Concentrations of Dissolved Solids and Nutrients in Water Sources and Selected Streams of the Santa Ana Basin, California, October 1998–September 2001

By Robert Kent *and* Kenneth Belitz

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FOREWORD

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

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

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

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

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

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

Robert M. Hirsch

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CONVERSION FACTORS

Multiply	By	To obtain
acre	4,047	square meters
acre-foot per year (acre-ft/yr)	1,233	cubic meter per year
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	2.54	centimeter
inch (in.)	25.4	millimeter
mile(mi)	1.609	kilometer
square mile (mi^2)	2.590	square kilometer

Temperature in degrees Celsius (^oC) may be converted to degrees Fahrenheit (^oF) as follows:

$$^oF=1.8\ ^oC+32.$$

WATER-QUALITY INFORMATION

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25^{o}C).

VERTICAL DATUM

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

ABBREVIATIONS AND ACRONYMS

Ca^{2+}	calcium
Cl^-	chloride
CO_3^{2-}	carbonate
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
EWI	equal-width increment
F^-	fluoride
FWA	flow-weighted average (stormflow)
HCO_3^-	bicarbonate

HIP	high-intensity phase (NAWQA data collection)
IBSP	Inorganic Blind Sample Project (USGS)
IR	interquartile range (in boxplots)
K^+	potassium
LRL	laboratory reporting level
MCL	maximum contaminant level (USEPA)
Mg^{2+}	magnesium
MWD	Metropolitan Water District
μm	micrometer
mi	mile
mi^2	square mile
Na^+	sodium
NO_2^-	nitrite
NO_3^-	nitrate
NWQL	National Water Quality Laboratory (USGS)
P	phosphorus
PVC	polyvinyl chloride
QC	quality control
RIX	rapid infiltration and extraction (treatment plant)
ROE	residue on evaporation at 180°C
RPD	relative percentage difference
SANA	Santa Ana Basin Study Unit (NAWQA)
SO_4^{2-}	sulfate
TDS	total dissolved solids
TN	total nitrogen
TON	total organic nitrogen
TP	total phosphorus

Organizations

NADP	National Atmospheric Deposition Program
NAWQA	National Water-Quality Assessment Program
OCWD	Orange County Water District
RWQCB	California Regional Water Quality Control Board
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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ABSTRACT

Concentrations of total dissolved solids (TDS) and nutrients in selected Santa Ana Basin streams were examined as a function of water source. The principal water sources are mountain runoff, wastewater, urban runoff, and stormflow. Rising ground water also enters basin streams in some reaches. Data were collected from October 1998 to September 2001 from 6 fixed sites (including a mountain site), 6 additional mountain sites (including an alpine indicator site), and more than 20 synoptic sites. The fixed mountain site on the Santa Ana River near Mentone appears to be a good representative of reference conditions for water entering the basin.

TDS can be related to water source. The median TDS concentration in base-flow samples from mountain sites was 200 mg/L (milligrams per liter). Base-flow TDS concentrations from sites on the valley floor typically ranged from 400 to 600 mg/L; base flow to most of these sites is predominantly treated wastewater, with minor contributions of rising ground water and urban runoff. Sparse data suggest that TDS concentrations in urban runoff are about 300 mg/L. TDS concentrations appear to increase on a downstream gradient along the main stem of the Santa Ana River, regardless of source inputs.

The major-ion compositions observed in samples from the different sites can be related to water source, as well as to in-stream processes in the basin. Water compositions from mountain sites are categorized into two groups: one group had a composition close to that of the alpine indicator site high in the watershed, and another group had ionic characteristics closer to those in tributaries on the valley floor. The water composition at Warm Creek, a tributary urban indicator site, was highly variable but approximately intermediate to the compositions of the upgradient mountain sites. Water compositions at the Prado Dam and Imperial Highway sites, located 11 miles apart on the Santa Ana River, were similar to one another and appeared to be a mixture of the waters of the upstream sites, Santa Ana River at MWD Crossing, Cucamonga Creek, and Warm Creek.

Rainfall usually dilutes stream TDS concentrations. The median TDS concentration in all storm-event discrete samples was 260 mg/L. The median flow-weighted average TDS concentration for stormflow, based on continuous measurement of specific conductance and hydrograph separation of the continuous discharge record, was 190 mg/L. However, stormflow TDS concentrations were variable, and depended on whether the storm was associated with a relatively small or large rainfall event. TDS concentrations in stormflow associated with relatively small events ranged from about 50 to 600 mg/L with a median of 220 mg/L, whereas concentrations in stormflow associated with relatively large events ranged from about 40 to 300 mg/L with a median of 100 mg/L.

From the perspective of water managers, the nutrient species of highest concern in Santa Ana Basin streams is nitrate. Most mountain streams had median base-flow concentrations of nitrate below 0.3 mg/L as nitrogen. Nitrate concentrations in both urban runoff and stormflow were near 1 mg/L, which is close to the level found in rainfall for the region. In fact, results from this study suggest that much of the nitrate load in urban storm runoff comes from rainwater. Nitrate concentrations in the Santa Ana River and its major tributaries are highest downstream from wastewater inputs, where median base-flow concentrations of nitrite+nitrate ranged from about 5 to 7 mg/L. About 4 percent of samples collected from sites receiving treated wastewater had nitrate concentrations greater than 10 mg/L. Rising ground water also appears to have high nitrate concentrations (greater than 10 mg/L) in some reaches of the river. Concentrations of other nitrogen species were much lower than nitrate concentrations in base-flow samples. However, storm events increased concentrations and the proportion of organic nitrogen, ammonia, and nitrite relative to nitrate.

Concentrations of total phosphorus at sites upstream from wastewater inputs were usually at or below 0.03 mg/L as phosphorus. Total phosphorus concentrations in base-flow samples from fixed sites below wastewater inputs were typically near 1 mg/L, indicating a departure from reference conditions and a potential for phosphorus-driven eutrophication.

INTRODUCTION

The Santa Ana River is the largest river in Southern California. In the Santa Ana Basin, which is home to over 4 million people, dissolved solids and nutrients (specifically inorganic nitrogen) have been identified as primary water-quality concerns (California Regional Water Quality Control Board, 1995). Given these concerns, the U.S. Geological Survey (USGS) completed a study of water-quality conditions in the river and selected tributaries with respect to total dissolved solids (TDS) and selected nutrients. Data were collected from October 1998 to September 2001 in the first high-intensity phase (HIP) of data collection for the Santa Ana Basin Study Unit (SANA) of the U.S. Geological Survey National Water Quality Assessment Program (NAWQA).

Human health issues related to nutrients in drinking-water sources stem chiefly from the nitrogen compounds of nitrite and nitrate. When infants consume water with relatively high nitrate concentrations, the nitrate may be converted to nitrite in the digestive tract. Once in the bloodstream, nitrite will combine with hemoglobin to form methemoglobin, which does not carry oxygen. Potentially fatal methemoglobinemia, or “blue-baby syndrome,” can then result from this internal suffocation, which actually causes infants to take on a peculiar lavender color (American Academy of Pediatrics, 1970; Johnson and Kross, 1990). Nitrite and nitrate also are suspected precursors of carcinogenic nitrosamines and nitrosamides (Neill, 1989), and there may be an increased risk for certain types of cancer in older women from even low-level nitrate exposure over many years (Weyer and others, 2001).

Regulatory criteria for the protection of aquatic life are generally not applied with respect to nitrate or nitrite because concentrations considered toxic to aquatic organisms rarely occur in nature (U.S. Environmental Protection Agency, 1986). However, Marco and others (1999) reported toxic responses by several amphibian larvae to nitrate and nitrite concentrations below limits recommended by the U.S. Environmental Protection Agency (USEPA) for drinking water and water inhabited by warm-water fishes. Three of the five species examined in that study [the red-legged frog (*Rana aurora*), the western toad (*Bufo boreas*), and the pacific tree frog (*Hyla regilla*)] are, or were, native to the Santa Ana River (Ed L. Ervin, Biological Resources Discipline, USGS, written commun., 2001).

Inorganic nitrogen in the form of ammonia (NH_3+NH_4^+) also carries potentially hazardous effects for aquatic life (Pocernich and Litke, 1997; U.S. Environmental Protection Agency, 1999). Finally, inorganic nitrogen and phosphorus are essential plant nutrients, and their concentrations are often limiting to algal growth in streams. When these nutrients are in excess, accelerated eutrophication can result in nuisance algal growth and dissolved oxygen depletion.

Purpose and Scope

The primary purpose of this report is to present an evaluation of dissolved solids and concentrations of selected nutrients in streams of the Santa Ana Basin as a function of water source. These sources include streamflow at reference sites in the foothills of two major mountain ranges (mountain sites), urban runoff (nonpoint source discharges unrelated to storm events), treated municipal wastewater, rising ground water, and stormflow. Constituent fluxes or loads are not presented in this report. The focus on water sources contrasts with the more common landscape-based approach to explain ambient surface-water-quality conditions. The hydrologic cycle of this semiarid, urban watershed differs from unaltered watersheds, and an understanding of the water quality related to each source may facilitate water-quality management decisions.

A secondary purpose of this report is to present a comparison of TDS and nutrient concentrations observed during the study to water-quality standards, goals, objectives, and reference conditions. Reference conditions refer to water quality that has been minimally affected by humans. High concentrations of dissolved solids and nutrients in surface water carry concerns for human as well as ecosystem health. Excessive concentrations of dissolved solids can collectively render water unfit for drinking (U.S. Environmental Protection Agency, 2002) and for supporting aquatic life. In addition, some individual dissolved constituents, such as chloride, sulfate, nitrate, and nitrite present their own water-quality concerns and have specific standards for maximum concentrations in drinking water or criteria for the protection of aquatic life (U.S. Environmental Protection Agency, 2002; 1999; 1988; 1986). Data used in this report are the product of more than 250 water samples collected from 37 stream sites during the study period of October 1998 to September 2001.

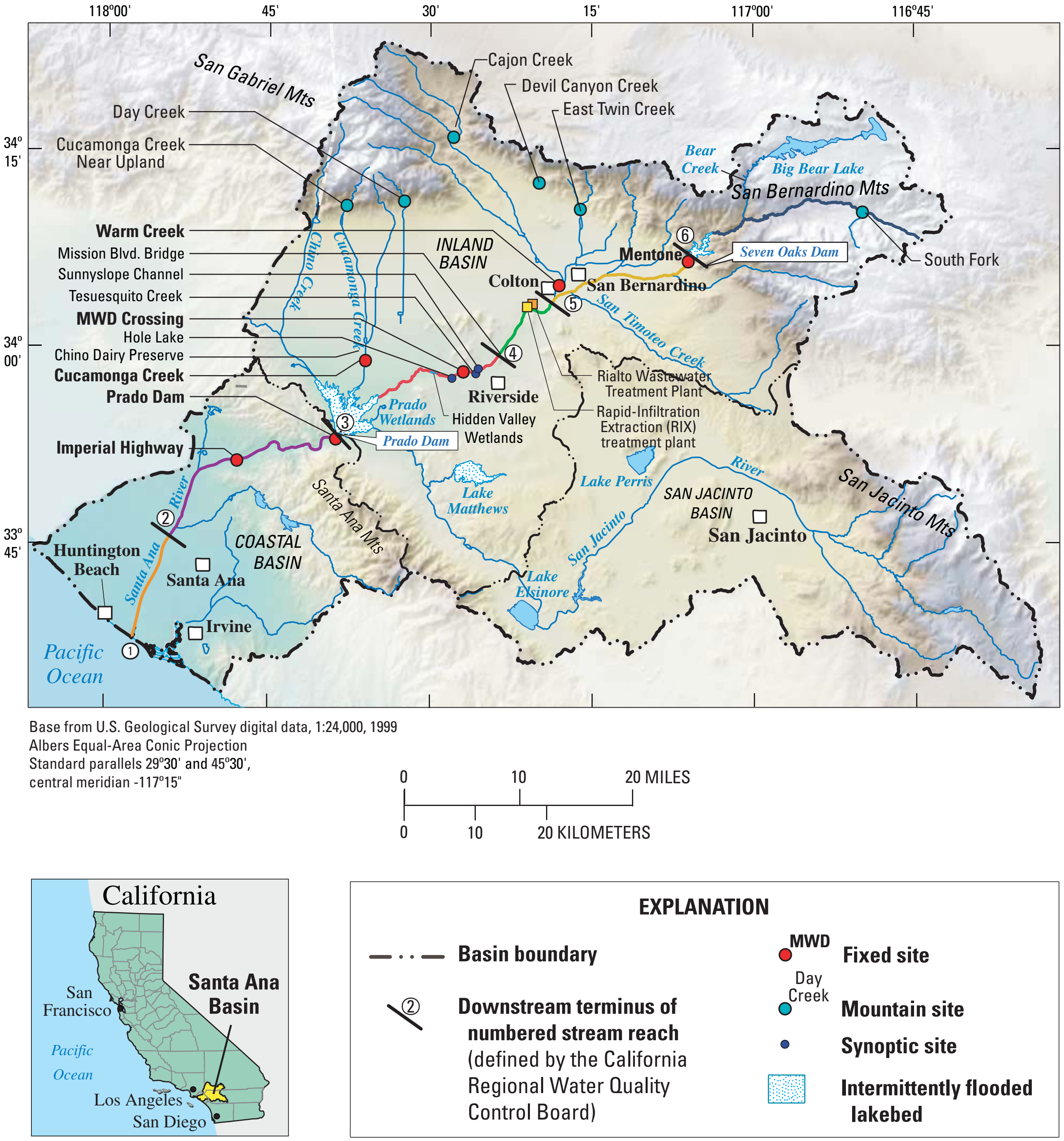
Description of Study Area

The Santa Ana NAWQA (SANA) study unit occupies about 2,700 mi^2 in the Transverse (San Gabriel Mountains, San Bernardino Mountains) Range and the Peninsular (Santa Ana Mountains, San Jacinto Mountains) Range Provinces of southern California (fig. 1). The Santa Ana River is the largest stream system in southern California, beginning in the San Bernardino Mountains (which reach elevations exceeding 10,000 ft above sea level) and flowing more than 100 mi to the Pacific Ocean near Huntington Beach. The 2,700 mi^2 watershed is home to over 4 million people, and the population is expected to increase by more than 50 percent by the year 2020. Water demand is expected to increase by somewhat less than 50 percent during the same period (Santa Ana Watershed Project Authority, 1998)

The climate is mediterranean with hot, dry summers, and cooler, wetter winters. Average annual precipitation ranges from about 10 to 24 in. in the coastal plain and inland valleys, and from 24 to 48 in. in the San Gabriel and the San Bernardino Mountains. However, during the period described in this report the area was experiencing a drought, and rainfall was only about a third of normal. As a result of the drought the Santa Ana River upstream from wastewater inputs recorded its second lowest annual flow in recorded history in 2001 (City of Redlands, 2002).

Natural vegetation in the drainage area ranges from riparian habitat and coastal sage at lower elevations, to chaparral and mixed deciduous and conifer forests at higher elevations. Alpine tundra is also present at the mountain summits. Sycamore, cottonwood, willow, and other riparian plants are common throughout the river flood plain, as are many aquatic plants. The San Gabriel, the San Bernardino, and the San Jacinto Mountains lie within the Southern California Mountains Ecoregion; the remainder of the study unit lies within the Southern and Central California Plains and Hills Ecoregion (Burton, 2002).

The study area can be subdivided into three primary subunits: the Coastal Basin, the Inland Basin, and the San Jacinto Basin. Within these subunits, water-bearing deposits can be identified in the alluvial-filled valleys and coastal plain, and in the relatively impervious uplands. The uplands are generally steep and remain undeveloped. Urban and agricultural land uses occur primarily in the alluvial-filled valleys and coastal plain. However, local land use has little influence on surface-water quality in the basin under base-flow conditions, because base flow in the Santa Ana River is maintained almost entirely by effluent from municipal wastewater treatment plants (Burton and others, 1998).



Base from U.S. Geological Survey digital data, 1:24,000, 1999
Albers Equal-Area Conic Projection
Standard parallels 29°30' and 45°30',
central meridian -117°15"

Figure 1. Location of study area and sampling sites, Santa Ana Basin, California.

Ground water is the main source of water supply in the watershed, meeting about two-thirds of the total water demand [about 1.2 million acre-feet per year (acre-feet/yr)] (Santa Ana Watershed Project Authority, 1998). Imported water from northern California and the Colorado River meet about one-quarter of the total consumptive demand. After delivery and domestic use, nearly all of the water is tertiary treated (Izbicki and others, 2000) in order to meet water-quality objectives established for the basin by the California Regional Water Quality Control Board (1995). This treated effluent is discharged to the Santa Ana River and several of its tributaries, and sites that receive wastewater constitute a major water-source group in this study. However, effluent quality at treatment-plant outfalls is variable, and its description is beyond the scope of this report.

In some cases wastewater receives further treatment after leaving the plant to remove inorganic nitrogen. Effluent from treatment plants in Colton and San Bernardino is pumped to a regional facility using a treatment called Rapid Infiltration and Extraction (RIX). The facility consists of about 43 acres of infiltration basins where effluent filters through the soil. It is then pumped from the aquifer beneath the infiltration basins along with a small amount of native ground water, disinfected, and discharged to the river (Wildermuth Environmental, Inc., 1998). The Hidden Valley Wetlands in Riverside also remove nitrate from effluent before it reaches the river. The Orange County Water District diverts about half of the Santa Ana River base flow though a series of artificial wetlands for the same purpose above the Prado Dam (O'Connor, 1995).

Other surface-water inputs besides treated wastewater include rising ground water in various parts of the basin and urban runoff (nonpoint source discharges not directly associated with storm events). Base flow in the Santa Ana River also is supplemented by intermittent releases of water imported from northern California and the Colorado River to increase streamflow available for ground-water recharge (Burton and others, 1998). The California Regional Water Quality Control Board (1995) refers to these releases as “non-tributary flow.”

A number of factors contribute to a disconnection between landscape and stream water quality in the Santa Ana Basin. Flow from the upper Santa Ana watershed is commonly diverted to detention basins located at the mountain front. Natural hydrologic processes also are short-circuited by the mostly concrete-lined urban storm-water conveyance network, which is designed to rapidly transfer water downstream. Base flow on the valley floor consists primarily of treated wastewater, which is discharged from several outfalls on the river and its tributaries.

The California Regional Water Quality Control Board (1995) divides the Santa Ana River into six reaches, numbered in ascending order from the mouth to the headwaters (fig. 1). For internal consistency in this report, these reaches are described from upstream to downstream. Reach 6 extends from the headwaters in the San Bernardino Mountains to just above the Seven Oaks Dam near Mentone. Flow in Reach 6 is perennial and consists of rising ground water, stormflow runoff and, on occasion, snowmelt. Reach 5 extends from the Seven Oaks Dam to the Bunker Hill Dike in San Bernardino (labeled “5” in fig. 1). Reach 5 has intermittent flow. Reach 4 extends from the Bunker Hill Dike to the Mission Blvd. Bridge in Riverside (labeled “4” in fig. 1). Reach 3 is located between Mission Blvd. Bridge and the Prado Dam. In contrast to the intermittent flow in Reach 5, discharges of treated wastewater enter the river along Reaches 3 and 4, resulting in perennial flow from near the top of Reach 4 to the recharge facilities at the bottom of Reach 2. Reach 2 extends from the Prado Dam to 17th Street in Santa Ana (labeled “2” in fig. 1). Reach 1 lies between 17th Street and the river mouth in Huntington Beach. This reach is usually dry because nearly all base flow of the Santa Ana River is captured by ground-water recharge facilities operated by the Orange County Water District near the downstream limit of Reach 2.

Study Design

Data for this study were collected from October 1998 to September 2001, corresponding to the high intensity phase (HIP) of the SANA study unit (Gilliom and others, 1995). In this report three general types of sites are identified: fixed sites, mountain sites, and synoptic sites (table 1).

Table 1. Stream sites from where samples were collected and analyzed for concentrations of dissolved solids and nutrients during this study, Santa Ana Basin, California, October 1998–September 2001

[Water quality data used in this interpretive report is available at http://waterdata.usgs.gov/ca/nwis/qwdata; RIX, rapid-infiltration and extraction (treatment plant); USGS, U.S. Geological Survey; WQC, water quality control; MWD, Metropolitan Water District]

USGS station ID No.	USGS station name	Site type(s)
11051500	Santa Ana River near Mentone	Fixed, Mountain
11060400	Warm Creek near San Bernardino	Fixed, Synoptic[1]
11066460	Santa Ana River at MWD Crossing	Fixed, Synoptic[1,2]
11073495	Cucamonga Creek near Mira Loma	Fixed, Synoptic[1]
11074000	Santa Ana River below Prado Dam	Fixed, Synoptic[1]
11075610	Santa Ana River above spreading diversion below Imperial Highway near Anaheim	Fixed
341014116494801	South Fork Santa Ana River near South Fork Campground near Angelus Oaks	Mountain
11058500	East Twin Creek near Arrowhead Springs	Mountain
11063680	Devil Canyon Creek near San Bernardino	Mountain
11063510	Cajon Creek below Lone Pine Creek near Keenbrook	Mountain, Synoptic[1]
11067000	Day Creek near Etiwanda	Mountain
11073470	Cucamonga Creek near Upland	Mountain, Synoptic[1]
340843117032501	Santa Ana River at Upper Powerhouse near Running Springs	Synoptic[1]
340552117172701	Warm Creek above Orange Show Grounds near San Bernardino	Synoptic[1]
340455117173801	Warm Creek above E Street near San Bernardino	Synoptic[1]
335913117080701	San Timoteo Creek near Eastside Ranch near Yucaipa	Synoptic[1]
335910117425801	Little Chino Creek above Pipeline Avenue near Los Serranos	Synoptic[1]
335835117412701	Chino Creek above Central Avenue near Los Serranos	Synoptic[1]
335655117395601	Chino Creek downstream of Pine Avenue at Prado Dam	Synoptic[1]
335506117381201	Mill Creek near Splatters Duck Club in Prado Wetlands	Synoptic[1]
340042117355901	Cucamonga Creek Main Channel at Chino Avenue near Ontario	Synoptic[1]
340041117355901	Cucamonga Creek Wastewater Effluent at Chino Avenue near Ontario	Synoptic[1]
340132117214401	Santa Ana River at Riverside Road near Riverside	Synoptic[1,2]
335835117253401	Sunnyslope Channel near Rubidoux Nature Center at Santa Ana River Regional Park	Synoptic[1]
335827117253801	Sunnyslope Channel at Santa Ana River Regional Park near Rubidoux	Synoptic[1,2]
340217117211401	Santa Ana River downstream Confluence of RIX Outflow	Synoptic[2]
335426117232701	Lake Evans Outflow at Riverside	Synoptic[2]
11066440	Santa Ana River at Mission Boulevard at Riverside	Synoptic[2]
335804117255201	Tesuesquito Creek near Mouth at Riverside	Synoptic[2]
335806117260501	Santa Ana River above MWD Crossing	Synoptic[2]
335748117275601	Riverside WQC Plant at Van Buren Boulevard near Riverside	Synoptic[2]
335743117280501	Hole Lake Discharge above Santa Ana River near Pedley	Synoptic[2]
335809117301001	Santa Ana River North of Hidden Valley Wetlands	Synoptic[2]
335759117300201	West Hidden Valley Wetlands Lake near La Sierra Heights	Synoptic[2]
335728117314101	Santa Ana River at Grulla Court at La Sierra	Synoptic[2]
335645117332601	Santa Ana River at Hamner Road above Norco	Synoptic[2]
335547117353601	Santa Ana River at Power Line Road near La Sierra Heights	Synoptic[2]

[1] Urban land-use gradient synoptic—19 sites (August 2000) (Burton and Brown, 2001)

[2] Dye tracer synoptic—15 sites (May 2001) (Mendez and Belitz, 2002)

Those sites listed here that do not appear on the figure 1 map of the study can be located on the map using their 15-digit station identification number and latitude/longitude coordinates bordering the map. The first six digits are latitude: digits 1–2, degrees; digits 3–4, minutes; digits 5–6, seconds. The next seven digits are longitude: digits 7–9, degrees; digits 10–11, minutes; digits 12–13, seconds. (The last two digits are sequence numbers without relevance for locating the site.)

Fixed Sites

In the NAWQA program, two types of fixed sites are recognized: indicator sites and integrator sites. Indicator sites are chosen to represent stream water-quality conditions resulting from specific land uses and important influences on water quality in the basin. In contrast, integrator sites are chosen to represent stream water-quality conditions affected by a combination of land uses, point sources, natural processes, and human influences. Fixed sites can be further divided into basic fixed sites and intensive fixed sites, the latter generally being sampled for more water-quality constituents and at greater frequency. The SANA fixed-site network consisted of six sampling locations (fig. 1). All of these were sampled at least monthly during the first two years of the high intensity phase (HIP), and nearly all storm sampling was conducted during this time. During the third year of the HIP, the fixed-site network was reduced to four sites.

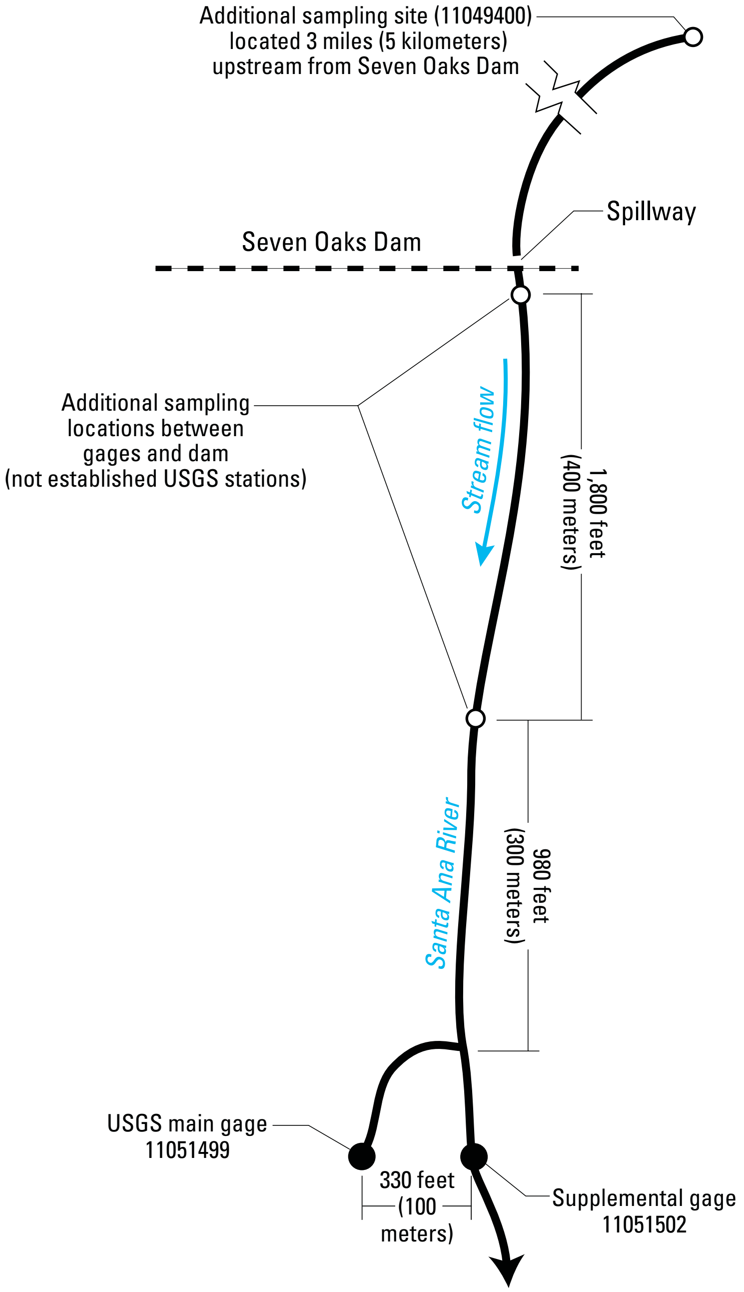
The Mentone site is a fixed mountain site located on the Santa Ana River, just upstream from where the Santa Ana River exits the San Bernardino Mountains. Owing to upstream diversions of the Santa Ana River, discharge at Mentone is primarily from Bear Creek, a major tributary of the Santa Ana River. During the time period of this study, construction of the Seven Oaks Dam affected the flow of the Santa Ana River in the area of the Mentone site. Therefore, water-quality samples were obtained from several locations (fig. 2). The first six samples (October 1998 to March 1999) were collected at the USGS main gage (site 11051499 in fig. 2). After March 1999 flow ceased at the main gage, and samples were collected at a supplemental gage (site 11051502), or at one of two non-permanent sites located between the supplemental gage and the dam outlet (fig. 2). The two gages and two non-permanent sites are located at the upper boundary of Reach 5, and water-quality data for all four sites is published and archived under USGS site 11051500. In February 2000, a sample was collected about 3 mi upstream from the dam, which is in Reach 6. This site was subsequently established as a NAWQA site for monitoring water-quality status and trends (site 11049400). Samples were collected monthly at the various Mentone sites from October 1998 to September 2001.

The Warm Creek urban indicator site (site 11060400) is concrete-lined; the drainage basin is small (12 mi^2) and entirely urban. Ground-water sources of water include a hot spring routed through a park and seepage that enters the stream through cracks in the concrete bottom and through drainage holes perforated in the vertical concrete sides. Urban runoff also contributes a substantial part of the discharge to the channel. Streamflow from this site enters the Santa Ana River near the downstream terminus of Reach 5 as identified by the California Regional Water Quality Control Board (1995). The Warm Creek site was sampled monthly from October 1998 to June 1999, twice-monthly from July 1999 to March 2000, and then monthly again from April 2000 to September 2001.

The site on the Santa Ana River at MWD Crossing (MWD, site 11066460) is an integrator on the Santa Ana River along Reach 3 downstream from the Rialto and RIX wastewater-treatment-plant outfalls (fig. 1). Although MWD is an integrator site, base flow is predominantly treated wastewater with minor contributions from rising ground water. Stormflow includes large contributions from tributaries that carry runoff from urban land use on the valley floor and from mountain runoff. Samples were collected monthly at this site from October 1998 to September 2000.

The Cucamonga Creek site (11073495) is located in the Chino Basin Dairy Preserve (fig. 1). However, discharge in Cucamonga Creek does not generally reflect land use in the adjacent area; the channel is concrete-lined and base flow consists primarily of treated wastewater with a small component of urban run-off. Under stormflow conditions, the discharge includes runoff from urban areas and undeveloped mountainous areas. Runoff from dairies also contributes to the discharge during intense rain events. Samples were collected here on the same schedule as at MWD. Cucamonga Creek becomes Mill Creek, as it enters the Prado Wetlands near the downstream terminus of Reach 3.

The Prado site (11074000), located downstream from the Prado Dam, is an integrator in space and time for the Inland Basin. The site is located near the upstream terminus of Reach 2. Water quality at this site is affected by a number of factors including wastewater, wetland processes in the Prado Wetlands, urban runoff, dairy runoff, and impoundment of stormflows. Samples were collected monthly at the Prado site during the entire high-intensity phase of data collection from October 1998 to September 2001.



(Not to scale, approximate distances)

Figure 2. Various sampling locations at the Mentone site, Santa Ana Basin, California (USGS, U.S. Geological Survey).

The Imperial Highway integrator site (11075610) is located on the Santa Ana River about 11 mi. downstream from the Prado Dam, and above diversion structures and ground-water recharge facilities maintained by the Orange County Water District (OCWD). This site is located in Reach 2. Under base-flow conditions, the discharge consists primarily of treated wastewater and minor amounts of urban runoff. Stormflows reaching this site have two sources: runoff from the Inland Basin that is released at Prado Dam, and runoff from urban areas located between the dam and the sampling site. The sampling schedule at Imperial Highway was the same as for Warm Creek until April 2001 when the last sample was collected for this study at Imperial Highway.

The routine monthly samples collected from each fixed site were typically collected during base-flow conditions. An additional six to eight samples were collected at each site during stormflow conditions. These were collected during the first two years and resulted from thirteen different storm events. One exception to the sampling strategy described above is that no samples were collected in November 2000.

Mountain Sites

One of the fixed sites, Mentone, was a mountain site. Beginning in January 2000, six additional mountain sites were sampled quarterly (fig. 1). The purpose of the quarterly sampling at these sites was to help establish a reference for water quality before it is altered by the urban landscape. One of the quarterly sites was initially identified as an alpine indicator fixed site (South Fork, 341014116494801—fig. 1, table 1) to serve as a reference site. However, initial data indicated that the stream water at South Fork contained substantially lower concentrations of dissolved and suspended materials than did most mountain stream water entering the basin. Therefore, the site was considered unrepresentative of basin reference conditions, and sampling there was reduced to quarterly after the first year of the HIP. The other five sites are mountain tributaries that contribute discharge to the Inland Basin. The sites include two tributaries that exit the San Gabriel Mountains [Cucamonga Creek near Upland (11073470) and Day Creek(11067000)], two tributaries that exit the San Bernardino Mountains [East Twin Creek (11058500) and Devil Canyon Creek (11063680)], and one tributary that receives runoff from both mountain ranges [Cajon Creek (11063510)]. Cajon Creek may be affected by human factors because it is located in a transportation corridor between the two mountain ranges.

Synoptic Study Sites

Two synoptic studies contributed to increased understanding of the role of spatial variability in controlling surface-water quality in the basin. One study was an urban land-use gradient study conducted in August 2000 (Burton and Brown, 2001). Nineteen sites were selected and characterized on the basis of water source and stream channel type; nutrients and dissolved solids were among the water-quality constituents sampled. The second study, a dye-tracer study, characterized the interaction between the Santa Ana River and the shallow ground-water system and quantified the percentage of wastewater and other sources of flow along an 18-mile reach (Mendez and Belitz, 2002). Dye-tracer measurements, along with additional data, were collected to characterize the water quality of the different water sources. These data, including nutrient samples, were collected over a 2-day period in May 2001 from nine sites on the main stem of the river and from six tributaries.

METHODS

Sample Collection

Water samples were collected by equal-width-increment [EWI] (USGS, variously dated), multiple-vertical, grab, or point (automatic) sampling methods, as site conditions dictated. The preferred method was EWI, because a discharge-weighted water-quality sample is collected along the sampling cross-section. The multiple-vertical sampling method also strives to represent water quality in a cross-section by integrating several verticals across a stream; multiple-vertical samples are usually not depth-integrated because shallow stream depths prohibit the use of isokinetic sampling equipment (USGS, variously dated). Grab samples, the least preferred method, are collected near midstream when streams are too narrow for EWI or multiple-vertical methods. Most samples collected for this study were obtained using the EWI method. Storm samples were usually collected near the stream bank by grab or automatic sampler (which also represented a grab sample).

Sample Processing

A cone splitter (USGS, variously dated) was used to divide the composited sample into subsamples, which theoretically contain equal concentrations of suspended and dissolved constituents (USGS, variously dated). Subsamples for whole-water nutrient analyses were collected directly from the cone splitter and preserved with 4.5 normal (N) sulfuric acid (U.S. Geological Survey Office of Water Quality, 1998). The subsamples analyzed for dissolved species were filtered through a capsule filter with an effective pore size of 0.45 micrometers (μm). All sample processing was carried out inside a clean mobile laboratory dedicated to this purpose. In addition, sample filtering was performed within a processing chamber, which consists of a clear plastic bag on a PVC frame to further avoid contamination from the atmosphere (Horowitz and others, 1994). Alkalinity and the concentrations of bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) were measured on filtered samples by field titration (USGS variously dated). Cleaning procedures for all sample-collection and processing equipment followed USGS protocols (USGS variously dated).

Laboratory Analyses

The USGS National Water Quality Laboratory (NWQL) analyzed the samples for dissolved and suspended species of nitrogen and phosphorus by colorimetric methods (Fishman, 1993; Patton and Truitt, 2000; Patton and Truitt, 1992; U.S. Environmental Protection Agency, 1993). These analyses quantified sample concentrations of dissolved nitrite, dissolved nitrite plus nitrate, dissolved total ammonia (ammonia plus ammonium), dissolved organic nitrogen plus ammonia, total organic nitrogen plus ammonia, dissolved orthophosphate, dissolved phosphorus, and total phosphorus. Analyses reported concentrations of nitrate and nitrite (nitrite+nitrate) as one analytical parameter. Nitrite was also reported as an isolated parameter. This allowed the determination that nitrite concentrations were a negligible proportion (typically less than 1 percent) of the nitrite+nitrate parameter in most samples. Therefore, the general term "nitrate" is used in the discussion of related water-quality issues. However, because health-related effects of exposure to high nitrate concentrations in water are a result of the metabolic conversion of nitrate to nitrite in an organism, concentration values are reported as the combined nitrite+nitrate parameter in order to present the entire concentration of concern. Total ammonia is reported by the NWQL as ammonia plus ammonium (NH_3+NH_4^+), although it exists in water primarily as the ammonium ion (Pocernich and Litke, 1997). Nutrient concentrations discussed in this report represent their concentrations expressed as either nitrogen or phosphorus. For example, a nitrate concentration expressed as 10 mg/L refers to a nitrate concentration of 10 mg/L as nitrogen.

Dissolved solids were measured both directly and indirectly. The NWQL provided direct analyses of dissolved solids by weighing the sample residue on evaporation at 180°C (Fishman and Friedman, 1989). In addition, the samples were analyzed for major ions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-}, F^-) and silica by ion chromatography (Fishman, 1993; Fishman and Friedman, 1989). Summing these with the nitrate concentrations and 0.6 times the field alkalinity value provides an additional measure of total dissolved solids and a rough check on the comprehensiveness of analysis (Howard, 1933). Finally, the six fixed sites were continuously monitored for specific conductance, a parameter strongly correlated with dissolved solids. Sensors on the specific-conductance monitors were calibrated by study unit personnel during all routine site visits, and long-term measurement drifts were corrected by applying data corrections to the continuous record following USGS protocol (Wagner and others, 2000). It was therefore possible to use the continuous record of specific conductance to calculate the concentration of dissolved solids for the basic fixed sites continuously throughout the high-intensity phase of data collection.

Data Analysis

As stated earlier, the primary purpose of this report is to evaluate TDS and nutrient concentrations in Santa Ana Basin streams as a function of water source. These sources include mountain runoff, urban runoff, treated municipal wastewater, rising ground water, and stormflow. The TDS and nutrient concentrations are also compared with water-quality standards, goals, objectives, and reference conditions.

Trilinear diagrams (Piper, 1944) are used to characterize the ionic composition of samples collected during base flow at the different sites in order to evaluate similarities and differences between sites. Piper diagrams are trilinear plottings that show the chemical character of a water sample on the basis of its relative concentrations of major cations (Ca^{2+}, Mg^{2+}, and Na^{+}+K^{+}) and anions (Cl^{-}+F^{-}+NO_2^{-}+NO_3^{-}, SO_4^{2-}, and HCO_3^{-}+CO_3^{2}). Boxplots are used to summarize concentration data. A boxplot, as used in this report, consists of a rectangle (box) divided by a line at the median (50th percentile) of the sample data. The lower and upper boundaries of the box itself extend from the 25th to the 75th percentiles, respectively, an interval referred to as the interquartile range (IR). Whiskers extend from the ends of the box as far as the last observed value within 1.5 times the IR. More extreme values appear as individual circles beyond the extent of the whiskers (fig. 3). Time-series graphs are used to show temporal variability for TDS and selected nutrients.

Data results are presented in the context of existing water-quality standards. These consist of primary or secondary standards in the form of maximum contaminant levels (MCLs) for drinking water (U.S. Environmental Protection Agency, 2002), water-quality objectives to protect designated beneficial water uses (California Regional Water Quality Control Board, 1995), and criteria to protect aquatic life or prevent stream eutrophication (U.S. Environmental Protection Agency, 1999, 1988, 1986). A primary drinking-water standard is legally-enforceable and applies to public water systems. A secondary drinking-water standard is a non-enforceable guideline regarding contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. Stream concentrations of total phosphorus also are compared with a reference condition determined using the 75th percentile (upper 25th percentile) of total phosphorus concentrations in samples from SANA mountain-stream sites (U.S. Environmental Protection Agency, 2000).

For some aspects of this study, specific conductance was used as a surrogate for TDS. For each fixed site a least-squares regression equation was calculated on the analytical values for TDS concentrations (mg/L) as a function of field-measured specific conductance (microsiemens per centimeter) for all samples collected. This relation then was used to estimate TDS concentrations at any time for each site using the continuous record of specific conductance. R-squared values for these linear regressions were at least 0.98 with better than 99 percent confidence for all sites except MWD, which had an r-squared value of 0.86 (fig. 4). Plots of residuals versus specific conductance indicate constant variance across values of specific conductance, except for the Prado and Imperial Highway plots. These showed error variances increasing with specific conductance. The residual standard errors were between 9 and 20 mg/L for all sites except MWD, which had a residual standard error of 39 mg/L. The weaker correlation and higher error for predicting TDS concentrations from specific conductance at MWD probably resulted from having the continuous monitor for specific conductance placed on one bank at a location where field data have shown that dissolved solids are not well-mixed across the stream.

From the perspective of water managers, the nutrient species of greatest concern in the Santa Ana Basin is nitrate. Therefore, emphasis is placed on nitrate in this discussion of nutrients. Concentration values for this form of nitrogen are reported here as they were analyzed, nitrite+nitrate, although sample nitrite concentrations were usually negligible.

To generate figures and summary statistics, concentration values reported as less than the laboratory reporting level (LRL), were replaced with values one-half of that level. During the study, the LRL for some analytes varied. When this occurred, one-half the highest common LRL applied to a given analyte during the study period was used to replace all values for that analyte reported as less than the LRL.

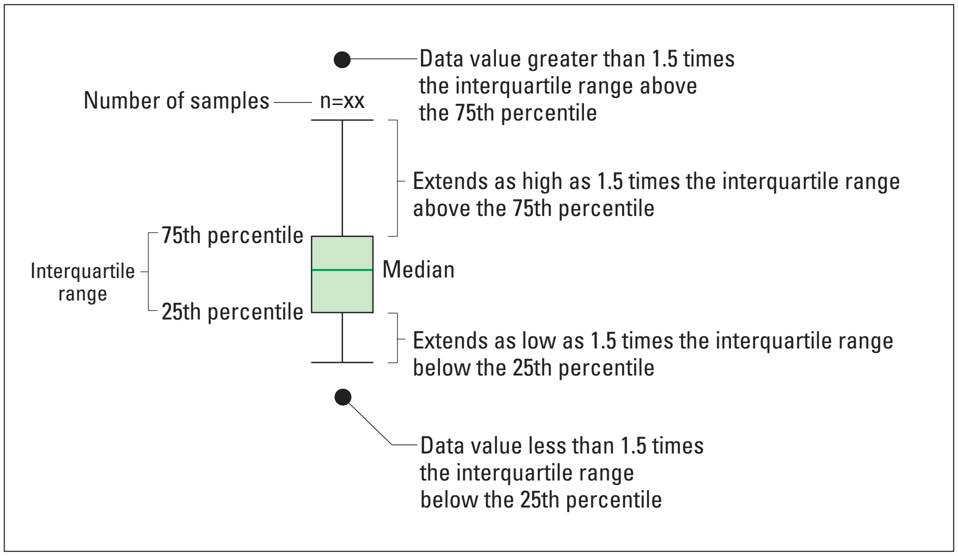


Figure 3. Elements of a boxplot as used in this report.

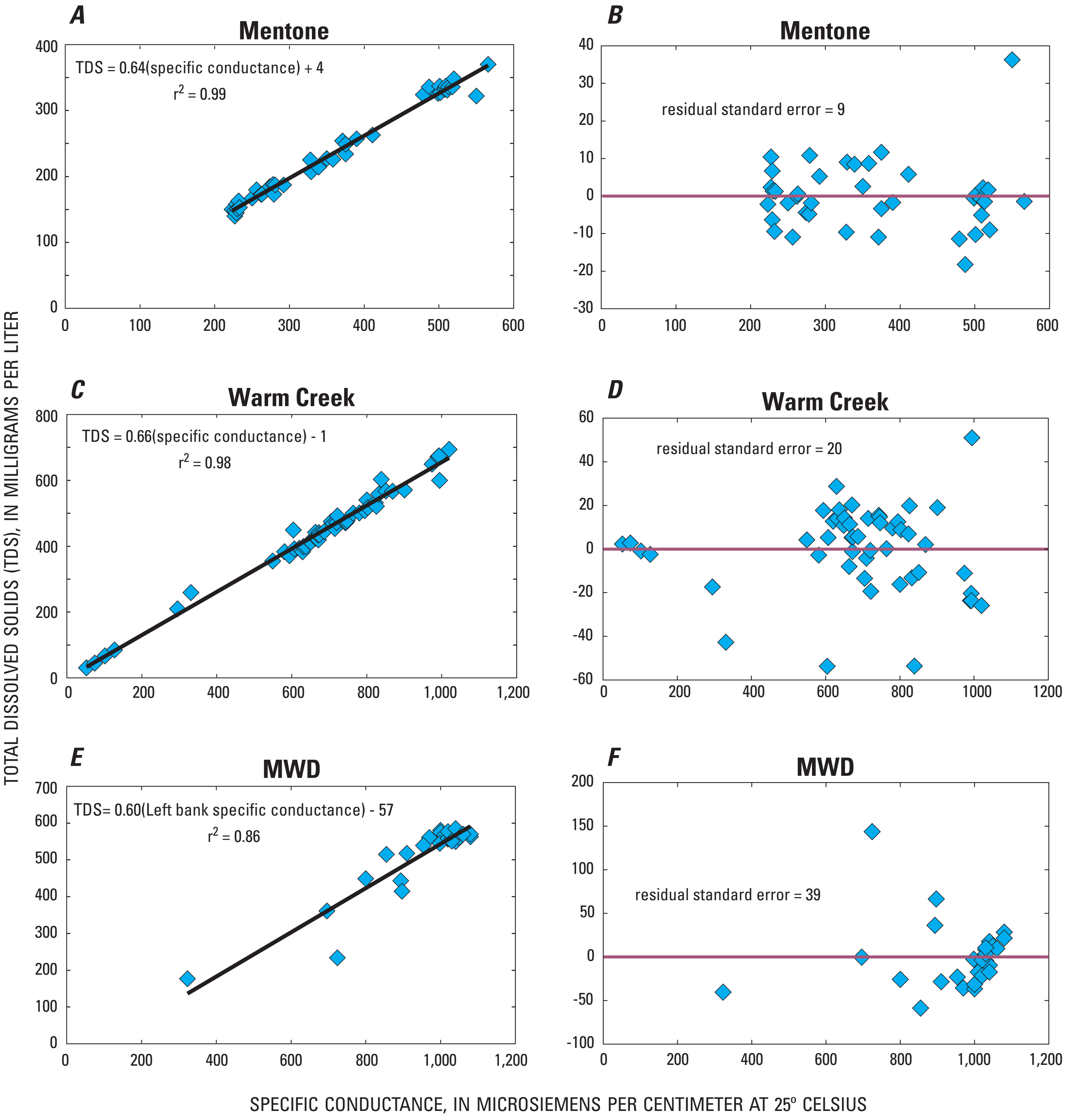


Figure 4. Regression and residual plots of total dissolved solids versus specific conductance at the six fixed sites, Santa Ana Basin, California.

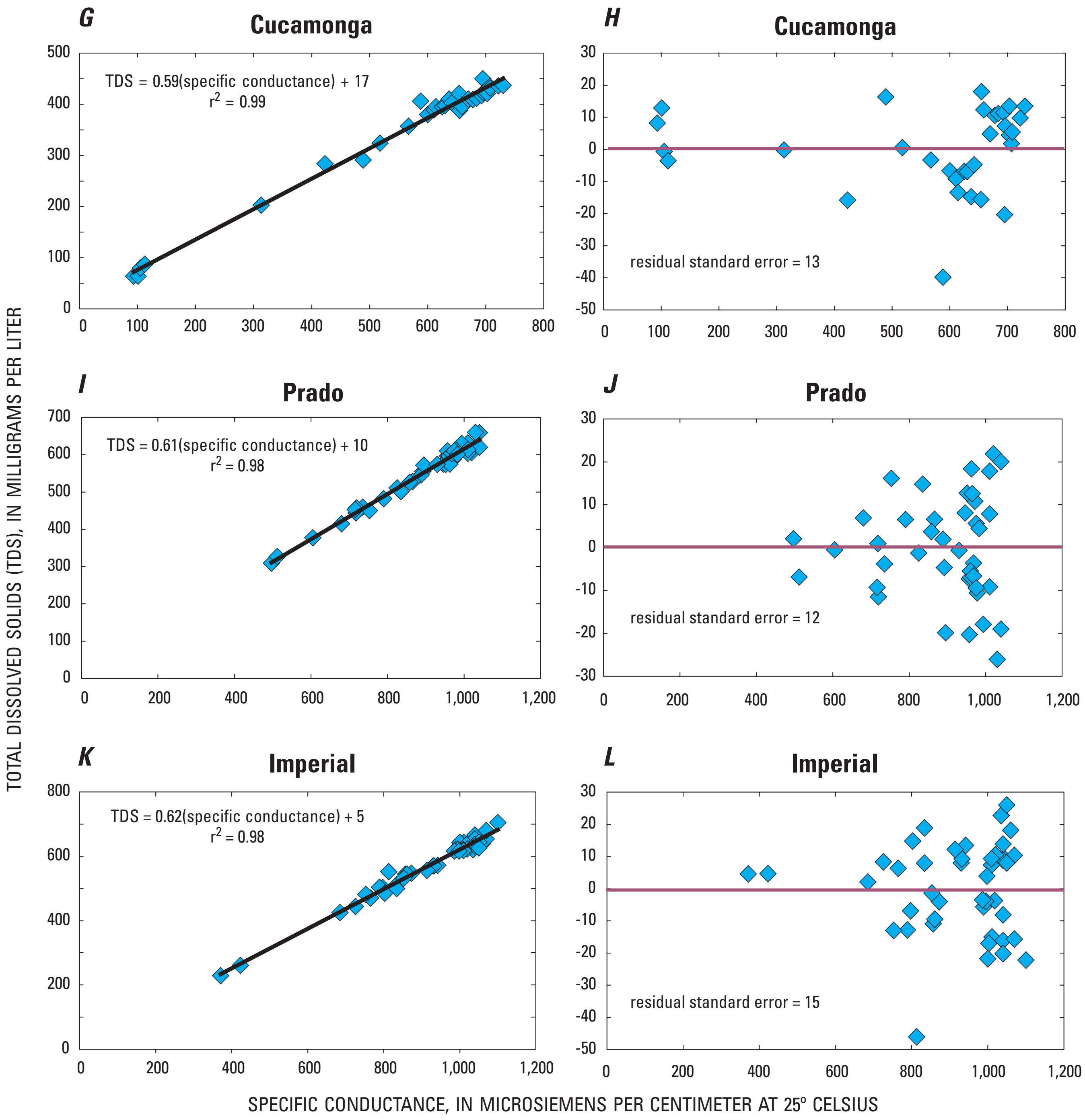


Figure 4.—Continued.

An important source of water in the Santa Ana Basin is stormflow, defined as stream discharge added to base flow during and temporarily after a rainfall event. It includes surface and subsurface runoff. The source of the water could be either precipitation from the storm or water that existed in the catchment prior to the storm. The stormflow end-member was evaluated by hydrograph separation at three sites: Warm Creek, MWD, and Cucamonga Creek. The hydrograph-separation technique was not applied to the other three fixed sites; controlled water releases at Prado Dam complicated attempts to perform hydrograph separations at the Prado and Imperial Highway sites. The continuous record for discharge at the Mentone site is complicated because it is created from the record of a combination of gages. In addition, the continuous monitor for specific conductance at the Mentone site was moved from one gage to another, and its record was difficult to relate to the record of discharge.

Separation of the hydrograph into base-flow and stormflow components was based primarily on the continuous record of discharge (Anderson and others, 2001; Rockwell and others, 2000), and secondarily on the continuous record of specific conductance. For each measurable rainfall event, discharge and TDS (calculated from specific conductance) values were determined for base-flow conditions before and after the event. Base-flow discharge (Q_b) during the storm was then estimated as a linear function of the discharge observed before and after the event:

$$Q_b = Q_{b(i)} + [(Q_{b(f)} - Q_{b(i)})(t - t_i)/(t_f - t_i)], \quad (1)$$

where

t	is time for which base-flow discharge is calculated (for $t_i < t < t_f$)
t_i	is initial time
t_f	is final time
$Q_{b(i)}$	is initial base-flow discharge at storm onset
$Q_{b(f)}$	is final base-flow discharge at storm onset

Stormflow discharge (Q_s) was estimated as the difference between the observed total discharge (Q_t) and the estimated base-flow discharge:

$$Q_s = Q_t - Q_b, \quad (2)$$

With the base-flow and stormflow discharge components estimated, an average TDS concentration for the stormflow can be evaluated from the load of TDS contributed by the stormflow. The stormflow load (Ls) can be obtained by subtracting the base-flow load (L_b) from the total load (L_t). The total load of TDS is a function of the observed discharge (Q_t) and the observed TDS concentration (C_t):

$$L_t = Q_t C_t \quad (3)$$

The dissolved-solids concentration is obtained from the continuous record of specific conductance converted to TDS concentration by the least-squares regression equation developed for each site. The base-flow load, (L_b), is a function of the base-flow discharge (Q_b) and the base-flow concentration (C_b):

$$L_b = Q_b C_b \quad (4)$$

The base-flow concentration is assumed to vary linearly from its pre-storm value to its post-storm value:

$$C_b = C_{b(i)} + [(C_{b(f)} - C_{b(i)})(t - t_i)/(t_f - t_i)], \quad (5)$$

where

$C_{b(i)}$	is initial base-flow TDS concentration at storm onset
$C_{b(f)}$	is final base-flow TDS concentration at storm end

With the total and base-flow loads calculated, the stormflow load (L_s) and the stormflow concentration of dissolved solids (C_s) can be calculated:

$$L_s = L_t - L_b, \text{ and} \quad (6)$$

$$C_s = L_s / Q_s . \quad (7)$$

Finally, the flow-weighted average stormflow TDS concentration (FWA) was calculated as:

$$FWA = \sum_{t_i}^{t_f} L_s / \sum_{t_i}^{t_f} Q_s \quad (8)$$

The point at which discharge began to increase was chosen as t_i, and t_f was chosen as the time when discharge began to level off on the recession limb of the hydrograph. As an example, the analysis of stormflow arriving at Warm Creek on March 15, 1999 is illustrated in figure 5. Figure 5*A* shows an increase in discharge from 8.2 to 49 cubic feet per second within a time span of 15 minutes; ti was chosen at 12:15. The concentration of TDS in the stream (Ct) can be seen to decrease rapidly as a result of the relatively low TDS concentration in the stormflow, the dominant source of water during most of the event. After the initial rapid decrease, C_t levels off. Observed discharge (Qt) returned to about 110 percent of discharge prior to the event, and was leveling off at 17:30. Therefore, this time was chosen for t_f. The flow-weighted average TDS concentration (fig. 5*C*) calculated for the event illustrated by this example is 220 mg/L.

In the analyses of some storms, the final base-flow discharge, $Q_{b(f)}$, was about equal to the initial value, $Q_{b(i)}$. In other cases it was about double the initial value. In general, the choice of t_f could vary by one to three hours. However, the calculated flow-weighted average TDS concentration was generally insensitive to changes of one to three hours in the selected value of t_f; changes of one to three hours in t_f generally resulted in changes to the calculated TDS of 0 to 5 percent. This lack of sensitivity to the selection of t_f is because the volume of stormflow near the end of an event is very small compared to the volume of water during peak flows.

The level-off point on the recession limb was chosen for t_f because, after this, flows were just as likely to increase as they were to decrease at the sites where these analyses were performed. This is especially true for Cucamonga Creek where wastewater discharges are variable and cause frequent hydrograph spikes that are unrelated to stormflow.

Nutrient concentrations associated with stormflow were also evaluated with the aid of hydrograph separation. For each of the discrete stormflow samples collected at the three sites—Warm Creek, MWD, and Cucamonga Creek—the proportion of stormflow at the time of sample collection was estimated using the described hydrograph separation technique. Discrete samples collected at a time when stormflow was equal to or exceeded 75 percent of the total observed streamflow were assumed to be representative of stormflow. This proportion was chosen because it is intermediate of samples consisting entirely of stormflow and samples consisting of equal parts stormflow and base flow.

QUALITY CONTROL

Two kinds of quality-control (QC) samples, blanks and replicates, were collected at frequencies determined by NAWQA guidelines (Mueller and others, 1997). Blank samples are collected and processed using specially prepared analyte-free water to identify potential sources of contamination in the sampling process that could lead to a positive bias in the data. Replicates are two or more samples collected and processed so that the samples are as identical in composition as possible in order to provide a measure of data variability introduced during sample collection, processing, and analysis.

Twenty-two equipment and field blank samples were collected for nutrients and constituents of TDS during the high-intensity phase (HIP) of data collection. Eight of these were collected through automatic samplers. Automatic samplers were used for routine samples only at the Prado site, and for storm samples at the Prado, Warm Creek, and Cucamonga Creek sites. Seventeen replicate samples were collected during this study; two of these were collected using automatic samplers.

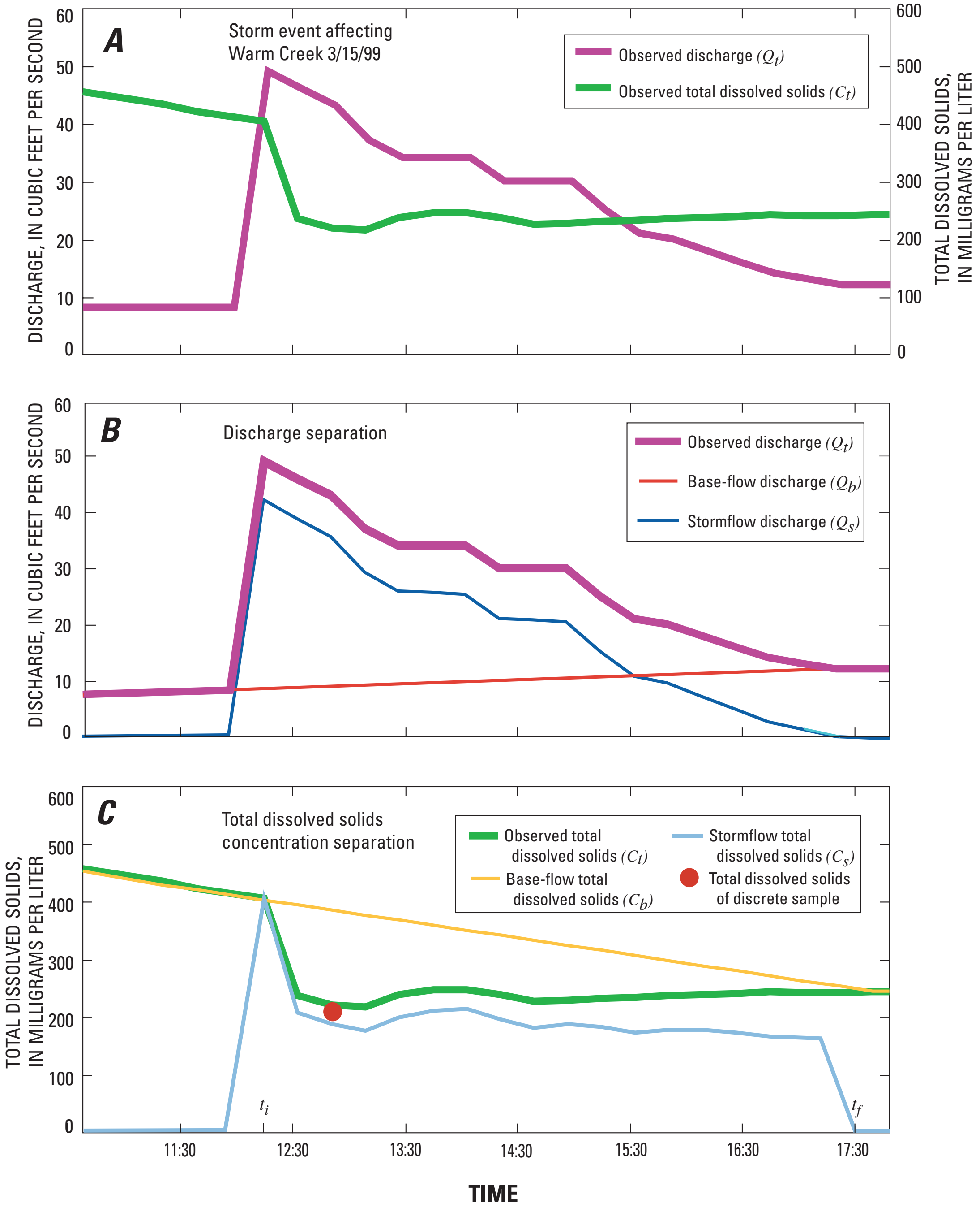


Figure 5. One result of the hydrograph-separation technique to isolate concentrations of total dissolved solids in stormflow, Santa Ana Basin, California.

In addition to quality-control measures performed by the study unit, the USGS operates an independent, external, quality-assurance project called the Inorganic Blind Sample Project (IBSP) to monitor and evaluate the quality of laboratory analytical results through the use of double-blind QC samples. Results from the project can be used to estimate the extent that laboratory errors contribute to overall errors in environmental data (Ludtke and Woodworth, 1997).

Field measurements of water temperature, dissolved oxygen, pH, specific conductance and alkalinity were performed on-site at the time of each sample collection. All USGS field personnel who perform water-sample measurements of specific conductance, alkalinity, and pH are required to demonstrate their proficiency in making these measurements by participating in the USGS National Field Quality Assurance Program (Stanley and others, 1998)

MAJOR-ION ANALYSES

Major-ion analyses for fixed and mountain sites are plotted on trilinear diagrams known as Piper plots (Piper, 1944) in figure 6. The plot shows that the variation of ionic composition at one particular site is generally smaller than between sites, indicating that water sources or instream processes are distinct and characteristic for each site. The ionic composition of the alpine indicator site—South Fork—was dominated by calcium bicarbonate, as were the sites fronting the San Gabriel Mountains: Cucamonga Creek near Upland and Day Creek. The mountain sites fronting the San Bernardino Mountains—Cajon Creek and Devil Canyon Creek—were dominated by calcium bicarbonate, with more chloride, sulfate, and magnesium than the other mountain sites. The other San Bernardino Mountains site, East Twin Creek, was dominated by a sodium/potassium sulfate composition.

The ionic composition of the urban indicator site—Warm Creek—appears to be intermediate to the compositions of the upgradient mountain sites: Cajon Creek, Devil Canyon Creek, and East Twin Creek. Even though surface water from these sites does not currently flow to Warm Creek, these streams have historically recharged the ground-water system. Discharge at Warm Creek is partially provided by rising ground water and, therefore, part of the ionic composition of water in Warm Creek is representative of the rising ground water. High variability in ionic composition of base flow at Warm Creek may reflect varying proportions of rising ground water and urban runoff in the samples.

The ionic compositions of samples from the Santa Ana River sites below Prado Dam and near Imperial Highway are similar to each other. These sites are integrators of water from the upper basin, and their composition is consistent with a mixture of the fixed sites sampled upstream: Warm Creek, MWD, and Cucamonga Creek (fig. 6). Although there are additional sources of water to these integrator sites, such as Chino Creek, rising ground water and additional wastewater treatment plant outfalls, either the compositions of the additional water sources are similar to those of the fixed sites sampled upstream or the contributions of these additional sources are small.

The ionic composition of samples collected from the sites located near Mentone was highly variable (fig. 7). The first six samples were collected at the main gage (site 11051499) (fig. 2), and are collectively referred to as “samples unaffected by dam construction.” TDS was low in these samples, and their composition on a trilinear plot was similar to that of the alpine indicator site (South Fork). After March 1999, construction of the Seven Oaks Dam stopped flow to this site and, as a result, samples were collected at three alternate sites. Water routed to these alternate sites passes through sand and rock that had been disturbed by dam construction. Water samples influenced by these disturbed materials were higher in dissolved solids and had a different ionic composition than the six samples collected at the initial site (fig. 7). Therefore, Mentone samples collected between April 1999 and September 2001 are collectively referred to as “samples affected by dam construction.” The samples affected by dam construction often had a composition tending toward that of samples from the East Twin Creek site Northwest of Mentone (fig. 6).

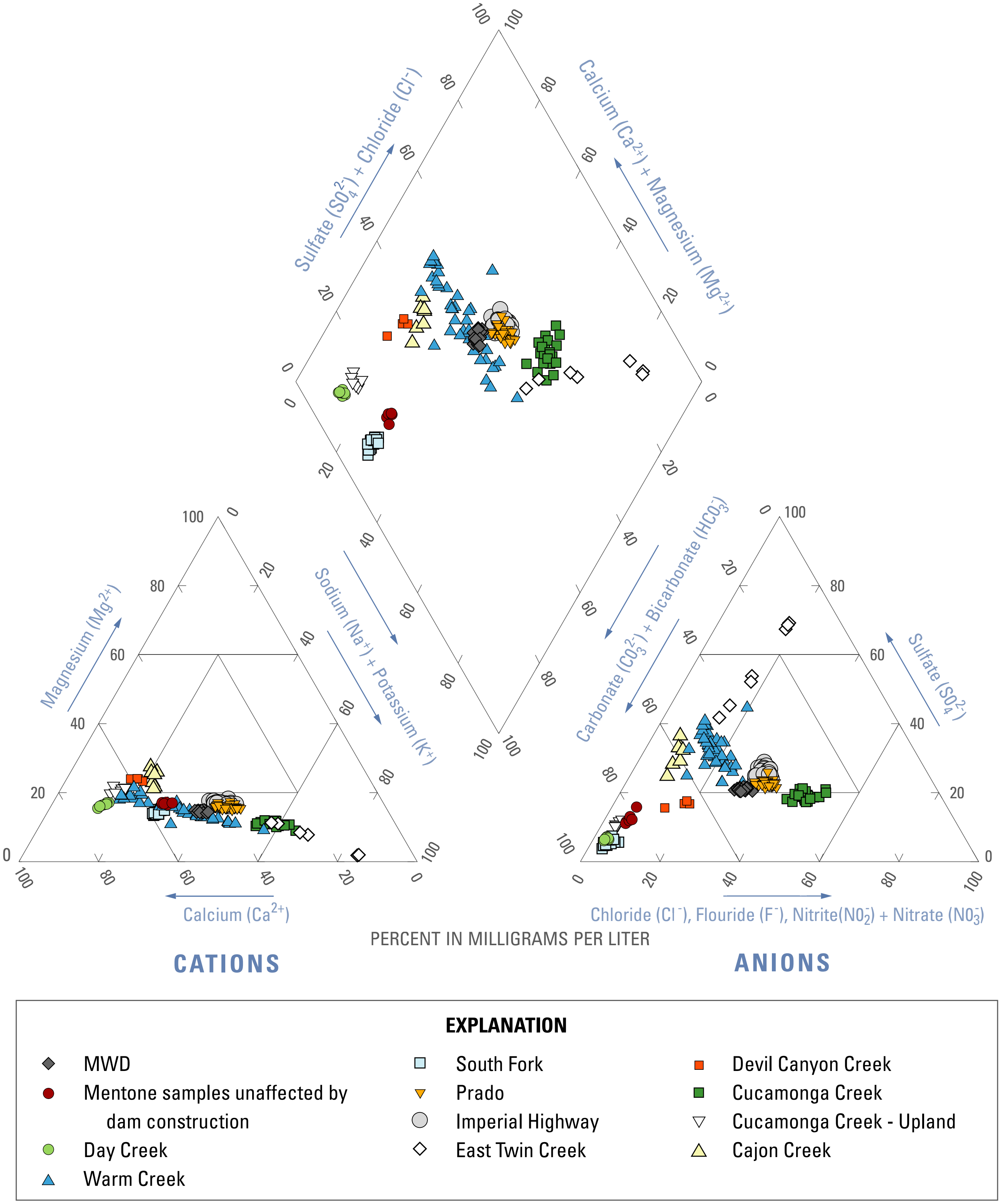


Figure 6. Base-flow water composition at fixed and mountain sites, Santa Ana Basin, California.

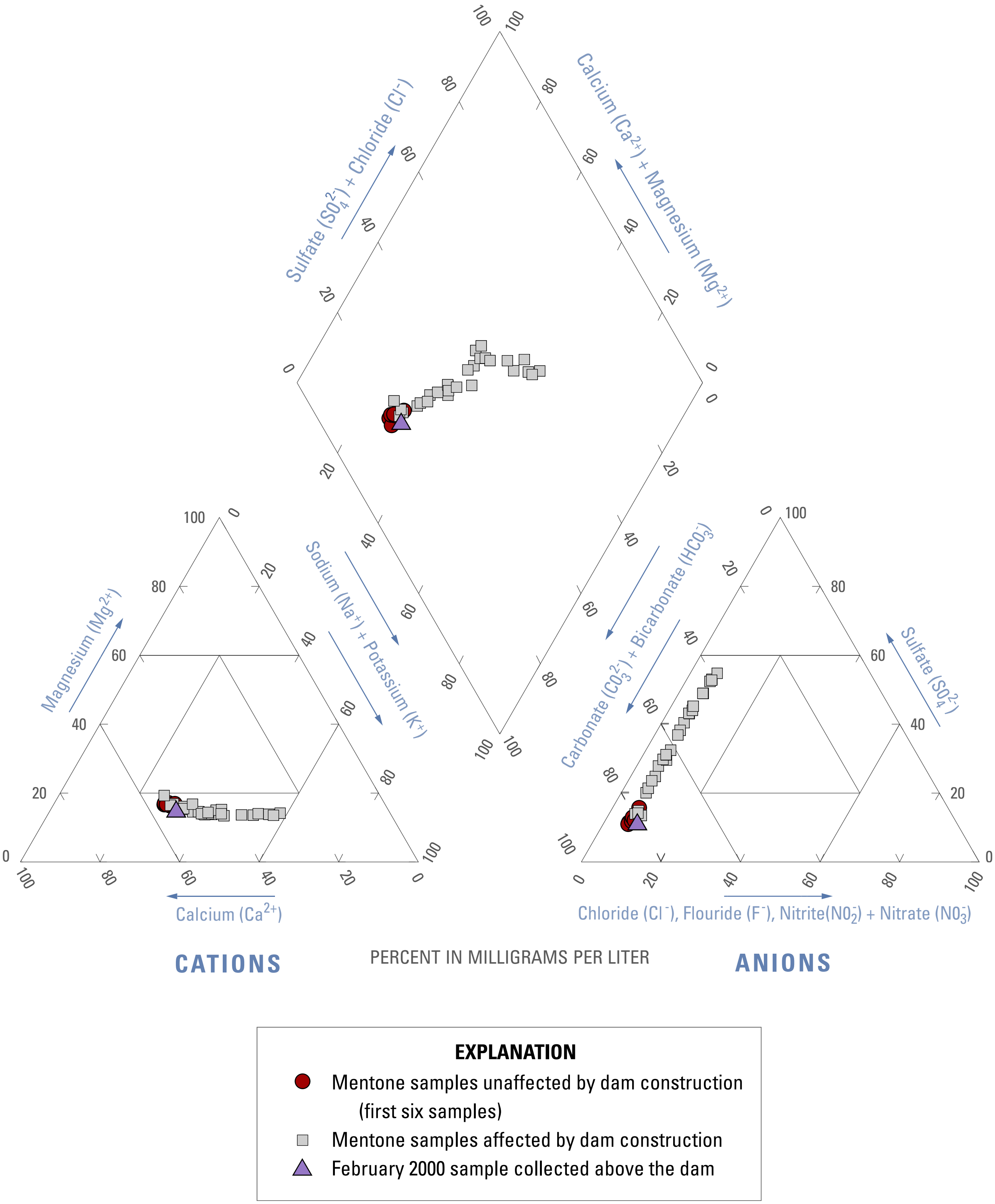


Figure 7. Base-flow water composition at the various sampling locations at the Mentone site, Santa Ana Basin, California.

In February 2000, a sample was collected upstream and beyond the influence of the dam construction. This sample was low in TDS and its ionic composition resembled that of the first six samples collected at the main gage (fig. 7). Additional measurements of specific conductance and analyses for selected anions made from October 2001 to April 2003 at this site above the dam are similar in value to those of the early Mentone samples. It appears that the initial six samples, along with the one collected above the dam, are most representative of water quality of mountain run-off at Mentone.

TOTAL DISSOLVED SOLIDS

Total Dissolved Solids and Concentrations of Some Individual Constituents Compared with Water-Quality Criteria

The USEPA has established water-quality criteria consisting of secondary maximum contaminant levels (MCLs) for total dissolved solids in drinking water, as well as for some individual dissolved constituents such as chloride, sulfate, fluoride, and manganese. The secondary MCL for TDS (500 mg/L) was exceeded in most of the base-flow samples from the valley-floor sites (fig. 8). Base-flow TDS concentrations at these sites were usually lower than the water-quality objectives (550 to 700 mg/L) set by the California Regional Water Quality Control Board [RWQCB](1995). Although municipal and domestic supply is not a designated beneficial use for the Santa Ana River (California Regional Water Quality Control Board, 1995), most of the river flow is used for aquifer recharge just downstream from the Imperial Highway site. The replenished aquifers are pumped as the primary water supply for about 2 million people (Orange County Water District, 1996). TDS in samples from mountain sites was generally less than the secondary MCL and the water-quality objectives for these sites (200 to 475 mg/L). However, TDS in samples from two mountain sites—East Twin Creek and Cajon Creek—often exceeded both the secondary MCL and water-quality objective levels (fig. 9).

The secondary MCL for chloride (250 mg/L) was not exceeded in water samples collected for this study. The secondary MCL for sulfate (also 250 mg/L) was exceeded at one site, East Twin Creek, in three of the seven samples collected there. Fluoride concentrations in samples from the East Twin Creek also exceeded the secondary MCL (2 mg/L) in six of the seven samples, and exceeded the primary MCL (4 mg/L) in four of these. The fluoride secondary MCL (2 mg/L) was also exceeded in 12 of the 50 samples (including storm samples) collected at Warm Creek. Prior to the construction of diversions that presently intercept flow from most mountain streams in the basin, East Twin Creek surface flows may have fed Warm Creek. The observation that East Twin Creek and Warm Creek streamflow presently share high fluoride concentrations provides additional evidence that basin ground water is a substantial source to Warm Creek.

Manganese concentrations exceeded the secondary MCL (0.05 mg/L) in most (30 of 41) samples collected from the Santa Ana River below Prado Dam. Manganese is considered a trace element because it is generally found in water at concentrations less than 1.0 mg/L. Therefore, manganese rarely contributes significantly to TDS concentrations in streams, even when it occurs at high concentrations. Manganese concentrations were mostly below 0.01 mg/L in samples collected for this study; however, it ranged from 0.02 to 0.35 mg/L in samples collected from the site below Prado Dam. The presence of manganese at concentrations exceeding the secondary MCL below the Prado Dam is probably a result of chemical reduction due to anaerobic conditions in the wetlands upstream from this site. Manganese is found in wetlands primarily in its reduced (manganous) form, which is more soluble than its oxidized (manganic) form (Mitsch and Gosselink, 1993). Three samples collected from the Santa Ana River below Imperial Highway also had manganese concentrations that exceeded the secondary MCL. This site is located 11 mi downstream from the site below Prado Dam. Samples were also collected from the Prado site on each of the days when the samples having unusually high manganese concentrations were collected from the Imperial Highway site. In each case, the sample collected from the Prado site had a higher manganese concentration than the sample collected from the Imperial Highway site. Therefore, it seems likely that the high manganese concentrations produced in the Prado Wetlands are occasionally carried downstream to the Imperial Highway site. Two samples collected from Cucamonga Creek, and one sample collected from Warm Creek also had manganese concentrations that slightly exceeded the secondary MCL. All three samples were collected under stormflow conditions.

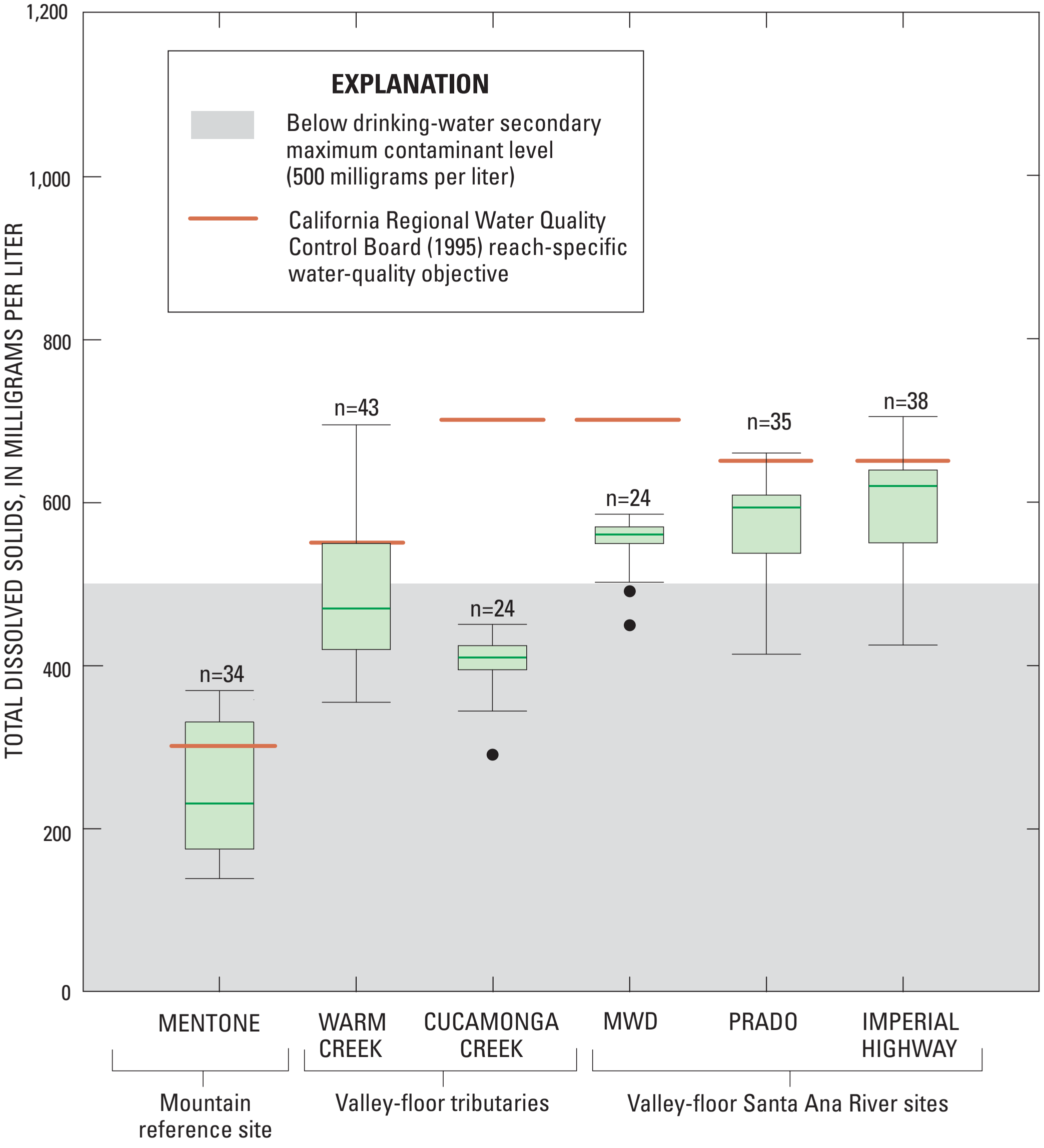


Figure 8. Base-flow total dissolved solids concentrations at fixed sites, Santa Ana Basin, California.

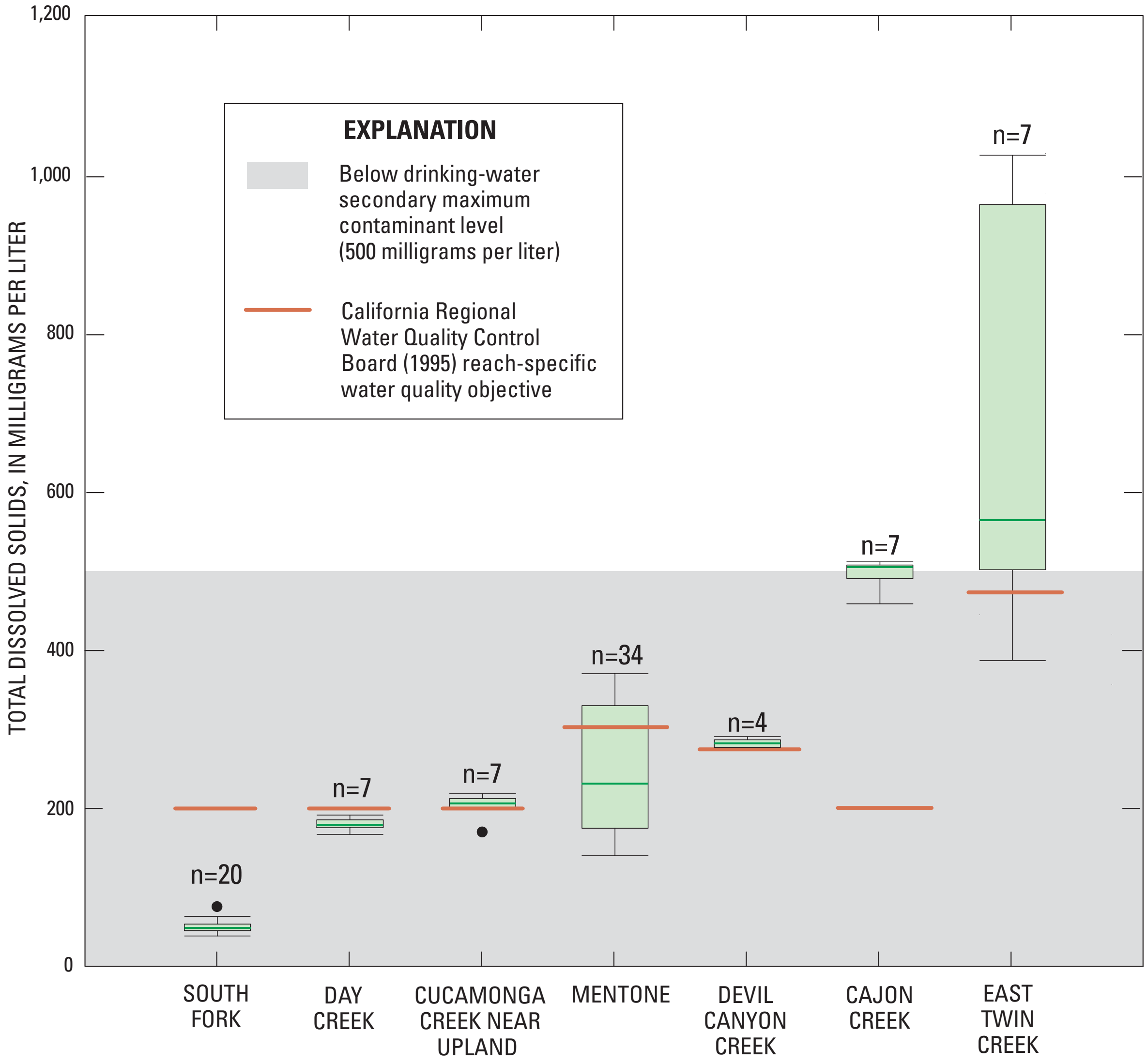


Figure 9. Base-flow total dissolved solids concentrations at mountain sites, Santa Ana Basin, California.

Base-Flow Total Dissolved Solids Concentration by Water Source

Of all the water sources sampled, mountain sites generally had the lowest TDS, with medians at most sites ranging from about 50 to about 300 mg/L (fig. 9). The Mentone site appears to be a good representative of reference conditions for water entering the basin, with a median TDS of 230 mg/L. That value is somewhat lower than the median at Devil Canyon Creek of 280 mg/L, but somewhat higher than the medians at the two sites in the San Gabriel Mountains: 180 mg/L at Day Creek and 200 mg/L at Cucamonga Creek near Upland. The alpine indicator site, South Fork of the Santa Ana River, had TDS concentrations of about 50 mg/L, which seem too low to represent reference conditions for water entering the basin. Two mountain sites (East Twin Creek and Cajon Creek) had high TDS: East Twin Creek receives drainage from the San Bernardino Mountains and had a median TDS of 560 mg/L; Cajon Creek receives drainage from both the San Bernardino Mountains and the San Gabriel Mountains and had a median TDS just over 500 mg/L. These concentrations are comparable to the highest levels found in samples collected from the valley floor.

Streams on the valley floor had median TDS ranging from about 400 to 600 mg/L (fig. 8), and generally increasing downstream (with decreasing reach number) along the main stem of the river. Median concentrations at the two tributary fixed sites, Warm Creek (tributary to Reach 5 of the Santa Ana River) and Cucamonga Creek (tributary to Reach 3), were 470 and 410 mg/L respectively. MWD, in Reach 3, had a median TDS of 560 mg/L. At the next integrator site, Prado Dam at the upstream terminus of Reach 2, the median TDS was 600 mg/L. About 11 mi downstream at the downstream terminus of Reach 2, the site below Imperial Highway had a median concentration of 620 mg/L.

The downstream increase in TDS appears to be independent of water source. Base-flow sources to Warm Creek are a mix of rising ground water and urban runoff, whereas base flow in Cucamonga Creek is usually about 90 percent treated wastewater with a small urban runoff component. Base flow at MWD in Reach 3 is about 70 percent wastewater (Mendez and Belitz, 2002), with rising ground water making up most of the balance. Base flow at Prado and Imperial Highway is predominantly wastewater.

Total dissolved solids in urban runoff range from about 250 to 370 mg/L, on the basis of sparse data (table 2). This is somewhat lower than concentrations observed at sites receiving treated wastewater, and closely approximates TDS in water delivered for domestic use in the Santa Ana Basin (City of Redlands, 2002; Metropolitan Water District of Southern California, 2002; Western Municipal Water District, 2002; San Bernardino Valley Municipal Water District, 2002). Some of the highest TDS in the basin may occur at sites on the valley floor that are dominated by rising ground water. However, this observation is based on just a few synoptic study samples collected from three valley-floor sites near MWD that are dominated by rising ground water. Total dissolved solids were 600 mg/L in two samples collected from the Sunnyslope channel in August 2000 (table 3). Samples collected in May 2001 from two other sites dominated by rising ground water—Tesuesquito Creek and Hole Lake—were not analyzed for dissolved solids. However, the specific conductance of samples from these sites was among the highest observed in this study, ranging from 1,230 to 1,550 µS/cm and indicating that TDS concentrations were likely also high.

Total Dissolved Solids in Stormflow

Stormflow is an important source of water to streams in the Santa Ana Basin, and it usually dilutes stream TDS. As a result, total dissolved solids in urban stormflow were generally low in comparison with urban runoff. During the period of this study, between six and eight samples were collected during storm events at each of the fixed sites. The median TDS in discrete samples collected under stormflow conditions was 260 mg/L. In addition to analyses of discrete stormflow samples, hydrograph separation was used to estimate TDS in the stormflow end-member at three sites: Warm Creek, MWD, and Cucamonga Creek. During the period of this study, 87 discrete storm events were identified in the study area from records of rainfall (U.S. Army Corps of Engineers, 2002) and stream discharge (Anderson and others, 2001; Rockwell and others, 2000). Each event affected one or more of the three evaluated sites.

Table 2. Nitrite+nitrate (mg/L as N) and total dissolved solids (mg/L) concentrations in samples consisting predominantly of urban runoff, Santa Ana Basin, California

[mg/L, milligrams per liter; <, less than indicated value; N, nitrogen; NO_2^-, nitrite; NO_3^-, nitrate; TDS, total dissolved solids; —, no data]

Site	Sample purpose[1]	Date	Time	$NO_2^-+NO_3^-$ (mg/L)	TDS (mg/L)
Cucamonga Creek below Hwy. 60	1	03/10/99	15:30	0.02	—
Cucamonga Creek below Hwy. 60	1	04/15/99	16:30	.16	—
Cucamonga Creek below Hwy. 60	1	05/19/99	16:10	.34	—
Cucamonga Creek Main Channel	2	08/09/00	12:30	.61	330
Cucamonga Creek Main Channel	3	08/15/01	22:20	3.78	—
Cucamonga Creek Main Channel	3	08/16/01	13:45	.54	—
Warm Creek near San Bernardino	4	06/13/02	09:30	.10	369
Warm Creek near San Bernardino	4	08/15/02	09:00	<.05	[2]316
Warm Creek near San Bernardino	4	10/16/02	11:00	.48	[2]315
Warm Creek near San Bernardino	4	12/02/02	09:00	.50	[2]333
Warm Creek near San Bernardino	4	01/16/03	09:00	.47	[2]353
Warm Creek near San Bernardino	4	03/13/03	09:00	.07	[2]334
Warm Creek near San Bernardino	4	06/12/03	09:00	.49	[2]352
Warm Creek near San Bernardino	4	08/14/03	09:00	.06	[2]265

[1] Sample purpose refers to topical study for which sample was collected: (1) dissolved organic carbon characterization study, (2) Urban Land Use Gradient study (Burton and Brown, 2001), (3) Algal assimilation study (Kent and Burton, 2001), and (4) Low-Intensity-Phase of data collection for the Santa Ana Basin Study Unit of the National Water-Quality Assessment Program (samples collected subsequent to report study period).

[2] Total dissolved solids (TDS) calculated from specific conductance (r^2=0.98)

Table 3. Nitrite+nitrate (mg/L as N) and total dissolved solids (mg/L) concentrations in samples consisting predominantly of rising ground water, Santa Ana Basin, California

[[mg/L, milligrams per liter; N, nitrogen; NO_2^-, nitrite; NO_3^-, nitrate; TDS, total dissolved solids]

Site	Sample purpose[1]	Date	Time	$NO_2^-+NO_3^-$ (mg/L)	TDS (mg/L)
Sunnyslope Channel	2	08/17/00	11:00	10.4	604
Sunnyslope Channel	2	08/17/00	14:10	10.5	605
Sunnyslope Channel	5	05/22/01	05:00	11.0	—
Tequesquito Channel	5	05/22/01	04:50	14.0	—
Hole Lake	5	05/23/01	00:10	16.5	—

[1] Sample purpose refers to topical study for which sample was collected: (2) Urban Land Use Gradient study (Burton and Brown, 2001),and (5) Dye-tracer study (Mendez and Belitz, 2002).

Eighty of the identified events affected Warm Creek. Rainfall events affecting Warm Creek typically measured from 0.05 to 0.40 in. (fig. 10*A*) and typically lasted from 4 to 12 hours (fig. 10*B*). The peak discharges resulting from these events typically exceeded pre-storm base flow by a factor of from 8 to 50 (fig. 11*A*), and receding discharges typically were leveling off ($Q_{b(f)}$) within 5 to 13 hours after the arrival of stormflow to the site (fig. 11*B*).

During this study, fewer rainfall events affected MWD and Cucamonga Creek. One reason for this is that the period for which hydrograph separation was performed coincided with the period of sample collection for each site; samples were collected from MWD and Cucamonga Creek during only two years, compared to three years for Warm Creek. Also, MWD and Cucamonga Creek receive higher base-flow discharges than Warm Creek due to inputs of treated wastewater, and they have larger contributing drainage areas. These factors probably diminished streamflow response to small rainfall events at these sites.

Twenty-three rainfall events affected MWD, typically measuring from 0.25 to 0.50 in. (fig. 10*A*) and lasting from 9 to 23 hours (fig. 10*B*). The peak stormflow discharges at MWD typically exceeded pre-storm base flow by a factor of from 3 to 8 (fig. 11*A*), and receding discharges typically leveled off 11 to 18 hours after the onset of stormflow (fig. 11*B*).

Thirty-one rainfall events affected Cucamonga Creek, typically measuring from 0.14 to 0.35 in. (fig. 10*A*) and lasting from 4 to 10 hours (fig. 10*B*). The peak stormflow discharges at Cucamonga Creek typically exceeded pre-storm base flow by a factor of from 9 to 24 (fig. 11*A*), and receding discharges typically leveled off 4 to 9 hours after the onset of stormflow (fig. 11*B*).

Storm events are usually of short duration in the Santa Ana Basin (fig. 10*B*). Stream channels are altered and base flow is sustained by other than natural processes, generally by treated wastewater or urban runoff. Stream response is rapid and also of short duration (fig. 11*B*) in these altered channels. The hydrograph separation technique typically delimited the periods of stormflow so that they were of duration similar to the rainfall events in order to limit analyses to periods during which stormflow was a major source of streamflow.

The median flow-weighted average TDS for stormflow, isolated by hydrograph separation at Warm Creek, MWD, and Cucamonga Creek, was 190 mg/L. This is less than the median of 210 mg/L for discrete samples collected under stormflow conditions at these three sites. However, the isolated stormflow TDS, which were calculated by hydrograph separation, were highly variable. Values were as high as 590 mg/L in stormflow reaching Warm Creek and as low as 35 mg/L in stormflow reaching Cucamonga Creek (fig. 12). Stormflow TDS concentrations are given as flow-weighted averages for each analyzed event.

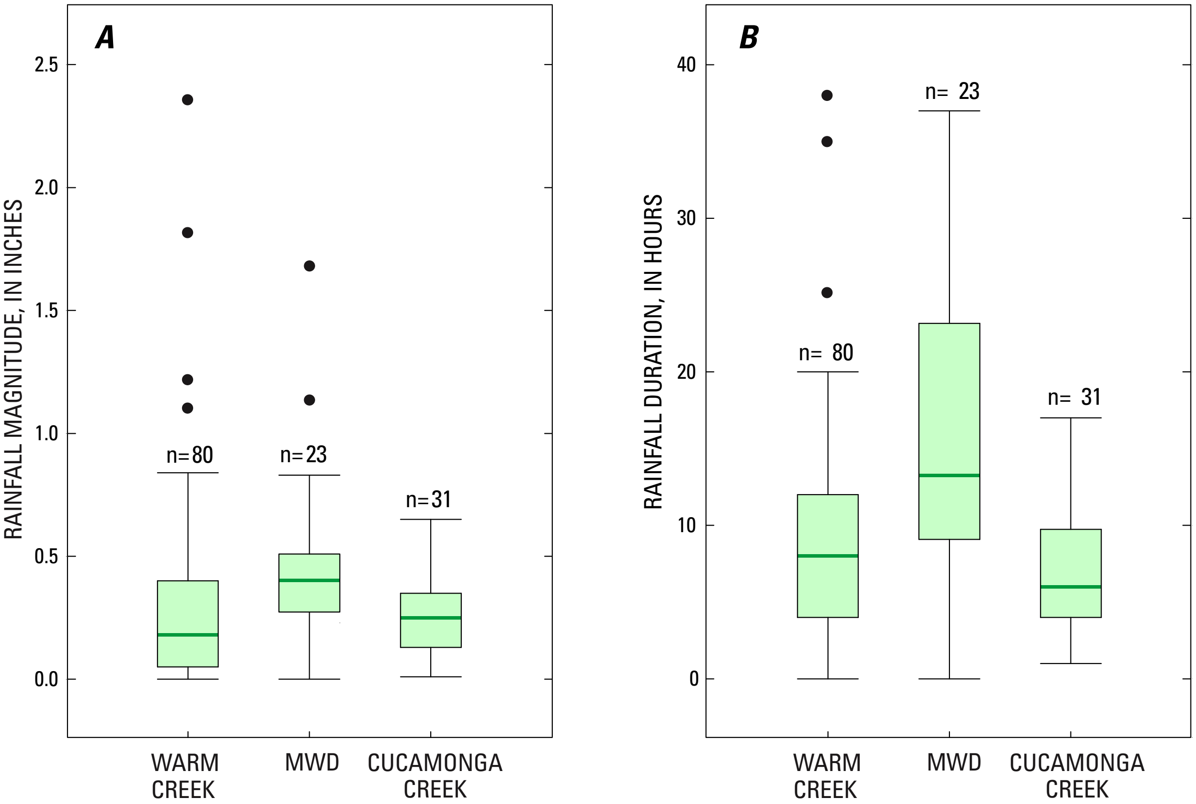


Figure 10. Rainfall magnitude (inches) and duration (hours) for storms analyzed by hydrograph separation, Santa Ana Basin, California.

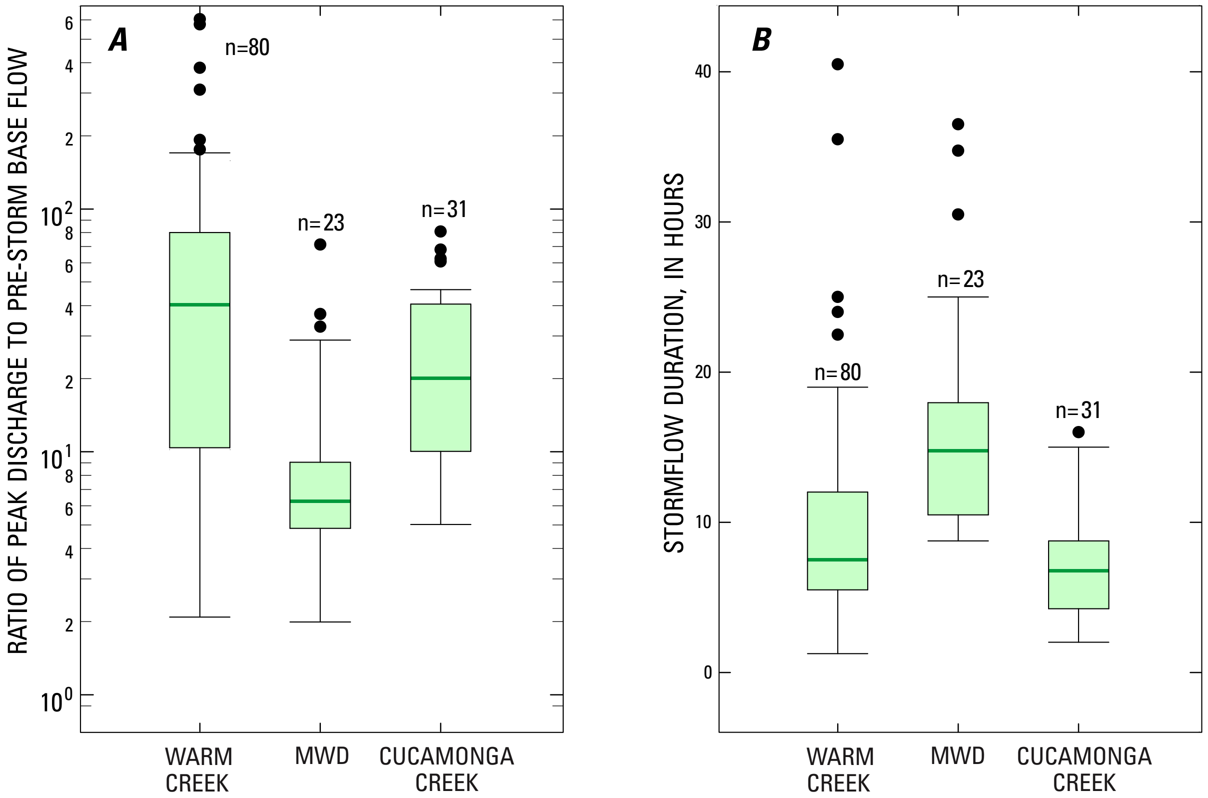


Figure 11. Stormflow magnitude (ratio of peak flow to pre-storm base flow) and duration (hours) for stormflow analyzed by hydrograph separation, Santa Ana Basin, California.

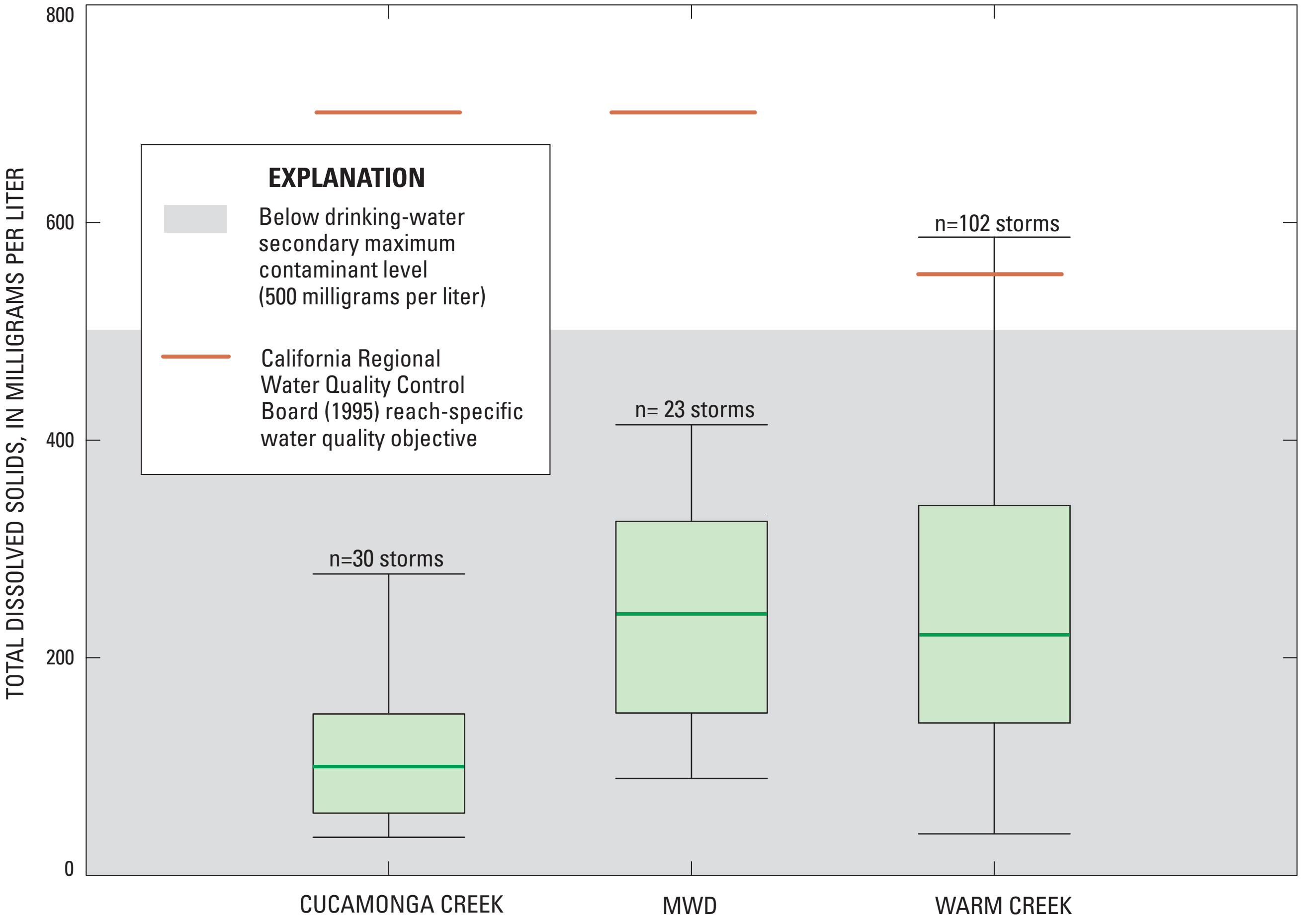


Figure 12. Total dissolved solids concentrations in stormflow (calculated by hydrograph separation) at three urban sites, Santa Ana Basin, California.

To help explain the variability observed over the entire population of storms analyzed by hydrograph separation, the results were divided into two groups: a low-rainfall group having a relatively high median, but variable TDS; and a high-rainfall group having a relatively low median and small variability in TDS (figs. 13, 14, and 15). The line dividing the two groups, or threshold-rainfall-magnitude, was chosen subjectively to minimize the concentration and variability of TDS in the high-magnitude rainfall group and, at the same time, include a substantial portion (greater than 20 percent) of the data in that group. Rainfall measurements were obtained from a U.S. Army Corps of Engineers (2002) website, which records rainfall to a precision of 0.01 inch. The values for the threshold-rainfall-magnitude were rounded to the nearest 0.05 inch.

The threshold rainfall magnitude was estimated at 0.45 in. for Warm Creek and MWD, and at 0.30 in. for Cucamonga Creek. The larger thresholds at Warm Creek and MWD may reflect the influence of ground-water inputs at these two sites. The dilution by rainfall at Warm Creek and MWD probably is offset by the input of high-TDS water stored in the catchment prior to the event as it is moved into the stream by increased potentiometric head in response to the rainfall.

The median flow-weighted average TDS concentrations for storm events when rainfall was less than the rainfall thresholds were 250 mg/L at Warm Creek, 300 mg/L at MWD, and 130 mg/L at Cucamonga Creek. When the rainfall thresholds were exceeded, the median flow-weighted average TDS was 140 mg/L at Warm Creek, 120 mg/L at MWD, and 70 mg/L at Cucamonga Creek. These results suggest that a characteristic TDS for large events is 70 to 140 mg/L, depending on location. These results also suggest that the characteristic TDS for small events is substantially higher. The relatively high TDS associated with low-magnitude events may provide significant annual stream TDS loads if small events collectively contribute significant proportions of the total yearly streamflow. This appears to be the case at Warm Creek, where even a small rainfall event can increase streamflow by one or two orders of magnitude (figs. 10*A*, 11*A*).

Storm samples collected near the beginning of a storm, as material is flushed from the landscape by stormwater runoff, would be expected to have higher TDS concentrations than those of samples collected later in the event. This was evident over the course of one event when two storm samples were collected from Cucamonga Creek. Prior to the storm, stream TDS was approximately 400 mg/L (based on the relation between TDS and continuously monitored specific conductance). The first sample was collected early in the event when, during a 15-minute time interval, discharge increased from 67 to 1,060 ft^3/s. The TDS of this sample was 284 mg/L (analyzed residue-on-evaporation). The second sample, collected 20 minutes later at peak discharge for the event (1,380 ft^3/s), had a TDS of 64 mg/L. The second sample apparently contained a lower concentration of dissolved materials flushed from the landscape, probably as a result of dilution by stormflow.

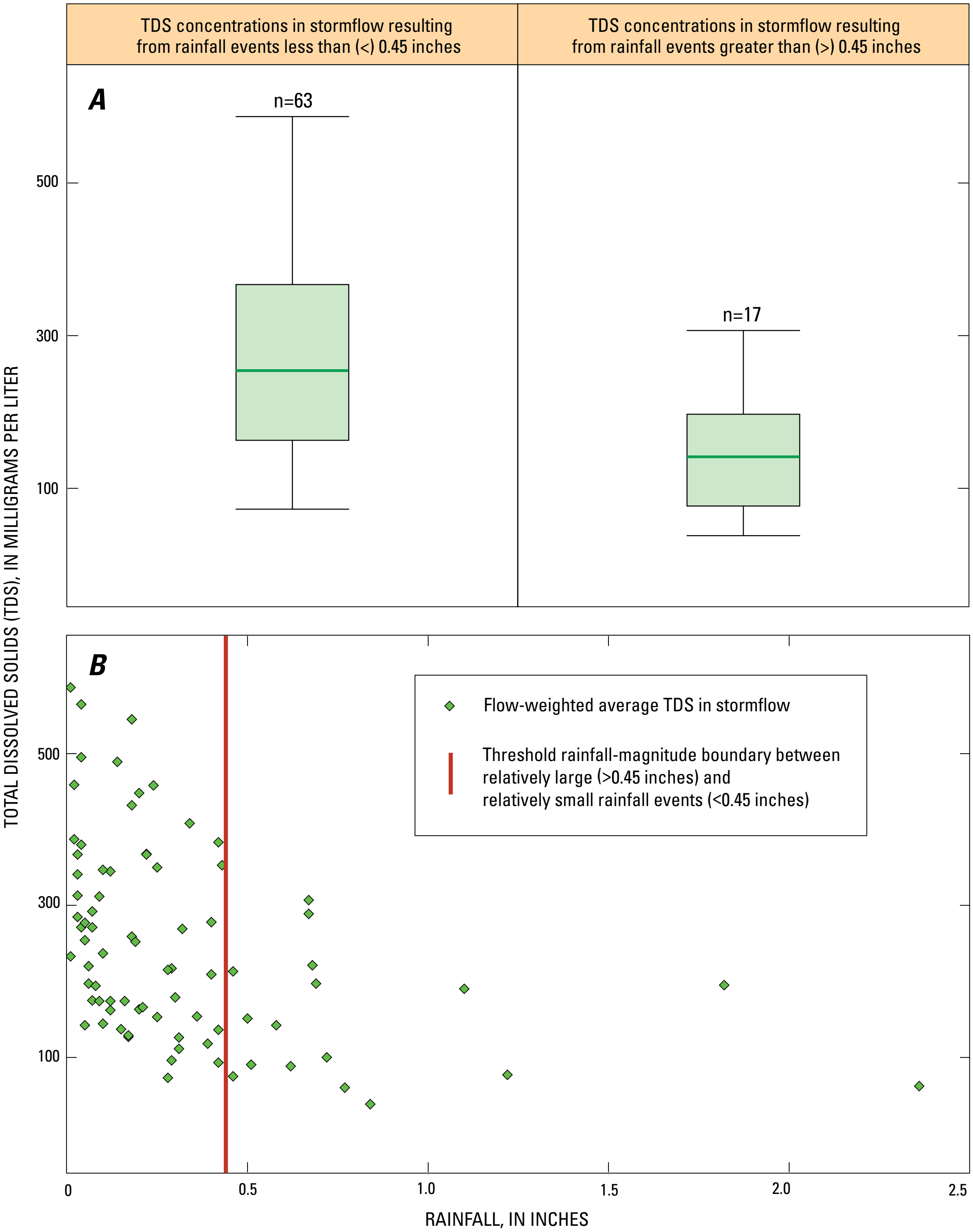


Figure 13. Stormflow concentrations of total dissolved solids (analyzed by hydrograph separation) as a function of rainfall magnitude at Warm Creek, Santa Ana Basin, California.

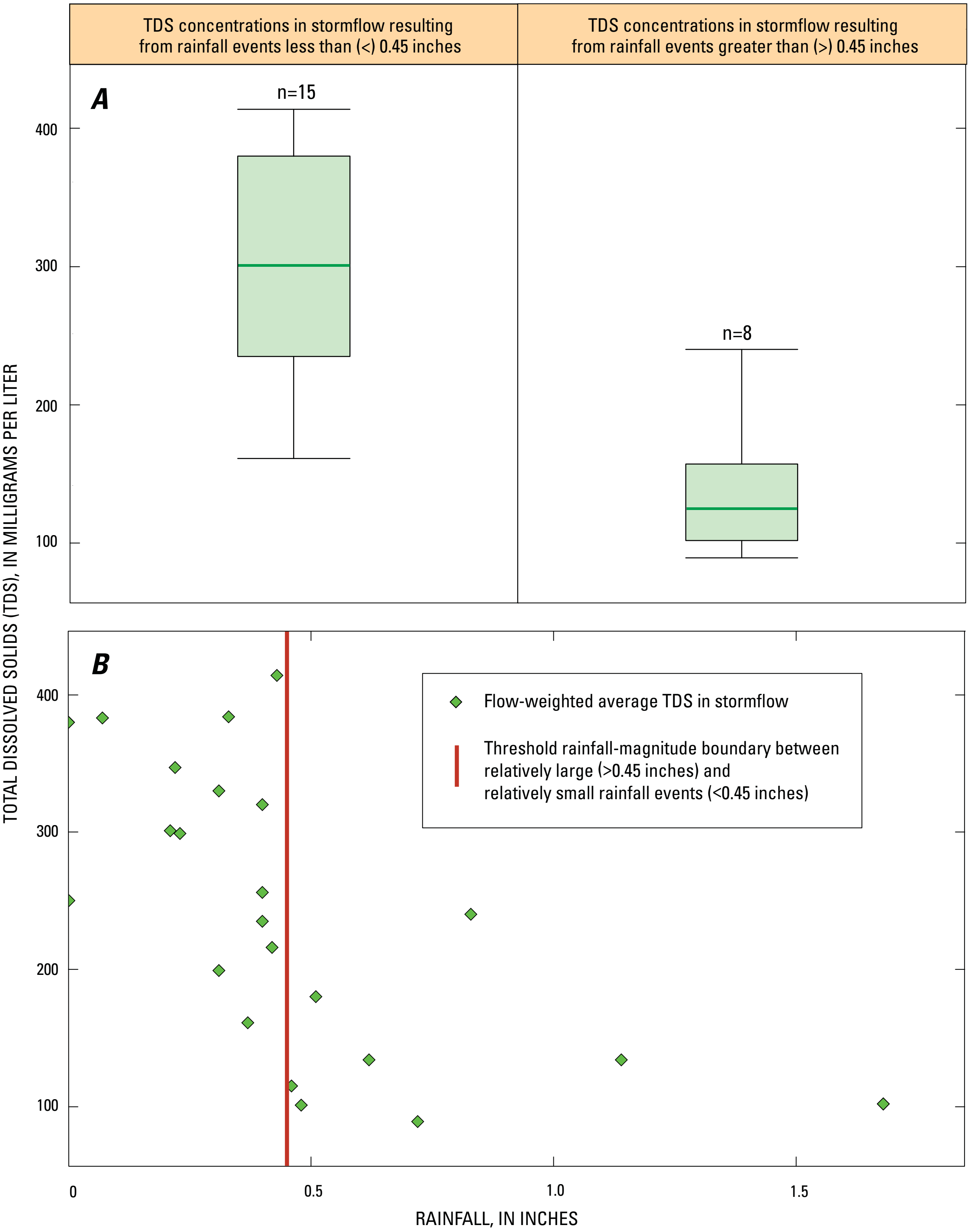


Figure 14. Stormflow concentrations of total dissolved solids (analyzed by hydrograph separation) as a function of rainfall magnitude at MWD, Santa Ana Basin, California.

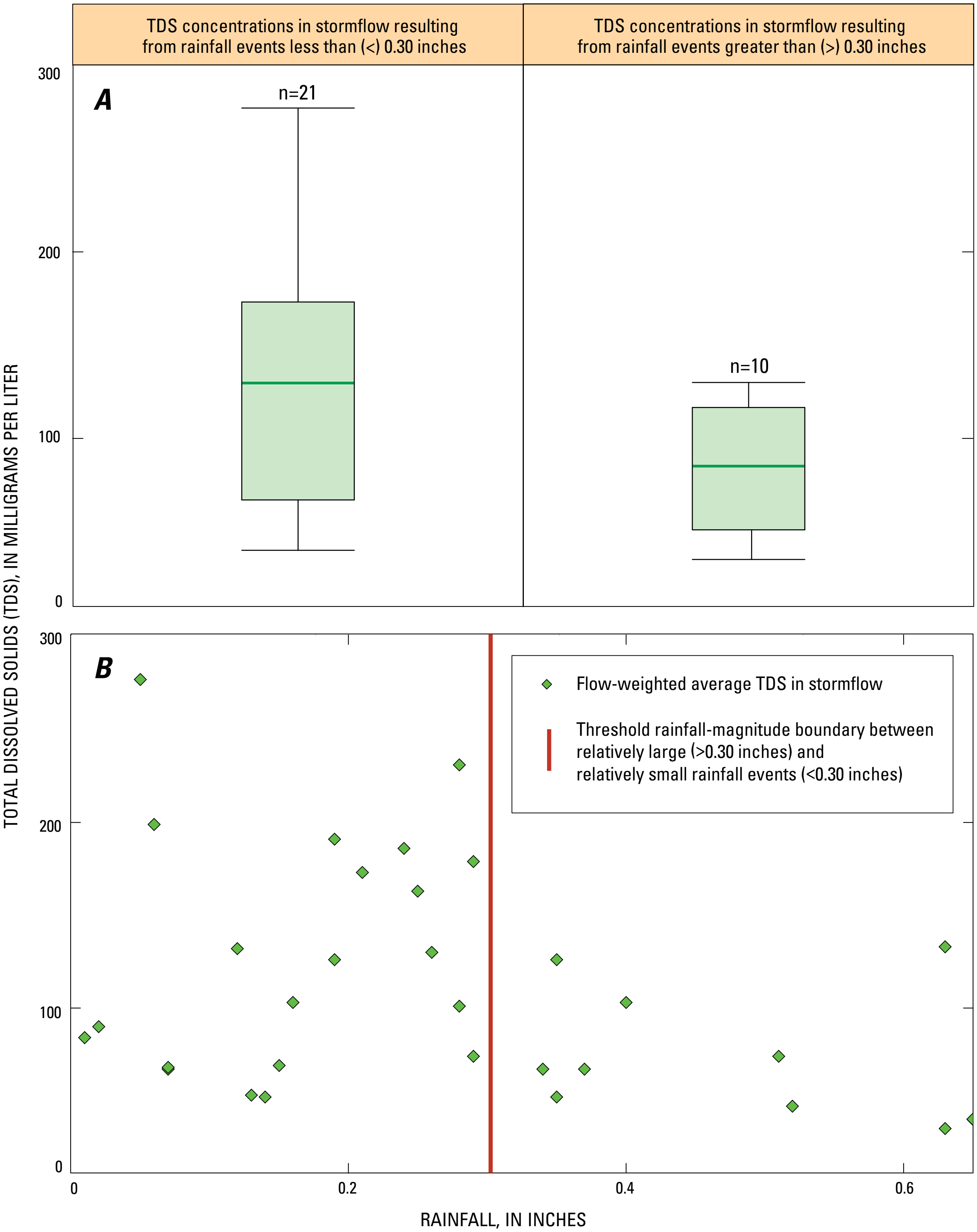


Figure 15. Stormflow concentrations of total dissolved solids (analyzed by hydrograph separation) as a function of rainfall magnitude at Cucamonga Creek, Santa Ana Basin, California.

Comparison of Calculated Mean-Daily, Discrete, and Flow-Weighted Average Stormflow Total Dissolved Solids Concentrations

Mean daily TDS, calculated from the continuous records of specific conductance, for the fixed sites during all or part of the period from October 1998 to September 2001 are shown in figures 16*A–F*. The concentrations obtained from laboratory analyses of discrete samples at base flow and stormflow are plotted with the concentrations calculated from the continuous record of specific conductance. Also plotted are the mean daily discharges for the period. For three of the sites, Warm Creek, MWD, and Cucamonga Creek, the flow-weighted stormflow TDS also are plotted (figures 16*B*, *C*, *D*). Note that the plots are not all at the same scale.

For all six sites, the mean daily TDS, calculated from specific conductance, is in close agreement with the TDS of discrete samples collected during base-flow conditions. The continuous record of mean daily specific conductance for the Imperial Highway site was unavailable. Therefore, published records of daily minimum and maximum values of specific conductance were used in place of mean daily values in figure 16*F*.

In figures 16*A–F*, the mean daily TDS calculated from specific conductance is commonly higher than concentrations in discrete storm samples. Storms often lasted less than 1 day and, consequently, daily averages typically included a higher proportion of base-flow discharge than did discrete stormflow samples. Figures 16*B*, *C*, *D* also show that the stormflow end-member, isolated by hydrograph separation at Warm Creek, MWD, and Cucamonga Creek had relatively low, flow-weighted average TDS.

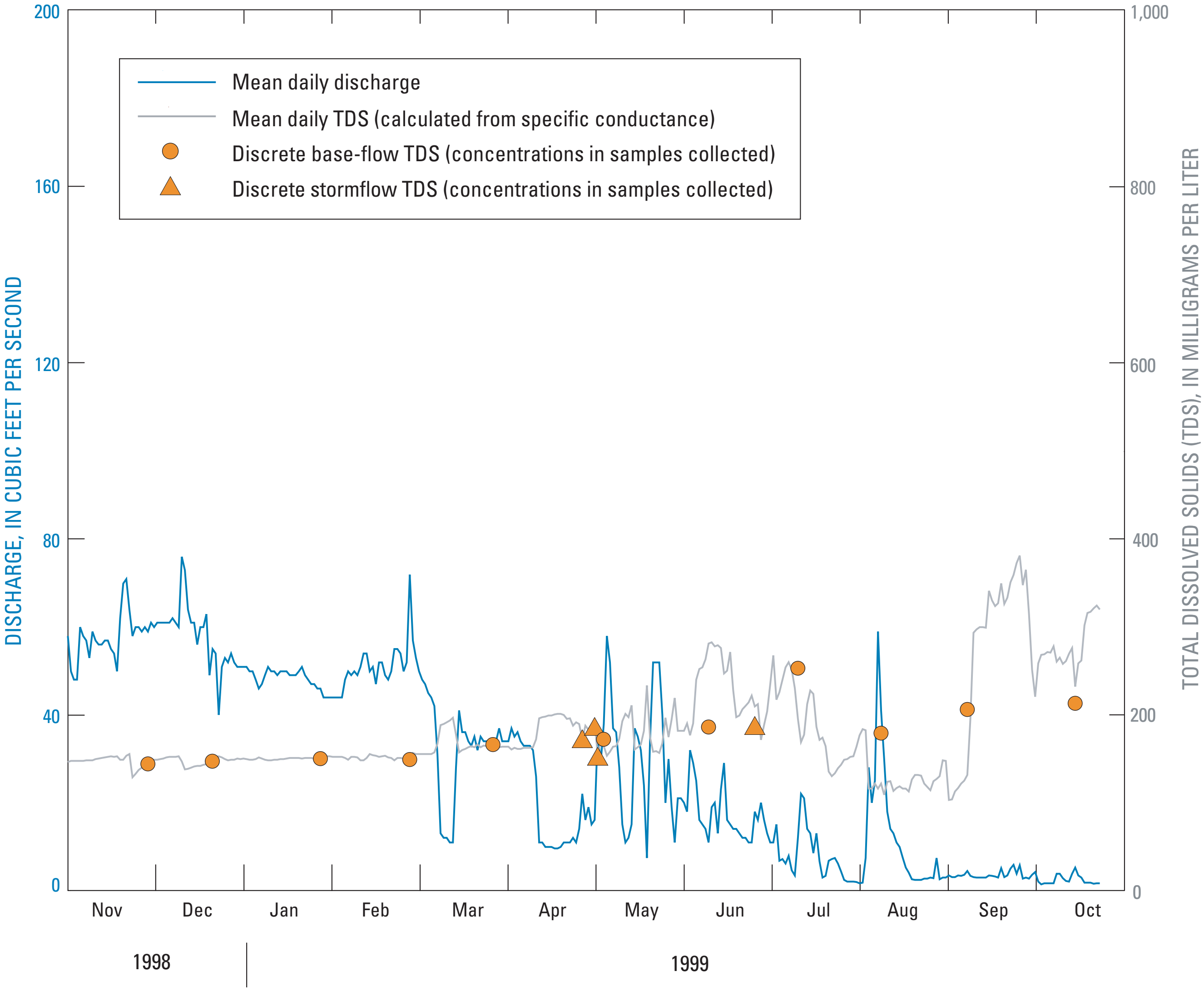
CONCENTRATIONS OF SELECTED NUTRIENTS

Total Nitrogen and Nitrogen Speciation

Mean total nitrogen concentrations in base-flow samples collected from fixed sites ranged from 0.3 mg/L for samples from Mentone to 7.9 mg/L for samples from Cucamonga Creek. Nitrogen at five of the six fixed sites was predominantly in the form of nitrate under base-flow conditions (fig. 17). More than seventy-five percent of the nitrogen in samples from the four fixed sites (MWD, Cucamonga Creek, Prado, and Imperial Highway that receive wastewater) was in the form of nitrate. Nitrogen in samples collected from Mentone was predominantly in the form of total organic nitrogen plus ammonia (TON+ammonia). Considering results from the other mountain sites sampled in the Santa Ana Basin, it appears that nitrogen speciation and concentrations of the different forms of nitrogen in samples from the Mentone site were representative of reference conditions for water entering the valley floor.

The concentration and proportion of TON+ammonia were usually higher in samples collected under stormflow conditions. This was most evident at Warm Creek, MWD, and Cucamonga Creek. Concentrations of all forms of nitrogen increased at Mentone and Warm Creek during stormflow, resulting in higher total nitrogen at these sites. At MWD, stormflow-related increases in concentrations of total organic nitrogen and ammonia were mostly offset by decreases in nitrate concentrations, resulting in little net change in total nitrogen concentrations. Nitrate concentrations also decreased at Cucamonga Creek during stormflow. However, total nitrogen at this site usually showed a net increase owing to stormflow and greater inputs of TON+ammonia. At the Prado and Imperial Highway sites, nitrogen concentrations and proportions of nitrogen species were similar under base-flow and stormflow conditions. This is likely due to flow regulation at Prado Dam.

A. Mentone



Figures 16*A–F*. Mean daily discharge, mean daily total dissolved solids (TDS), and TDS in discrete base-flow and stormflow samples at the six fixed sites, Santa Ana Basin, California. Graphs for B, C, and D also have flow-weighted average stormflow TDS obtained by hydrograph separation.

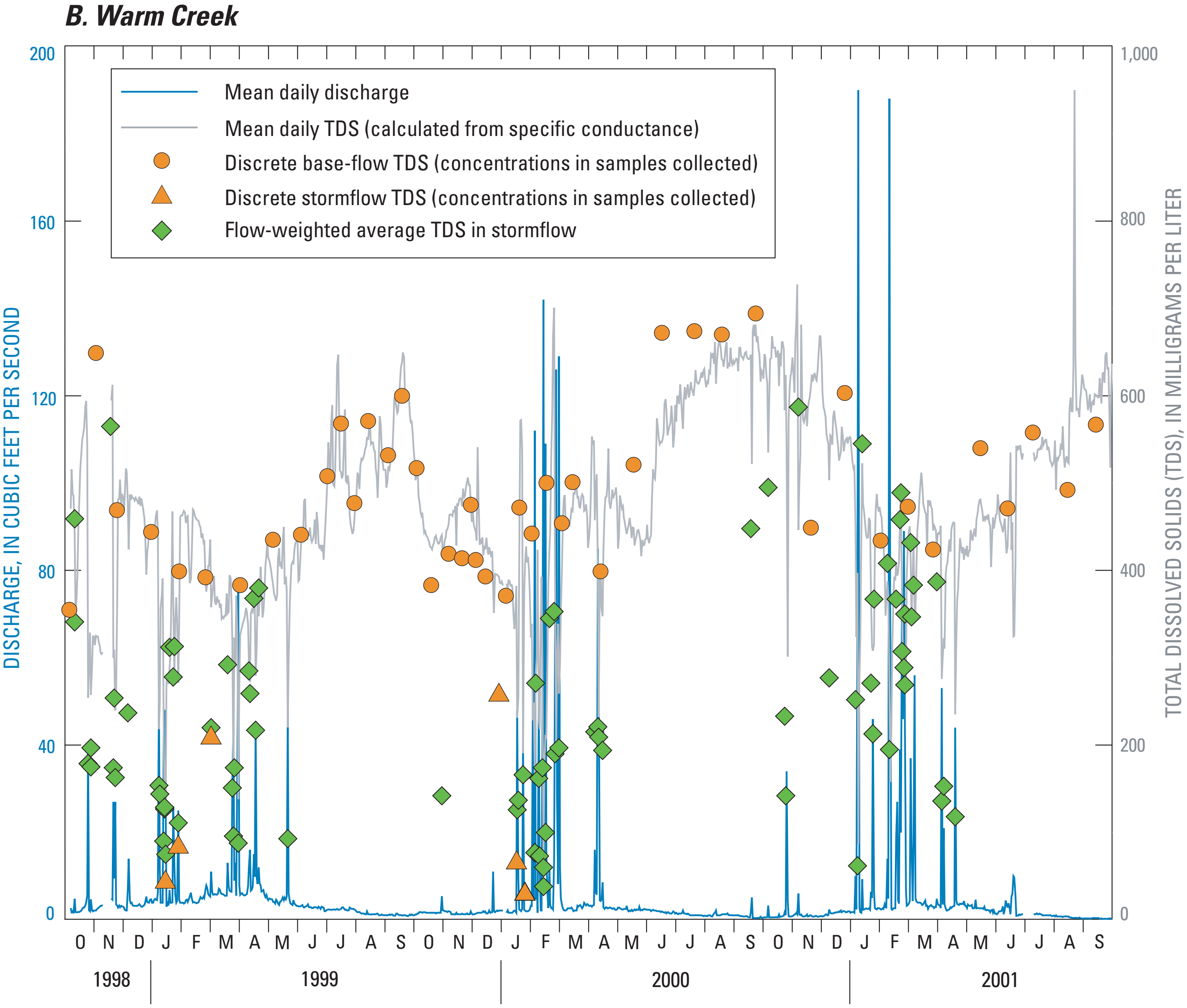


Figure 16.—Continued.

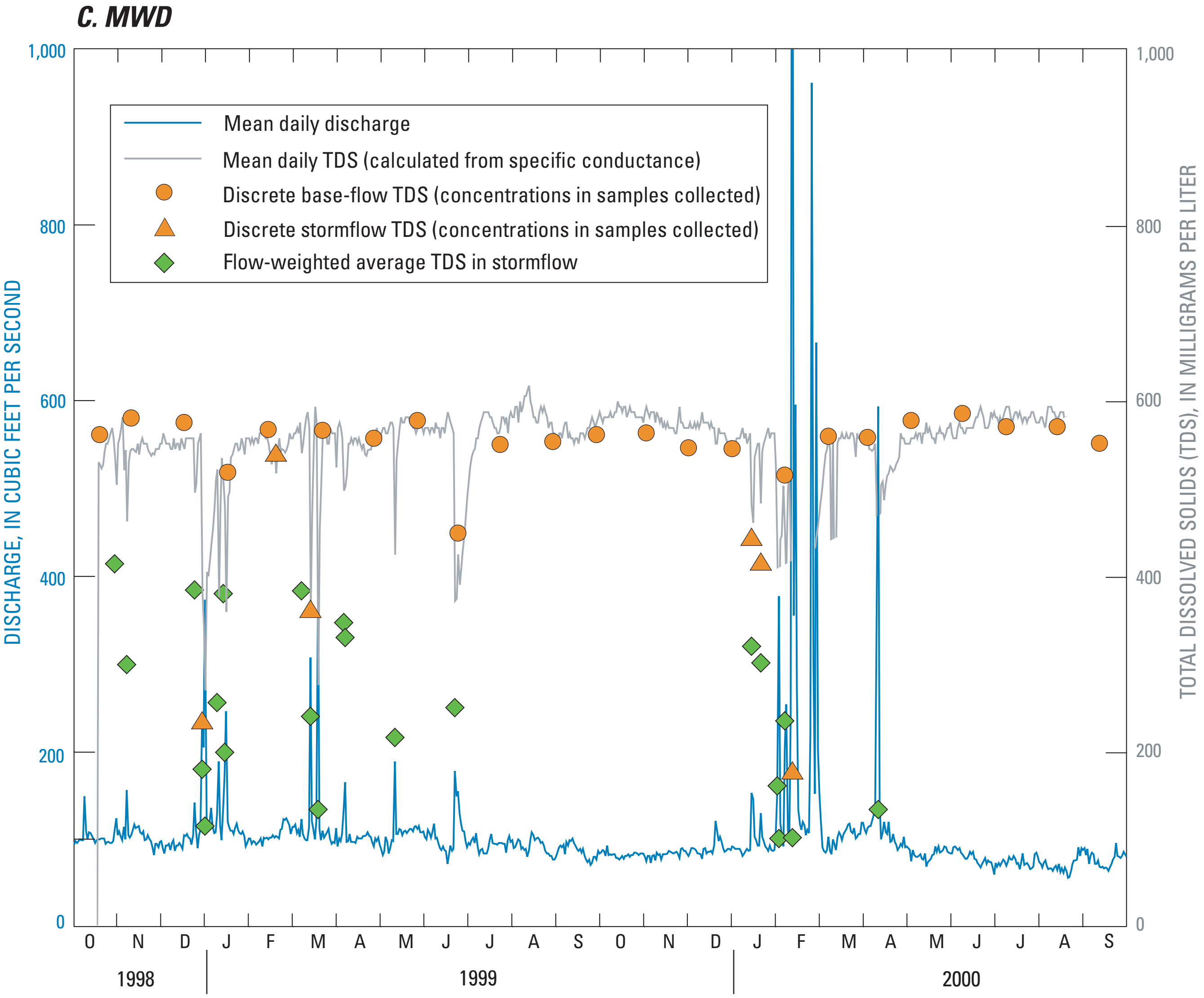


Figure 16.—Continued.

D. Cucamonga Creek

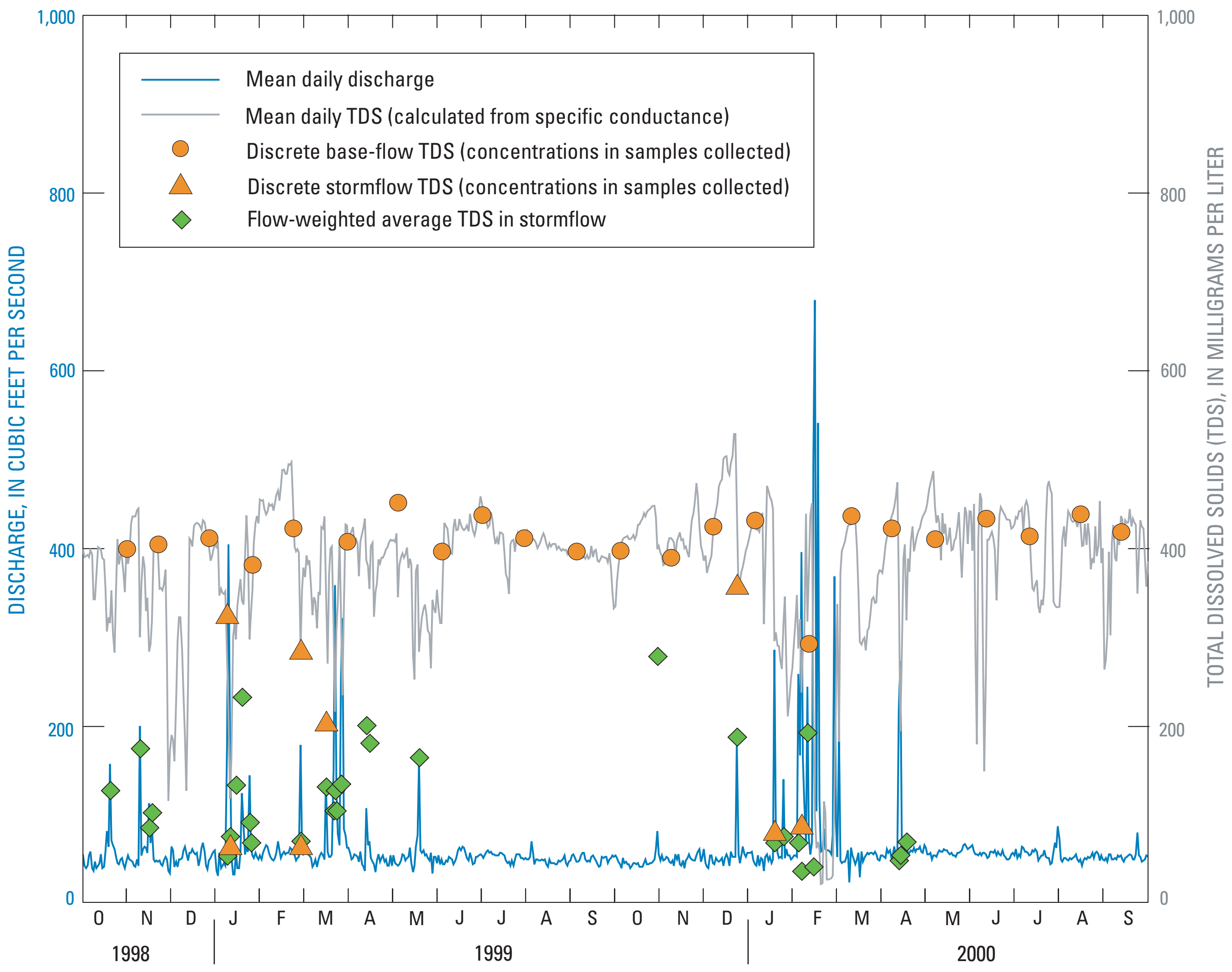


Figure 16.—Continued.

E. Prado

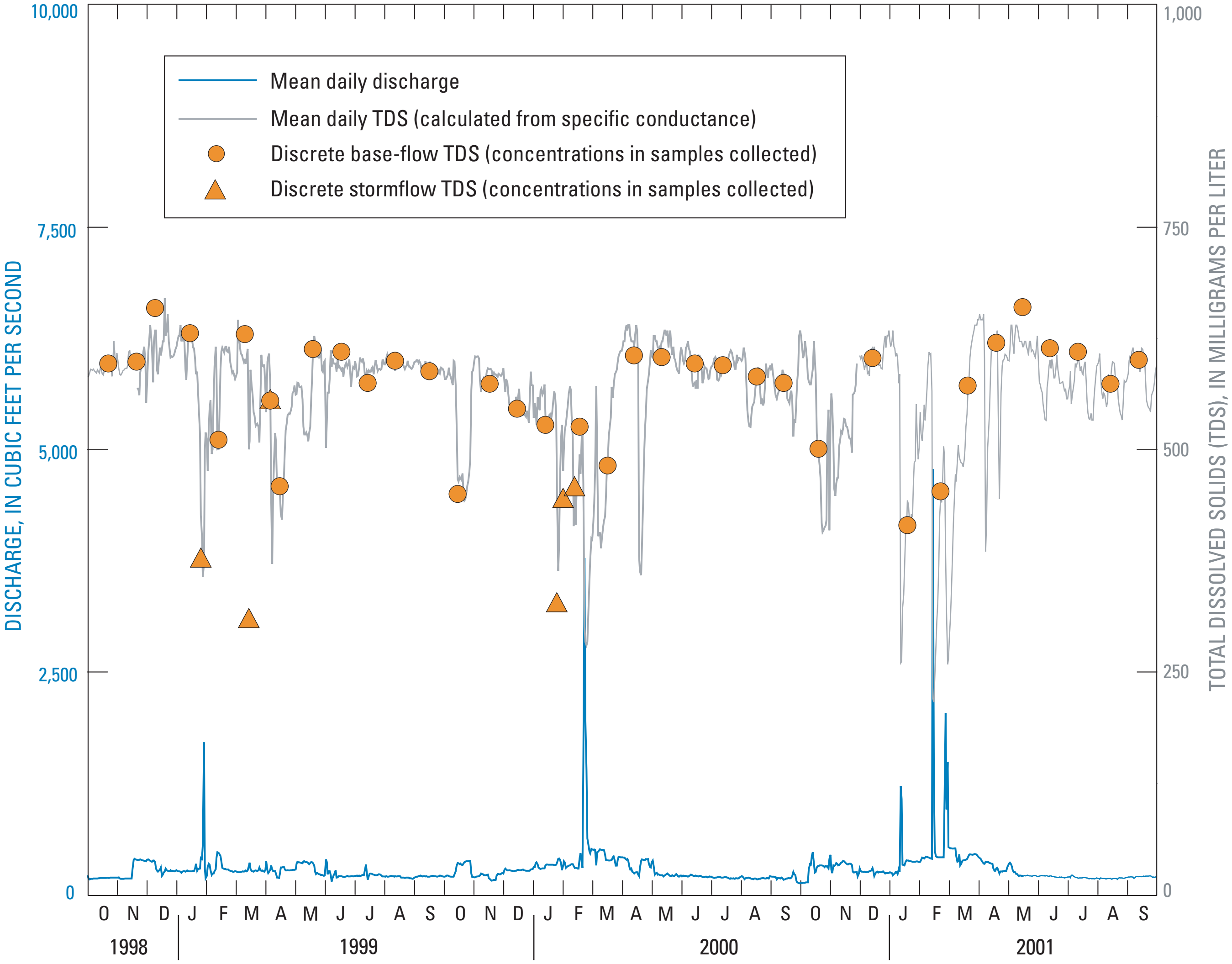


Figure 16.—Continued.

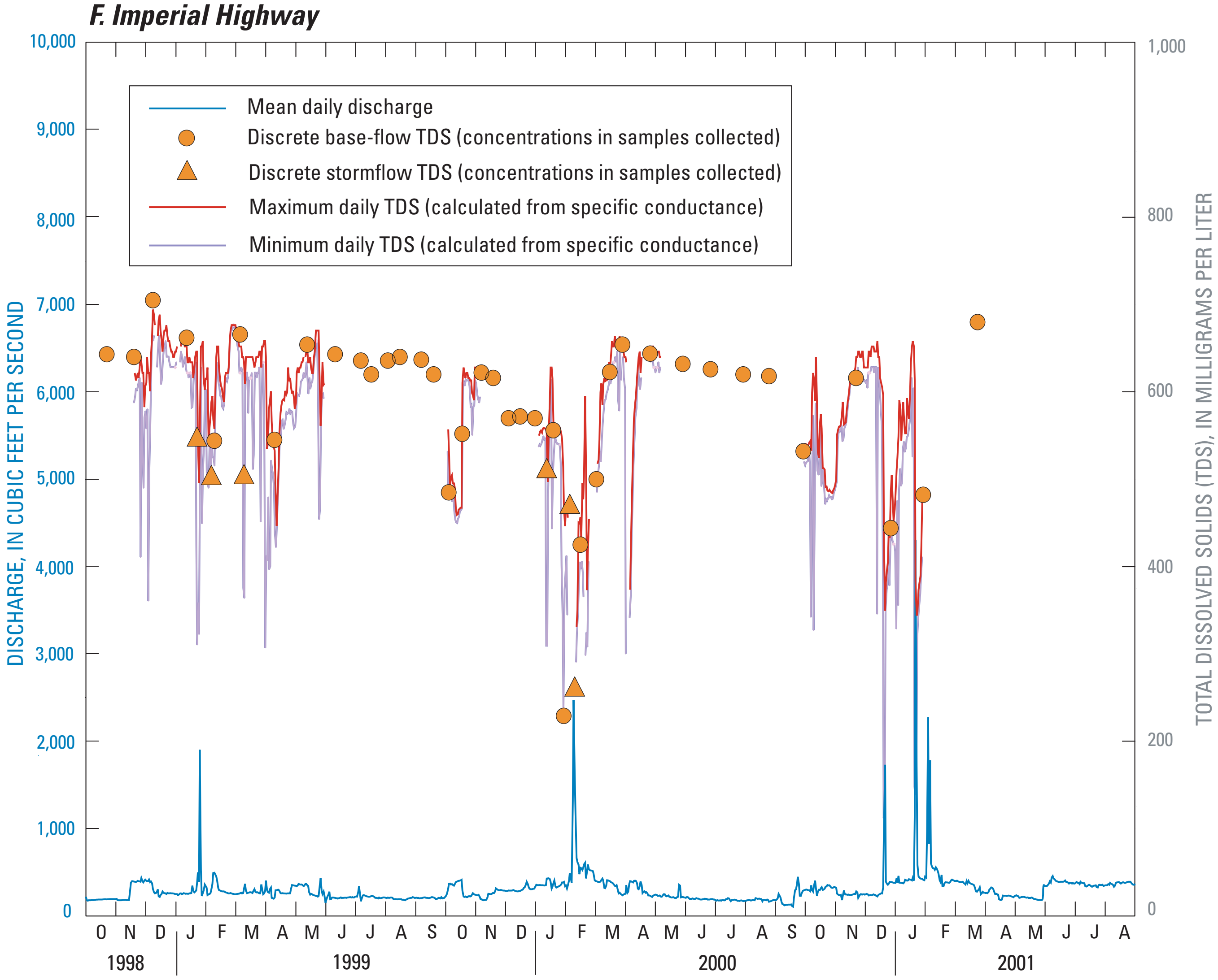


Figure 16.—Continued.

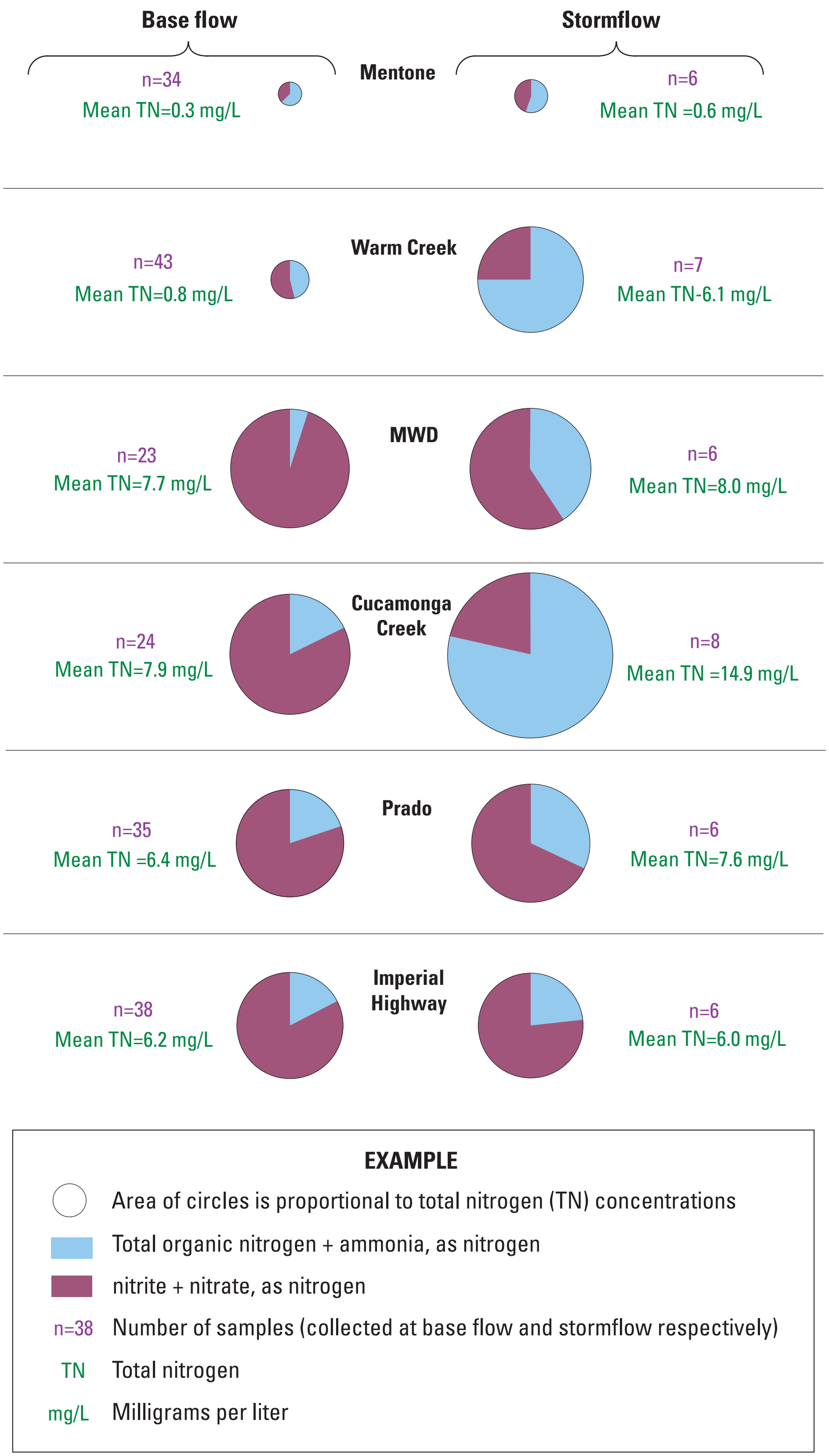


Figure 17. Mean nitrogen concentrations and speciation at fixed sites under base-flow and stormflow conditions, Santa Ana Basin, California.

Base-Flow Nitrate Concentrations by Water Source

Nitrate concentrations are higher in Santa Ana Basin streams receiving treated wastewater than in most streams that have other sources of water. Median base-flow concentrations at the four fixed sites located downstream from wastewater-treatment-plant outfalls (MWD, Cucamonga Creek, Prado Dame, and Imperial Highway) ranged from 4.9 to 6.7 mg/L. Nitrite+nitrate concentrations exceeded the U.S. Environmental Protection Agency (2002) drinking water standard of 10 mg/L in four samples collected at Cucamonga Creek and in one sample collected at MWD (fig. 18). Sites on stream reaches not receiving wastewater inputs had relatively low concentrations of nitrite+nitrate, with medians mostly below 1 mg/L (fig. 19).

Streams fed by mountain runoff in the Santa Ana Basin (the Mentone site and the other mountain sites) had median base-flow concentrations of nitrite+nitrate mostly below 0.3 mg/L (fig. 19). This agrees well with a national study by Clark and others (2000), which produced a mathematical model for predicting nitrate concentrations in undeveloped basins. Their model predicts that the flow-weighted mean nitrate concentration in undeveloped basin streams in the Santa Ana region should fall between 0.20 to 0.34 mg/L (fig. 19). The mountain site on Cajon Creek had relatively high nitrite+nitrate concentrations with a median of 1.4 mg/L. This is more than twice the median concentrations found at other basin sites that receive mountain run-off, and exceeds the California Regional Water Quality Control Board (1995) objective of 1 mg/L for this site. The site is located in a pass between the San Bernardino and the San Gabriel Mountains and, therefore, its water source is not strictly mountain runoff. The pass also serves as a transportation corridor, possibly resulting in highway and railway runoff to the stream.

Nitrite+nitrate concentrations in urban runoff in the Santa Ana Basin seem to be mostly below 1 mg/L (table 2). This estimate for urban runoff is based on fewer data than other water sources because none of the fixed sites had urban runoff as the sole source of water during the high-intensity phase (HIP) of data collection. Flow at the urban indicator site on Warm Creek usually consists of both urban runoff and rising ground water, and it had a mean nitrite+nitrate concentration of 0.4 mg/L (fig. 18). In eight samples collected subsequent to the HIP at this site, from June 2002 to August 2003, the typical rising ground-water contribution was absent, leaving only the urban runoff component. The nitrite+nitrate concentrations for these samples all have been less than 1 mg/L (table 2) and are comparable to the concentrations observed at this site when it is receiving ground-water inputs.

Results for those eight samples are presented in table 2, along with results for six samples collected from Cucamonga Creek upstream from the wastewater input where the flow is predominantly urban runoff. Nitrite+nitrate concentrations in all but one of these samples were less than 1 mg/L. The sample with a higher nitrite+nitrate concentration (3.8 mg/L) was collected at night from Cucamonga Creek. Conditions in this stream vary diurnally, with dissolved-oxygen concentrations ranging from 4 to more than 20 mg/L and pH ranging from 7.5 to more than 10 standard pH units in a single 24-hour period. Such extreme fluctuations can be attributed to high daytime primary productivity by attached algae. At night, the abundant algae may release nitrogen compounds, thus increasing the concentration of nitrite+nitrate.

Some streams receiving rising ground water have high concentrations of nitrate. Samples collected from three ground-water-fed tributaries contributing to Reach 3 (fig. 1) had some of the highest nitrate concentrations observed in this study. The five samples collected from these tributaries had nitrite+nitrate concentrations ranging from about 10 to 16 mg/L (table 3). One of the tributaries—Sunnyslope Channel—emerges from a culvert below street level as a concrete-lined channel. From where it is first exposed to sunlight the channel is blanketed with algae, indicating eutrophy. Although these tributaries have high nitrate concentrations, their relative contribution to streamflow in the Santa Ana Basin is small by volume.

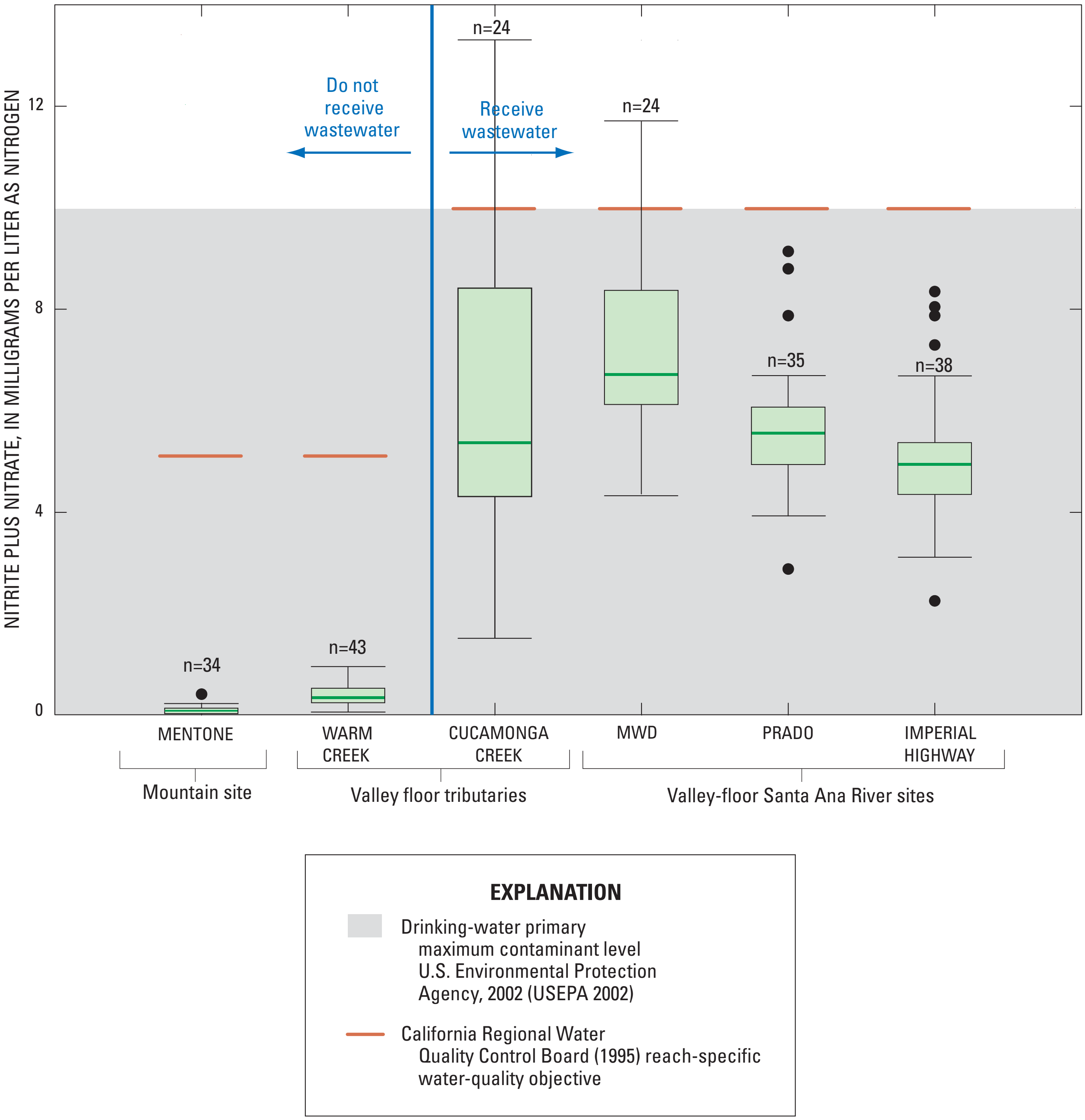


Figure 18. Nitrite+nitrate concentrations at fixed sites, Santa Ana Basin, California.

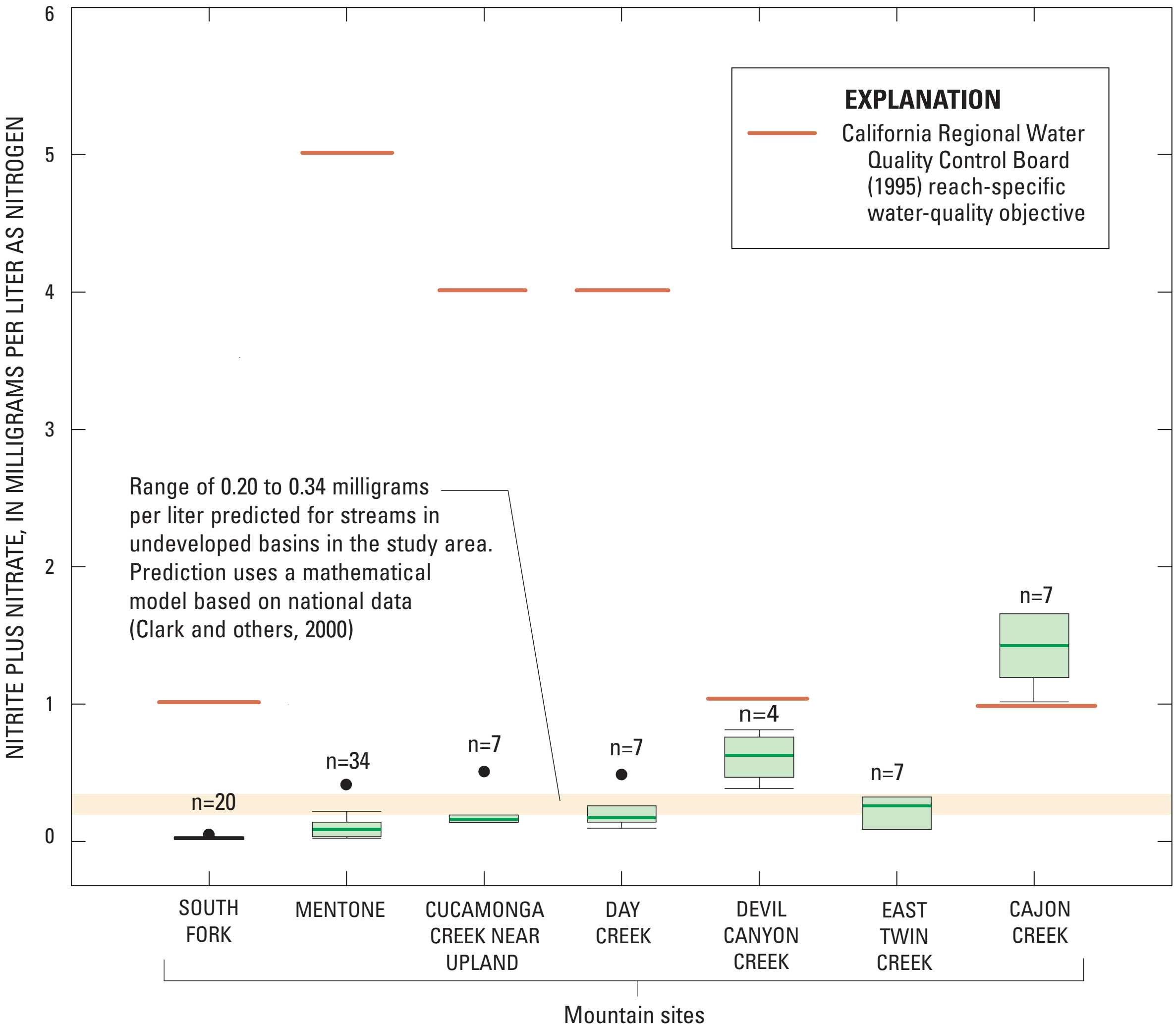


Figure 19. Nitrite+nitrate concentrations at mountain sites, Santa Ana Basin, California.

Nitrate in Stormflow

Nitrate concentrations are higher in stormflow samples than in base-flow samples from SANA sites not receiving wastewater inputs (fig. 20). The difference was small for the Mentone site. Concentrations in storm samples there ranged from 0.11 to 0.77 mg/L, with a median of 0.17 mg/L; base-flow samples had nitrite+nitrate concentrations ranging from not detected (less than 0.05 mg/L) to 0.42 mg/L, with a median of 0.09 mg/L. The difference was greater for Warm Creek. Storm-sample concentrations at Warm Creek ranged from 0.27 to 3.8 mg/L, with a median of 0.98 mg/L; base-flow samples had nitrite+nitrate concentrations ranging from 0.07 to 1.3 mg/L, with a median of 0.34 mg/L.

One storm sample also was collected at each of the mountain sites on Cajon Creek and Devil Canyon Creek. Nitrite+nitrate concentrations in these storm samples were substantially higher than the concentrations observed in base flow at these sites. Concentrations in seven base-flow samples collected from Cajon Creek ranged from 1.0 to 1.7 mg/L, with a median of 1.4 mg/L. The storm sample collected from this site had a concentration of 4.3 mg/L. Nitrite+nitrate concentrations in four base-flow samples collected from Devil Canyon Creek ranged from 0.38 to 0.81 mg/L, with a median of 0.63 mg/L. The storm sample collected from this site had a concentration of 2.6 mg/L.

When nitrate concentrations increase as a result of stormflow in streams without point sources of nitrate, the increase is often attributed to nitrate running off the landscape from nonpoint sources (Schnoebelen and others, 1999; Mueller and others, 1995). In the Santa Ana Basin, rainwater has higher nitrate concentrations than does stream base flow at sites not receiving wastewater. The National Atmospheric Deposition Program (NADP) (2002) estimated nitrate concentrations in Santa Ana Basin precipitation at between 0.7 to 1.3 mg/L during the three years of this study. Base-flow nitrate concentrations at Santa Ana Basin sites not receiving wastewater inputs are usually lower than 1 mg/L. Therefore, part of the increase in nitrate concentrations at these sites during storm events may be contributed by rainfall itself. Other sources of nitrate to streams during storm events include nitrate washed in from land surfaces or nitrate that enters streams with ground water that existed in the catchment prior to the event (Kendall and McDonnell, 1998).

In streams receiving wastewater, nitrate concentrations are lower in stormflow samples than in base-flow samples (fig. 20). The lower concentrations are a result of dilution of the relatively high nitrate concentrations of wastewater. Other researchers have observed similar decreases in nitrate concentrations as a result of storms and have also attributed them to dilution of point-source nitrate (Mueller and others, 1995; Izbicki and others, 2000).

The dilution of nitrate concentration by stormflow can be assessed by regressing nitrate concentration as a function of the percentage of stormflow in the stream discharge at the time of sample collection. Hydrograph separations, performed on data from three urban sites, allowed such a regression on 21 storm samples. It appears that nitrite+nitrate concentrations are inversely correlated with percentage stormflow. However, there is wide variability in the stormflow nitrate concentrations (fig. 21). Possible sources of this variability include: first-flush effects in samples collected early in the rainy season, first-flush effects in samples collected early during individual storms, and variable inputs from the landscape (for example, releases from waste-stabilization ponds). Although the correlation coefficients are relatively low for the individual regressions, the slopes of the regression lines are similar. The linear correlation for all 21 storms represented in figure 21 was significant at the $\alpha = 0.05$ level using Kendall's Tau, a non-parametric test of correlation (Helsel and Hirsch, 1992). In addition, nitrate concentrations in samples with the highest percentage stormflow tend to approach concentrations estimated by National Atmospheric Deposition Program (2002) for rain.

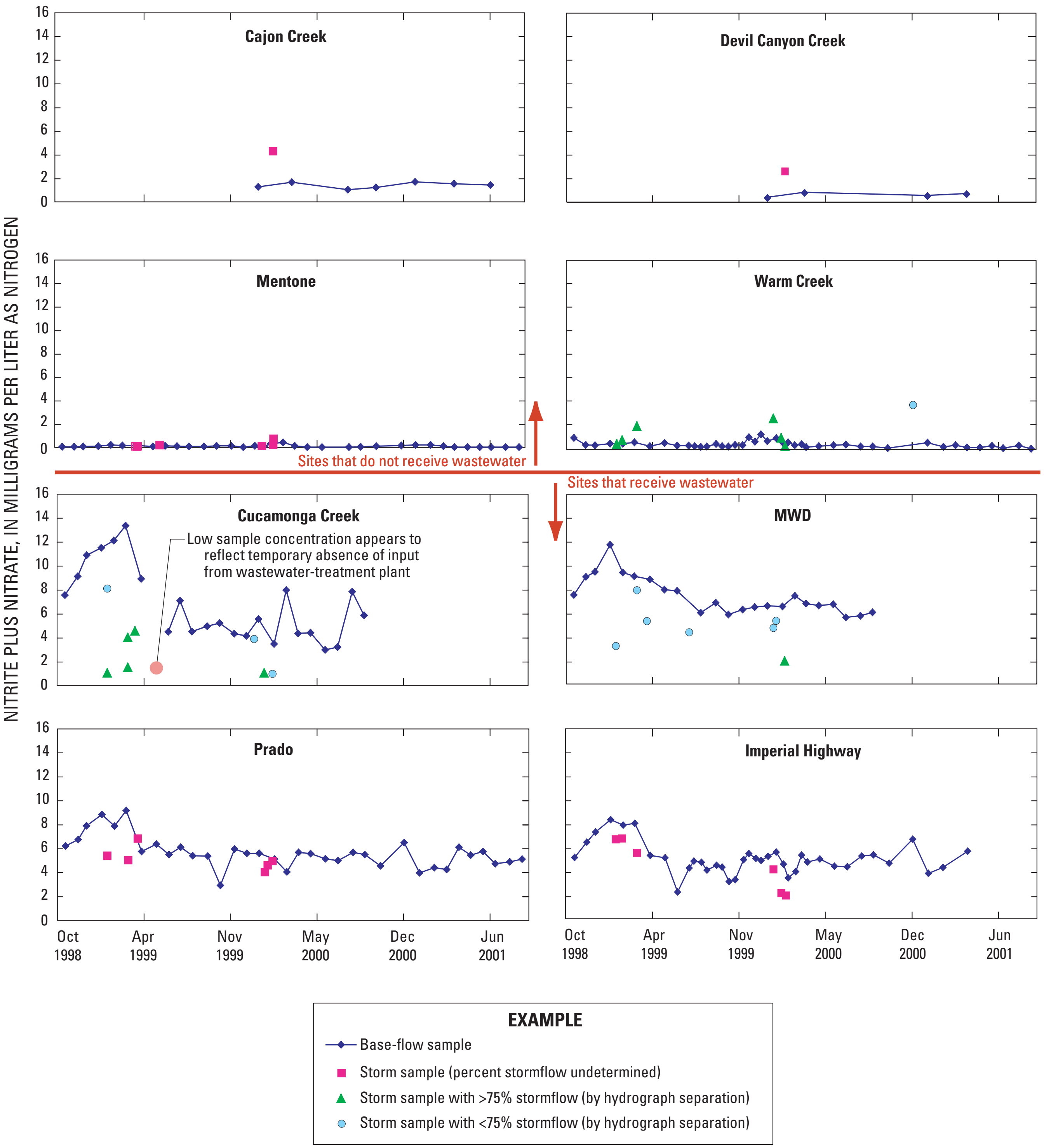


Figure 20. Time-series of nitrite plus nitrate concentrations in samples from sites where at least one stormflow sample was collected, Santa Ana Basin, California (>, greater than; <, less than).

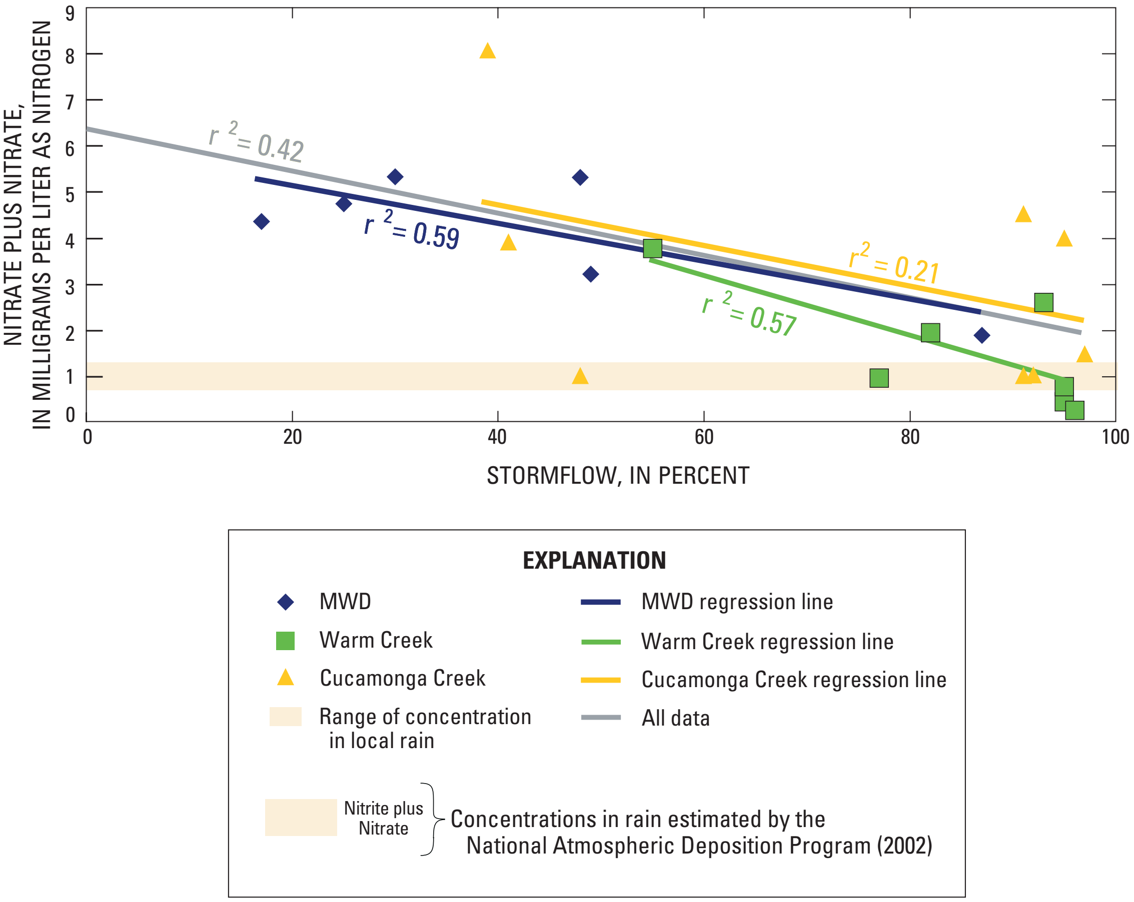


Figure 21. Nitrite+nitrate concentrations in stormflow samples as a function of percentage of stormflow in the stream (determined by hydrograph separation) at the time of sample, Santa Ana Basin, California.

The regressions for the three urban sites suggest that nitrite+nitrate concentrations are approximately 1 to 2 mg/L as stormflow approaches 100 percent of stream discharge. Twelve storm samples were collected when hydrograph-separation results indicate that total stream discharge consisted of at least 75 percent stormflow (fig. 22). The median nitrite+nitrate concentration of the 12 storm samples was 1.3 mg/L. This suggests that stormflow nitrate comes mostly from rain and picks up little additional nitrate from the urban landscape. A study by Ebbert and Wagner (1987) also suggests that much of the nitrate load in urban storm runoff comes from rain.

Ammonia

In addition to nitrite and nitrate, inorganic nitrogen also exists in the form of ammonia (dissolved NH_3 plus NH_4^+). Concentrations of ammonia in base-flow samples for this study were usually well below 1 mg/L, and contributed far less to total stream nitrogen than did nitrate. Mountain sites, including Mentone, usually had concentrations of ammonia below the LRL (0.02 or 0.04 mg/L) in base-flow samples. Sites on the valley floor frequently had relatively low, but detected, concentrations of ammonia in base-flow samples (fig. 23). The generally low concentrations of ammonia in base flow at all sites showed little annual variability, except at the Prado site, where marked winter peaks occurred during all three years of the study. These peaks are dampened, but still visible in the time series for the site below Imperial Highway, 11 mi downstream from Prado.

At most fixed sites, ammonia concentrations were higher in storm samples than in base-flow samples (fig. 23). The National Atmospheric Deposition Program (NADP) (2002) estimates that ammonia in precipitation for this region ranged from 0.17 to 0.35 mg/L during the period of this study. This is higher than base-flow median concentrations observed at any of the 12 fixed and mountain sites (less than 0.02 to 0.12 mg/L). However, the values estimated by the NADP are lower than the median storm-sample concentrations observed at three sites: 0.75 mg/L at Warm Creek, 1.18 mg/L at Cucamonga Creek, and 0.57 mg/L at Prado. The 12 samples that were determined, by hydrograph separation, to consist of at least 75 percent stormflow provide the best estimate of stormflow concentrations of ammonia. The median concentration in those 12 samples was 0.9 mg/L (fig. 22).

These storm-related ammonia concentrations of about 1 mg/L are above the concentrations found in local rain, according to NADP estimates. This suggests that, either the NADP estimates are low, or that stormflow ammonia enters valley-floor streams from the surrounding landscape. Alternatively, or in addition to this process, ammonia could be mobilized from streambed sediments to the water column by stormflow-induced turbulence. There were 11 storm samples that had ammonia concentrations greater than or equal to 1 mg/L. Six of these were collected at Cucamonga Creek. Relatively high stormflow concentrations of ammonia at this site, located in the Chino Basin Dairy Preserve, may indicate a landscape contribution as a result of rainfall. This contribution could occur as nonpoint runoff, or as point releases, either intentional or unintentional, from waste-stabilization ponds.

Ammonia concentrations also were elevated by storm events at Warm Creek. Storm-sample concentrations were between 0.2 and 1.6 mg/L at this site, where base-flow concentrations were typically near or below the laboratory reporting limit of 0.02 to 0.04 mg/L (fig. 23). Three of the six storm samples collected at the Prado site also had relatively high concentrations (0.7 to 1.2 mg/L) that were between 6 and 10 times the base-flow median concentration (0.12 mg/L). However, stormflow did not appear to appreciably increase total ammonia concentrations at MWD, Imperial Highway, or the mountain sites.

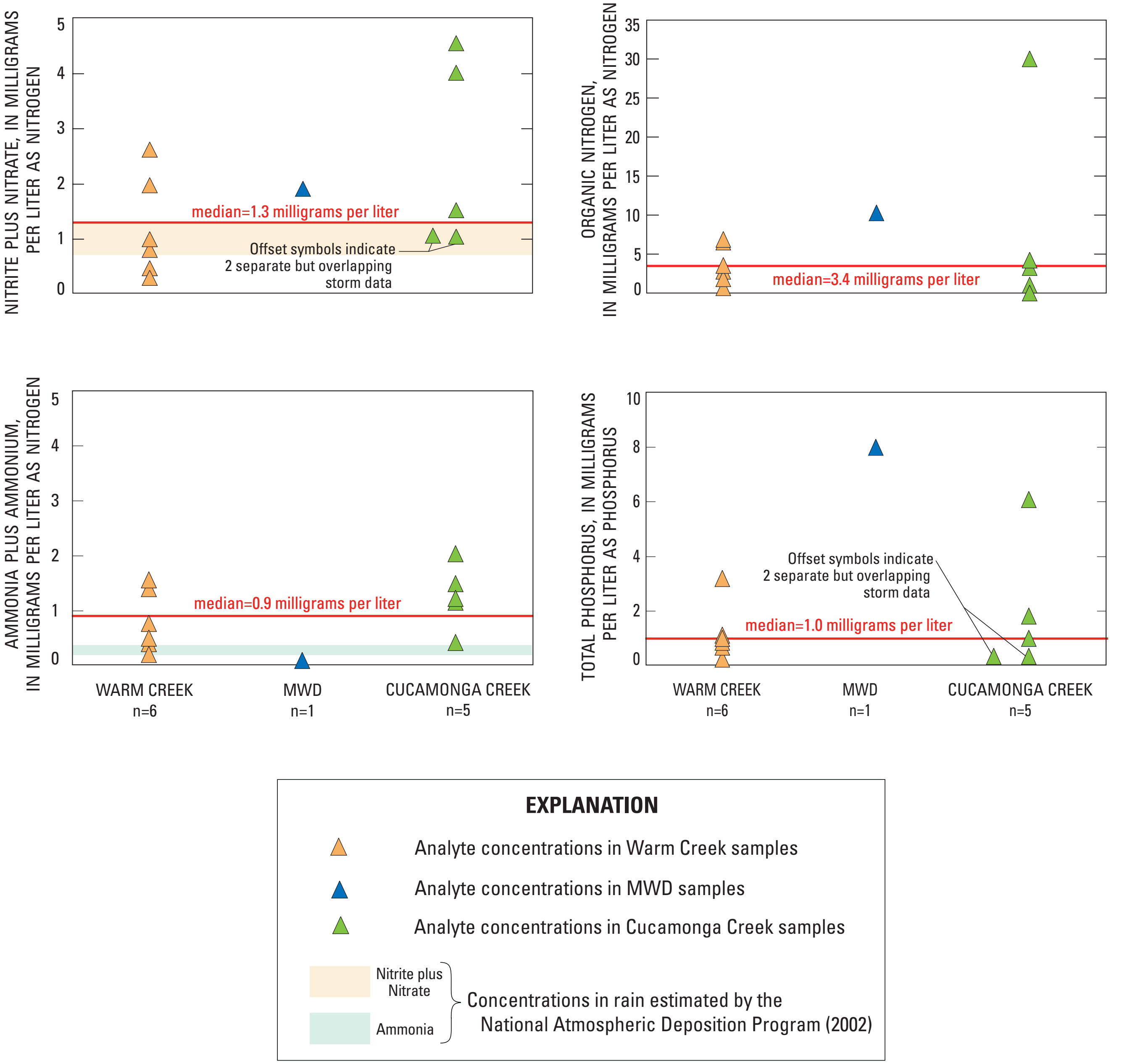


Figure 22. Concentrations of selected nutrients in 12 samples consisting of at least 75 percent stormflow (determined by hydrograph separation), Santa Ana Basin, California.

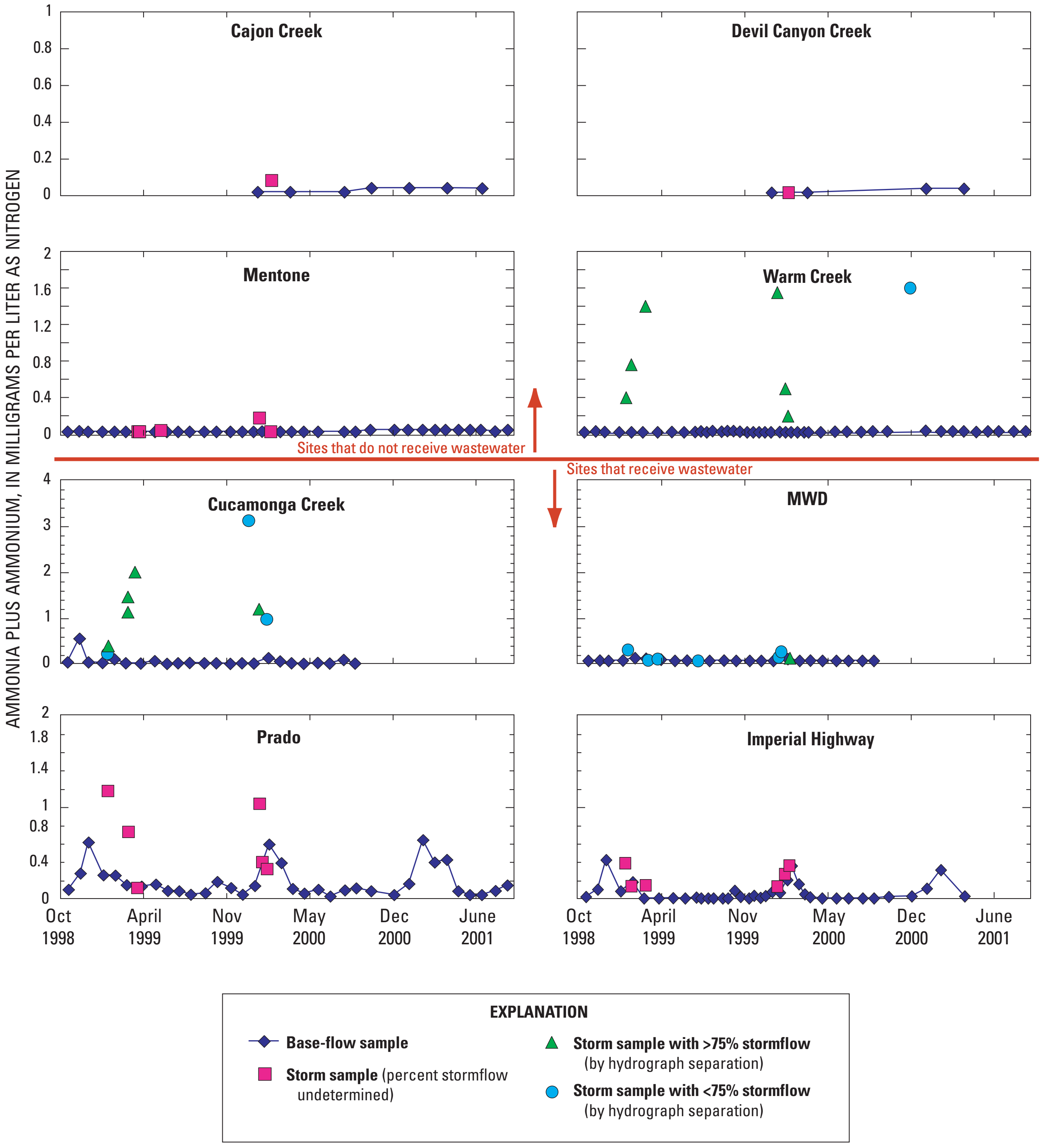


Figure 23. Time-series of ammonia plus ammonium concentrations in samples from sites where at least one stormflow sample was collected, Santa Ana Basin, California (>, greater than; <, less than).

Un-ionized ammonia NH_3 is far more toxic to aquatic organisms than is the ammonium ion NH_4^+. The U.S. Environmental Protection Agency (1999) has an ammonia criterion to protect freshwater aquatic life from acute and chronic effects of ammonia. Ammonia speciation and toxicity depend on pH and temperature. Therefore, the criteria take into consideration the concentration of total ammonia (NH_3+NH_4^+), sample pH and, in the case of the chronic effects criterion, the ambient water temperature. Neither the acute nor the chronic ammonia criteria were exceeded in surface-water samples collected for this study.

Organic Nitrogen

Concentrations of organic nitrogen, like ammonia, were usually low in comparison with nitrate in base flow, typically representing less than 20 percent of total stream nitrogen (suspended and dissolved). Mountain sites had base-flow concentrations of organic nitrogen as high as 0.8 mg/L, but the medians were less than 0.1 mg/L for all mountain sites. Base-flow organic nitrogen concentrations at Warm Creek ranged from less than 0.1 to 0.9 mg/L, with a median of 0.3 mg/L. Fixed sites downstream from wastewater inputs had base-flow concentrations ranging from 0.2 to 3.0 mg/L, with a collective median of 1.0 mg/L.

Concentrations of organic nitrogen often increased in basin streams under stormflow conditions. Mountain sites (including Mentone) had storm-sample organic nitrogen concentrations ranging from less than 0.1 to 1.8 mg/L, with a median of 0.3 mg/L. Warm Creek had storm-sample organic nitrogen concentrations ranging from 0.7 to 6.9 mg/L, with a median of 3.4 mg/L. Storm-sample organic nitrogen concentrations for fixed sites receiving wastewater inputs were variable, ranging from less than 0.1 to 41 mg/L, with a median of 1.6 mg/L. The median concentration of organic nitrogen in the 12 samples that consisted of at least 75 percent stormflow was 3.4 mg/L (fig 22). The highest observed concentration of organic nitrogen in any sample was 41 mg/L. This occurred in a storm sample from Cucamonga Creek that was shown to have only 41 percent storm flow. Such an extreme concentration of organic nitrogen at Cucamonga Creek in response to a storm event may be evidence of a dairy-landscape contribution to the stream.

Phosphorus

No Federal or State drinking-water standard or maximum contaminant level exists for phosphorus, and phosphorus compounds that are typically found in streams (as opposed to elemental P) are not generally considered toxic to aquatic life. Using the 75th percentile of total phosphorus concentration data from SANA mountain sites, the reference condition is about 0.02 mg/L total phosphorus (TP) (fig. 24). That value agrees closely with the level of 0.03 mg/L determined by the USEPA using reference conditions in streams for this ecoregion (U.S. Environmental Protection Agency, 2000). As an alternative, the USEPA (1986) has suggested a general goal that TP not exceed a concentration of 0.10 mg/L as P to control accelerated eutrophication in streams not discharging directly to lakes or impoundments.

Base-flow TP concentrations in samples from sites receiving mountain runoff rarely exceeded even the U.S. Environmental Protection Agency (2000) reference criterion of 0.03 mg/L, let alone their general goal level (U.S. Environmental Protection Agency, 1986) of 0.1 mg/L (fig. 25*A*). Base-flow TP concentrations at the urban indicator site on Warm Creek, which receives rising ground water and urban runoff, were typically at about 0.03 mg/L. This level indicates minimally impacted conditions using the statistical criterion based on reference conditions but is well within the general goal to control eutrophication. TP concentrations in samples from fixed sites with wastewater inputs typically have TP concentrations near 1 mg/L, indicating that phosphorus may be a factor in the eutrophication observed in many of the streams (fig. 25*A*). TP concentrations in stormflow were variable, but were typically higher than concentrations in base flow. The median concentration in the 12 samples that were determined to consist of at least 75 percent stormflow was 1.0 mg/L (fig. 22).

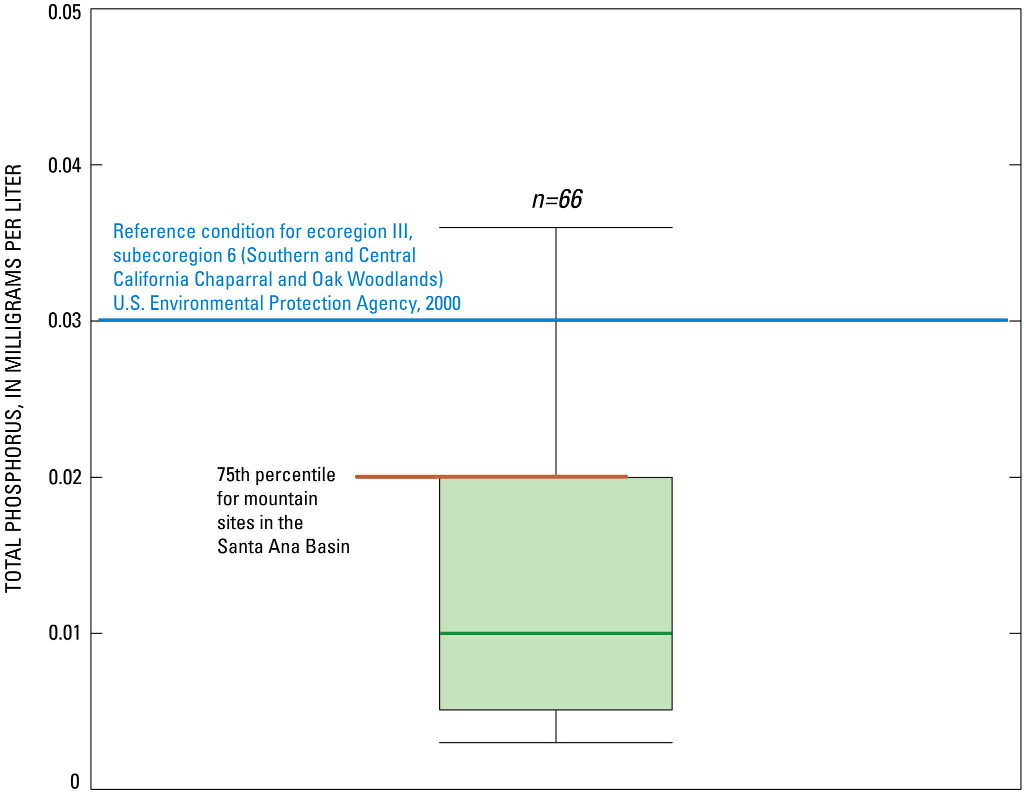


Figure 24. Base-flow total phosphorus concentrations at mountain sites compared with reference conditions, Santa Ana Basin, California.

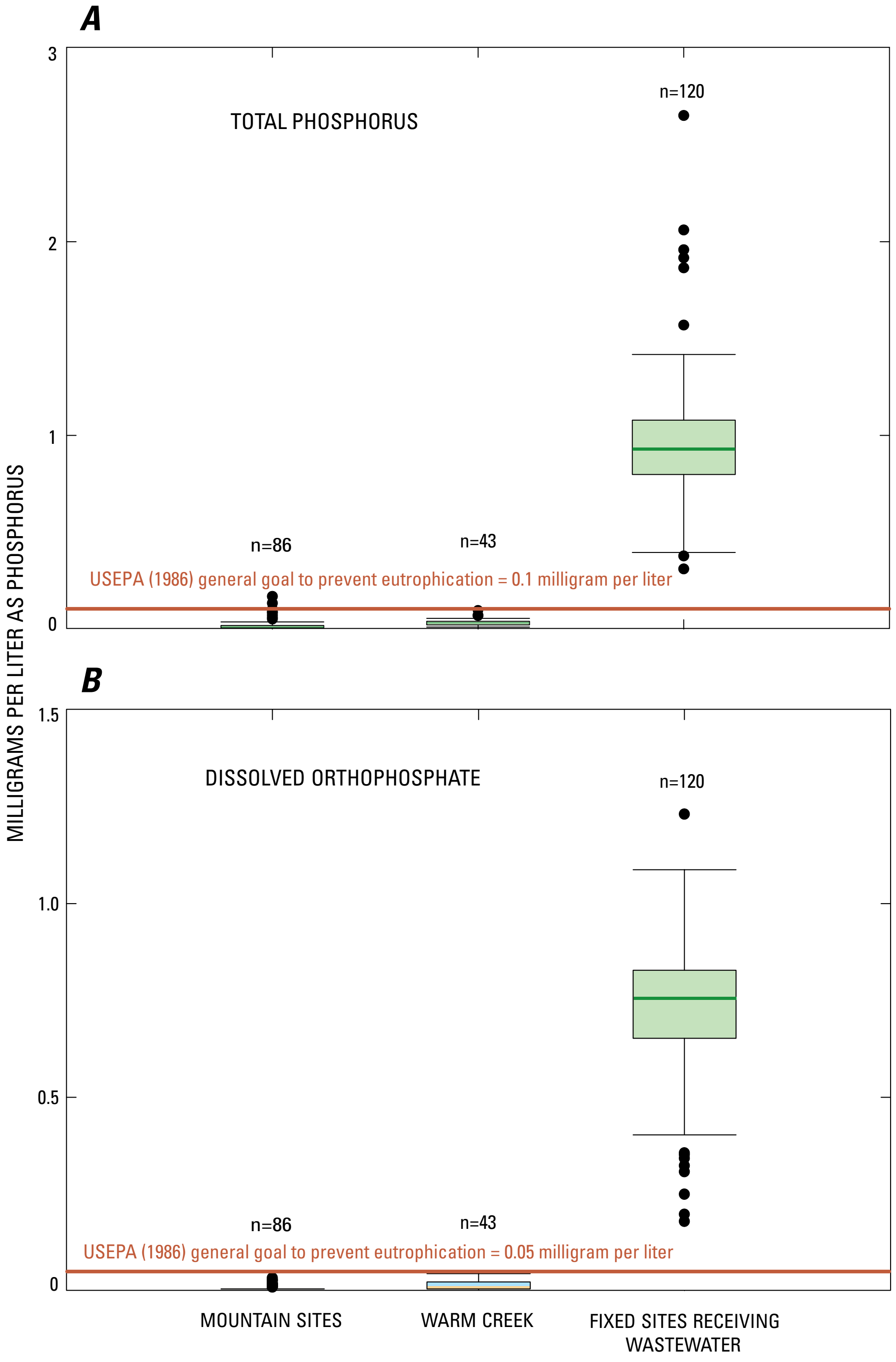


Figure 25. Base-flow total phosphorus (A) and dissolved orthophosphate (B) at sites grouped by water source, Santa Ana Basin, California (USEPA, U.S. Environmental Protection Agency).

Most phosphorus in base-flow samples collected for this study was in the form of dissolved orthophosphate, and this is the form of phosphorus most biologically available to aquatic organisms.

The U.S. Environmental Protection Agency (1986) has set a general goal of less than 0.05 mg/L for phosphates in streams to control accelerated eutrophication. As with total phosphorus, sites not receiving wastewater usually had orthophosphate concentrations less than the goal. Dissolved orthophosphate was usually less than or equal to the LRL (0.01–0.02 mg/L) at mountain sites. Therefore, establishing a reference-condition criterion for dissolved orthophosphate based on the 75th percentile of environmental sample concentrations at Santa Ana Basin reference sites (U.S. Environmental Protection Agency, 2000), as was done for total phosphorus, would not be meaningful. Most base-flow dissolved orthophosphate concentrations at Warm Creek were also less than 0.02 mg/L, and no base-flow sample collected from Warm Creek had a concentration above 0.05 mg/L. Fixed sites that received wastewater usually had concentrations above the U.S. Environmental Protection Agency (1986) goal of 0.05 mg/L, and the collective median for these sites was 0.76 mg/L (fig. 25*B*).

QUALITY-CONTROL RESULTS

Quality-control results generally indicate high data integrity, although blank samples collected using automatic samplers were more prone to show carryover contamination than were blanks collected by equipment cleaned using USGS protocols. Therefore, QC sample results are summarized in two tables: table 4 summarizes QC results for samples collected using standard USGS protocols (USGS, variously dated), and table 5 summarizes the results for samples collected by automatic samplers.

Nutrient compounds usually were not detected in field and equipment blanks or, at most, were detected at only a few hundredths of a milligram per liter above the laboratory reporting level (LRL). There were two cases where detections of nutrient compounds (orthophosphate and nitrite) in blanks were of potential concern. In each of these cases, the compound was detected at a concentration that exceeded the lowest concentration detected in environmental samples, and the concentration was greater than the applicable LRL. In one case, dissolved orthophosphate was detected at a concentration of 0.024 in a blank collected using standard USGS protocols (USGS, variously dated). The concentration of dissolved orthophosphate in environmental samples collected from the mountain sites and from Warm Creek was commonly less than or equal to 0.01 mg/L (fig. 25*B*). Therefore, concentrations detected between 0.01 and 0.024 mg/L should be used with caution.

In another blank, collected with an automatic sampler, nitrite was detected at a concentration of 0.029. The LRL for nitrite varied from 0.006 to 0.01 mg/L, and the lowest nitrite concentration detected in an environmental sample collected with an automatic sampler was 0.014 mg/L. However, nitrite concentrations isolated from the parameter nitrite+nitrate are not reported in this study because they were nearly always negligible in comparison with nitrate concentrations. Therefore, such a slight positive bias in sample nitrite levels would not affect the interpretation of data presented in this report.

There were no detections of nitrite+nitrate in blank samples collected using standard USGS protocols. There was one detection of nitrite+nitrate in a blank collected by automatic sampler (0.054 mg/L). However, the lowest nitrite+nitrate concentration detected in any environmental sample collected by these samplers (0.27 mg/L) was five times greater than the concentration detected in the blank sample. Therefore, the potential positive bias introduced by carryover contamination of nitrite+nitrate appears to be negligible, even when automatic samplers were used.

Table 4. Summary of quality-control sample results when standard U.S. Geological Survey (USGS) protocols (USGS, variously dated) were used, Santa Ana Basin, California

[LRL, laboratory reporting limit; mg/L, milligrams per liter; >, greater than indicated value; <, less than indicated value; E, estimated value; ºC, degrees Celsius; N, nitrogen; P, phosphorus; RPD, relative percentage difference; —, not detected]

Constituent (LRL, in mg/L) [USGS parameter code]	Number of equipment or field blank detections >LRL/analyses	Maximum concentration detected in blank samples (mg/L)	Minimum concentration detected in surface-water samples (mg/L)	RPD in 14 replicate samples (percent)		Number of replicate samples with greater than 10 percent RPD
Major ions				**Median**	**Maximum**	
Calcium (0.01–0.02) [00915]	1/13	E0.03	6.5	0.49	3.9	0
Magnesium (0.004–0.014) [00925]	0/13	—	.89	1.5	5.0	0
Potassium (0.1–0.24) [00935]	0/13	—	.69	2.3	9.5	0
Sodium (0.06–0.09) [00930]	0/13	E.076	3.0	1.5	3.5	0
Chloride (0.1–0.29) [00940]	0/13	—	.29	1.1	6.7	0
Fluoride (0.1) [00950]	0/13	—	<.1	3.2	11	1
Silica (0.05–0.09) [00955]	0/13	E.047	3.9	1.1	6.2	0
Sulfate (0.1–0.31) [00945]	0/13	—	1.3	.19	1.3	0
Residue on evaporation at 180ºC (10) [70300]	0/13	—	38	.52	2.1	0
Nutrients						
Nitrogen species (as N)						
mmonia (0.02–0.04) [00608]	1/14	.020	<.02	.73	14	1
Ammonia + Dissolved Organic N (0.1) [00623]	0/14	E.079	<.10	3.5	>136	2
Ammonia + Total Organic N (0.1) [00625]	1/14	.143	<.10	13	51	9
Nitrite + Nitrate (0.05) [00631]	0/14	—	<.050	1.5	8.2	0
Nitrite (0.006–0.01) [00613]	0/14	—	<.010	.00	67	2
Phosphorus species (as P)						
Dissolved Phosphorus (0.004–0.05) [00666]	1/14	.0060	<.050	1.2	88	3
Dissolved Orthophosphate (0.01–0.02) [00671]	2/14	.024	<.010	2.3	22	2
Total Phosphorus (0.004–0.05) [00665]	0/14	—	<.050	2.1	110	2

Table 5. Summary of quality-control sample results when automatic samplers were used, Santa Ana Basin, California

[LRL, laboratory reporting limit; mg/L, milligrams per liter; >, greater than indicated value; <, less than indicated value; °C, degrees Celsius; N, nitrogen; P, phosphorus; RPD, relative percentage difference; —, not detected]

Constituent (LRL, in mg/L) [USGS parameter code]	Number of equipment or field blank detections >LRL/analyses	Maximum concentration detected inblank samples (mg/L)	Minimum concentration detected in surface-water samples(mg/L)	RPD in 3 replicate samples (percent)		Number of replicate samples with greater than 10 percent RPD
Major ions				**Median**	**Maximum**	
Calcium (0.01–0.02) [00915]	6/8	0.61	5.7	1.6	3.3	0
Magnesium (0.004–0.014) [00925]	2/8	.20	.58	1.4	2.8	0
Potassium (0.1–0.24) [00935]	0/8	—	<.10	4.8	5.6	0
Sodium (0.06–0.09) [00930]	5/8	1.5	2.3	1.1	3.7	0
Chloride (0.1–0.29) [00940]	1/8	.61	2.0	.03	.90	0
Fluoride (0.1) [00950]	0/8	—	.11	2.4	8.4	0
Silica (0.05–0.09) [00955]	2/8	.36	1.3	1.6	3.1	0
Sulfate (0.1–0.31) [00945]	1/8	1.3	2.2	.24	.54	0
Residue on evaporation at 180°C (10) [70300]	0/8	—	31	.57	3.4	0
Nutrients						
Nitrogen species (as N)						
Ammonia (0.02–0.04) [00608]	1/8	.021	.027	.34	2.0	0
Ammonia + Dissolved Organic N (0.1) [00623]	0/8	—	.37	.74	46[1]	1
Ammonia + Total Organic N (0.1) [00625]	0/8	—	.75	16	17	2
Nitrite + Nitrate (0.05) [00631]	1/8	.054	.27	1.4	3.2	0
Nitrite (0.006–0.01) [00613]	2/8	.029	.014	2.6	2.8	0
Phosphorus species (as P)						
Dissolved Phosphorus (0.004–0.05) [00666]	0/8	—	.076	.81	9.9	0
Dissolved Orthophosphate (0.01–0.02) [00671]	2/8	.024	.057	1.3	1.5	0
Total Phosphorus (0.004–0.05) [00665]	0/8	.020	.22	2.0	5.1	0

[1] The RPD of 46 percent occurred for a replicate performed to compare the equal-width-increment (EWI) method with the automatic-sampling method. The large RPD may have been a result of the different sampling methods.

Residue-on-evaporation at 180°C (ROE), the analytical measure of TDS, was never detected in blanks at the LRL of 10 mg/L. Concentrations of some major ions (constituents of TDS) were occasionally detected, up to a few tenths of a milligram per liter above their LRL in blanks collected with automatic samplers. However, no major ions were ever detected in blanks from either group (collected by standard USGS protocols or using automatic samplers) at concentrations exceeding the minimum concentration detected in environmental samples from the respective groups.

Replicate results were evaluated for each analyte of interest by calculating the relative percentage difference (*RPD*) between the analyte concentrations in environmental samples and the concentrations in their corresponding duplicate samples. The *RPD* is calculated for each sample pair using the following equation:

$$RPD = 100 \times |S_1 - S_2| / (S_1 + S_2)/2,$$

where

S_1 is the concentration of the environmental sample; and

S_2 is the concentration of the duplicate sample.

Seventeen replicates comparing analyzed concentrations of 17 nutrient and TDS constituents were performed for this study. Three of the seventeen replicates were performed using automatic samplers. Summarized in tables 4 and 5 are the RPDs calculated from the results of these replicates for each analyte.

Seven nutrient analytes had an RPD of more than 10 percent in at least one replicate. Most of the large RPDs were observed for the analyte consisting of total organic nitrogen plus ammonia (TON+ammonia). Eleven out of the seventeen replicates had RPDs greater than 10 percent for this analyte; the highest of these occurred in three replicates with relatively low sample concentrations (less than 0.1 mg/L) of TON+ammonia. These three replicates had RPDs of 37, 50, and 51 percent. Replicates having more typical concentrations of TON+ammonia (0.1 to 2 mg/L) had lower RPDs ranging from 4 to 22 percent. However, even a replicate sample having extremely high concentrations of TON+ammonia (44 and 37 mg/L) had an RPD of 17 percent. High analytical variability for TON+ammonia could lead to substantial error in the calculation of total nitrogen in samples having high proportions of nitrogen in these forms. Such variability is of less consequence when most of the nitrogen in the sample is in the form of nitrate.

Three RPDs for dissolved organic nitrogen + ammonia (DON+ammonia) were greater than 10 percent in three replicates, but the high variability for two of these cases has possible explanations. In one of these the RPD was greater than 136 percent. For this replicate, DON+ammonia was not detected in the environmental sample at the LRL of 0.1 mg/L. The corresponding duplicate sample had a concentration of 0.5 mg/L. Typically, DON+ammonia was not detected at the site where this replicate was collected (South Fork). Therefore, it seems likely that the duplicate sample was contaminated during processing, shipping, or analysis. In another replicate with a high RPD for DON+ammonia (46 percent), the environmental sample (0.71 mg/L) was collected by equal-width-increment (EWI), and the duplicate sample (1.1 mg/L) was collected with an automatic sampler. The large variability in this case may have resulted from the different sampling methods. The third case of an RPD greater than 10 percent for DON+ammonia had an RPD of 14 percent, which represented a difference of less than 0.1 mg/L between the environmental sample (0.64 mg/L) and the corresponding duplicate (0.56 mg/L). This level of analytical variability in dissolved organic nitrogen + ammonia would not affect our ability to understand nitrogen dynamics in the study basin.

For phosphorus species, RPDs were sometimes greater than 10 percent, but this usually only occurred at low sample concentrations (less than 0.1 mg/L). Only one replicate had an RPD greater than 10 percent for a phosphorus analyte at a concentration of potential environmental concern. In that case the environmental sample had a dissolved phosphorus concentration of 0.98, and the corresponding duplicate sample had a concentration of 0.38—resulting in an RPD of 88 percent. Considering the concentrations of other forms of phosphorus in both the environmental and duplicate samples, and the range of dissolved phosphorus observed in other base-flow samples collected from the site in question (Imperial Highway), it appears that the duplicate sample was compromised before analysis for this parameter. The result is considered an isolated case. Replicate analyses for ROE (the analytical measure of TDS) and major ions (constituents of TDS) generally did not show high variability.

The Inorganic Blind Sample Project (IBSP), a USGS quality-assurance program, reported laboratory variability and biases for some methods of nutrient analysis used by the USGS National Water Quality Laboratory for this study. Periodic quality-assurance summaries from their database reported analytical variability during at least some of the study period for dissolved phosphorus, ammonia, and nitrate. Additional information on the IBSP can be found at the following URL:
http://bqs.usgs.gov/bsp/mainpage.html.

SUMMARY

Total dissolved solids (TDS) and concentrations of nutrients in selected Santa Ana Basin streams were examined as a function of water source. The principal water sources are mountain runoff, wastewater, urban runoff, and stormflow. Six fixed surface-water sites were sampled at least monthly from October 1998 to September 2000 for species of nitrogen and phosphorus, residue on evaporation (the analytical measure of TDS), and individual major ions (the main constituents of TDS). At least six storm-event samples were collected from each fixed site during this period. Monthly sampling continued through April 2001 at one fixed site (Imperial Highway), and until September 2001 at three of the fixed sites (Mentone, Warm Creek, and Prado), with the exception that no samples were collected in November 2000 at any site. One of the fixed sites (Mentone) was located at the base of the San Bernardino Mountains. Six additional mountain sites were sampled quarterly from January 2000 to July 2001, including single storm-event samples collected at two of the sites. Water quality at the Mentone site appears to be representative of reference conditions for water entering the valley floor.

The major-ion compositions in samples from the different sites indicate distinct sources of water and in-stream processes in the basin. Base-flow samples from most mountain sites tended to have a calcium-bicarbonate composition. However, the major-ion composition of East Twin Creek base-flow samples was dominated by sodium/potassium-sulfate, and the Mentone samples which were affected by the construction of Seven Oaks Dam also tended toward that composition. The water composition at Warm Creek was highly variable, but was approximately intermediate to the compositions of the mountain sites located upgradient of the site (Cajon Creek, Devil Canyon Creek, and East Twin Creek). Water compositions at the Prado Dam and Imperial Highway sites were similar and appeared to be a mixture of the waters at the MWD, Cucamonga Creek, and Warm Creek sites.

The median TDS in base-flow samples from mountain sites, including the fixed site near Mentone, was 200 mg/L. Base-flow TDS from valley-floor sites typically ranged from 400 to 600 mg/L regardless of water source. Sparse data indicate that TDS in urban runoff range from about 250 to 370 mg/L, which approximate levels reported for the basin domestic supply (City of Redlands, 2002; Metropolitan Water District of Southern California, 2002; Western Municipal Water District, 2002; San Bernardino Valley Municipal Water District, 2002). TDS increases downstream along the main stem of the Santa Ana River, regardless of source inputs.

Rainfall usually dilutes stream TDS. The median TDS of all samples collected during or shortly after storms was 260 mg/L. However, stormflow TDS was highly variable, especially during relatively small rainfall events. Hydrograph separations were performed to isolate stormflow from base flow for 87 rainfall events at three fixed sites. The median flow-weighted average TDS concentration for isolated stormflow during these events was 190 mg/L. However, stormflow TDS concentrations were lower and far less variable during relatively large events (greater than 0.30 to 0.45 in. of rain), with values typically closer to 100 mg/L.

Base-flow nutrient concentrations, like TDS, were usually lowest in samples from sites receiving mountain runoff. From the perspective of water managers, the nutrient species of greatest concern in the Santa Ana Basin is nitrate. Laboratory analyses for nitrate included a mostly negligible contribution of nitrite. However, because the nitrite compound carries the same concerns as nitrate, concentrations for the combined parameter (nitrite+nitrate) are presented in this report. Streams fed by mountain runoff had median base-flow concentrations of nitrite+nitrate mostly below 0.3 mg/L. Nitrite+nitrate concentrations in both urban runoff and stormflow were near 1 mg/L, which is close to the level found in rainfall for the region. Nitrite+nitrate concentrations in the Santa Ana River and its major tributaries are highest where stream flow is dominated by wastewater effluent. Nitrite+nitrate concentrations in samples collected from the four fixed sites located downstream from these inputs ranged from about 5 to 7 mg/L, mostly representing the wastewater discharges. In addition, rising ground water along this stretch of the river also had high nitrite+nitrate concentrations. Five samples were collected from sites dominated by rising ground water, and all five samples had nitrite+nitrate concentrations above 10 mg/L, the U.S. Environmental Protection Agency (2002) drinking-water standard.

Concentrations of other nitrogen compounds were much lower than nitrate in base-flow samples. Ammonia (dissolved NH_3+NH_4^+) was usually less than 0.04 mg/L in samples from mountain sites, and concentrations tended to be well below 1 mg/L in samples from the valley-floor sites. Using criteria established in 1999 by the USEPA, ammonia was not observed at levels considered toxic to aquatic life in samples collected for this study. Mountain sites typically had base-flow concentrations of organic nitrogen below 0.1 mg/L. Base-flow organic nitrogen concentrations at Warm Creek ranged from less than 0.1 mg/L to 0.9 mg/L, with a median of 0.3 mg/L. Fixed sites downstream from wastewater inputs had base-flow concentrations ranging from 0.2 to 3.0 mg/L, with a median of 1.0 mg/L. Storm events increased concentrations and the proportions of organic nitrogen, ammonia, and nitrite relative to nitrate.

Concentrations of total phosphorus (TP) were usually below 0.03 mg/L in samples from sites receiving mountain runoff. Base-flow TP concentrations at the urban indicator site on Warm Creek, which receives rising ground water and urban runoff, were typically at about 0.03 mg/L. These levels were well under the general goal set (in 1986) by the USEPA of less than 0.1 mg/L to control for eutrophication. TP concentrations in samples from fixed sites below wastewater inputs typically have TP concentrations near 1 mg/L, indicating a departure from reference conditions and a potential for phosphorus-driven eutrophication. The USEPA also set (in 1986) a general goal for total phosphates in streams of less than 0.05 mg/L to control for accelerated eutrophication. As with total phosphorus, sites not receiving wastewater usually had concentrations of dissolved orthophosphate under the goal, whereas sites that received wastewater usually had concentrations above the goal.

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