Copper	10/71–5/91	112	50	22	[3]1,000	—	40
Iron	12/67–9/94	227	10	187	[3]300	6	1,700
Lead	10/71–5/91	112	10	9	[4]15	9	580
Manganese	5/73–9/94	96	10	96	[3]50	89	510
Molybdenum	11/82–9/94	51	100	3	—	—	20
Nickel	1/80–9/94	69	100	0	100	0	<100
Selenium	5/73–9/94	96	1	2	50	0	3.0
Silver	5/73–9/94	82	1	0	[3]100	0	1
Vanadium	11/82–9/94	51	1	51	—	—	9
Zinc	11/71–5/91	112	10	85	[3]5,000	0	110
			Selected organic compounds				
Aldrin	12/70–9/86	96	0.01	17	[5]0.05	0	0.01
Atrazine	11/95–8/78	7	.05	0	3	0	<.05
Chlorodane	12/70–9/86	96	.1	0	2	0	.1
Diazinon	12/70–9/86	95	.01	72	[5]14	0	.3
Dieldrin	12/70–9/86	96	.01	35	[5].05	0	.02
Endosulfan	1/79–9/86	36	.01	18	—	—	.01
Lindane	12/70–9/86	96	.1	1	.2	0	.11
Malathion	12/70–9/86	96	.01	32	160	0	.3
Mirex	1/79–9/86	36	.01	17	—	—	.01
Parathion	12/70–9/86	96	.01	20	[5]30	0	.03
Perthane	12/70–9/86	36	.1	0	—	0	<.1
Silvex	12/70–9/86	90	.01	20	50	—	.01
Simazine	8/76–8/78	6	.1	0	4	0	<.1
DDT	12/70–9/86	96	.05	1	—	0	.06
DDE	12/70–9/86	96	.03	3	—	—	.03
DDD	12/70–9/86	96	.05	0	—	0	<.01
PCB's Total	11/72–9/86	82	.1	0	—	—	.1
2,4-D	12/70–9/86	90	.01	65	70	0	.75

[1]If detection limit has changed through time because of changes in analytical techniques, the higher detection limit is used in this table.
[2]From California Department of Water Resources (1995), unless noted otherwise.
[3]U.S. EPA Secondary Maximum Contaminant Level (SMCL) from California Department of Water Resources (1995).
[4]U.S. EPA action level (at tap) from California Department of Water Resources (1995).
[5]California Department of Health Services action level from California Department of Water Resources (1995).

TRACE ELEMENTS AND ORGANIC COMPOUNDS IN THE SANTA ANA RIVER

Trends were not calculated for trace elements and organic compounds in the Santa Ana River below Prado Dam because most of the values for these constituents were less than analytical detection limits and because changes in sample collection, handling, and laboratory methods may have affected the comparability of the data for some constituents. Trace-element and organic-compound data collected for this study, however, are included in this report (table 4) so that the data could be compared with water-quality standards and with data collected as part of future studies. Although additional data are available from other agencies, a summary of these data was beyond the scope of this report.

Trace-element data presented in table 4 show that cadmium has exceeded the U.S. Environmental Protection Agency's (1994) maximum contaminant level (MCL) of 5 µg/L for drinking water in about 5 percent of the samples. No flow-adjusted trend in cadmium concentrations was observed in the Santa Ana River below Prado Dam for water years 1974–81 by Smith and others (1987). However, a significant upward flow-adjusted trend in cadmium concentrations was calculated for the same period in nearby Los Angeles River basin (Smith and others, 1987) which also is highly urbanized. Important sources of cadmium to the environment include fossil fuel combustion, primary-metals manufacturing, electroplating, and solid-waste disposal (Delos, 1985). Lead also has exceeded the U.S. Environmental Protection Agency (1994) action level (15 µg/L at tap) for drinking water in about 8 percent of the samples (table 4). No trend in lead concentrations was observed in either the Santa Ana or the Los Angeles Rivers by Smith and others (1987) between 1974 and 1981. Prior to 1981, gasoline was a large source of lead to the environment (Ethyl Corporation, 1982). Lead from gasoline decreased after 1981 when unleaded gasoline was introduced. Neither cadmium or lead have been detected in the Santa Ana River below Prado Dam at concentrations greatly above their respective detection limits since 1981—this indicates that, at present, these metals may not be important water-quality concerns.

Iron and manganese concentrations have exceeded the U.S. Environmental Protection Agency's (1994) secondary maximum contaminant level (SMCL) of 300 µg/L and 50 µg/L, for drinking water 3 percent and 90 percent of the time, respectively. The SMCLs are primarily for esthetic purposes and are not enforceable by law. Although iron concentrations have not exceeded the U.S. Environmental Protection Agency's SMCL since 1976, manganese concentrations commonly exceed the SMCL throughout the entire period of record.

Data for 18 organic compounds collected from 1970 to 1986 show that none of these compounds were detected at concentrations above their respective MCLs (table 4). However, 12 of those compounds (aldrin, diazinon, dieldrin, endosulfan, lindane, malathion, mirex, parathion, and silvex, DDT, DDE, and 2,4-D) have been detected at least once in the Santa Ana River below Prado Dam. Because of changing regulations and changes in the use of many of these organic compounds, some of these compounds, such as DDT, may not be present in the Santa Ana River under present-day (1997) conditions. However, six compounds (butylbenzyl phthalate, DEHP, diazinon, di-n-butylphthalate, methoxychlor, and simazine) were detected in samples of stormflow runoff collected by the U.S. Geological Survey at Imperial Highway in December 1995 and January 1996 and analyzed by Orange County Water District (Orange County Water District, 1996b). These data suggest that organic compounds may be important water-quality concerns in the Santa Ana River. Additional data are necessary to characterize the concentration of selected organic compounds present in stormflow runoff in the Santa Ana River.

When interpreting trace-element and organic-compound data from the Santa Ana River, it is important to remember that water from the Santa Ana River is not used directly as a source of public supply but rather as a source of recharge for aquifers that are pumped for public supply. As a result, trace elements and organic compounds may be sorbed and organic compounds may be degraded before the water is pumped.

SUMMARY

The Santa Ana River drains an extensively urbanized area of about 2,670 mi^2 near Los Angeles. Population in the area has increased rapidly since the 1940's and in 1990 was about 4.5 million. About 2 million people in Orange County are dependent on the Santa Ana River as a source of recharge for aquifers that are pumped for water supply.

In recent years, base flow in the Santa Ana River has increased as a result of the discharge of treated municipal wastewater, and high flows have increased as a result of increased precipitation and urbanization and its resultant runoff. Against this complex background of climatic and man-made influences, it is difficult to interpret trends in terms of cause and effect. Instead, the results of trend calculations presented in this report are intended to illustrate overall changes in the concentrations of selected constituents through time.

For the Santa Ana River below Prado Dam, concentrations of nitrite plus nitrate, total dissolved nitrogen, and phosphorus were generally lower during the wetter seasons and higher during the dryer seasons. In contrast, concentrations of ammonia, organic nitrogen, ammonia plus organic nitrogen, total organic carbon, and chemical oxygen demand were lower in the dryer seasons and higher during the wetter seasons. Although some seasonal variations were present, concentrations of orthophosphate and dissolved organic carbon did not show large seasonal changes. For the Santa Ana River at MWD Crossing, statistically significant relations with streamflow were calculated for specific-conductance values and dissolved-solids concentrations. For the Santa Ana River below Prado Dam, statistically significant relations with streamflow were calculated for specific-conductance values and for dissolved-solids, nitrite plus nitrate, total dissolved nitrogen, phosphorus, and orthophosphate concentrations. These relations were used to calculate flow-adjusted trends.

At MWD Crossing, significant, flow-adjusted downward trends of -1.1 µS/cm per year and -1.6 mg/L per year were calculated for specific conductance and dissolved solids, respectively. In contrast, below Prado Dam, flow-adjusted upward trends of 2.2 µS/cm per year and no flow-adjusted trends were detected for specific-conductance values and dissolved-solids concentrations, respectively. Specific-conductance values and dissolved-solids concentrations in the Santa Ana River below Prado Dam, when not adjusted for changes in streamflow, had statistically significant downward trends of -8.3 µS/cm per year and -6.0 mg/L per year, respectively. For the Santa Ana River below Prado Dam, statistically significant downward trends (not adjusted for streamflow) were calculated for ammonia (-0.04 mg/L per year) and total organic carbon (-0.19 mg/L per year); statistically significant, flow-adjusted upward trends were calculated for nitrate (0.13 mg/L per year), nitrite plus nitrate (0.15 mg/L per year), total dissolved nitrogen (0.39 mg/L per year), and orthophosphate (0.03 mg/L per year); statistically significant trends were not obtained for nitrite, organic nitrogen, ammonia plus organic nitrogen, phosphorus, and dissolved organic carbon.

Although data were insufficient to calculate trends for trace elements and organic compounds, the concentrations of cadmium and lead occasionally exceeded their respective maximum contaminant levels for drinking water in the Santa Ana River below Prado Dam. Of the 18 organic compounds for which data are available for 1970 to 1986, none were detected at concentrations above their respective MCLs.

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