An Assessment of Optical Properties of Dissolved Organic Material as Quantitative Source Indicators in the Santa Ana River Basin, Southern California

By Brian A. Bergamaschi, Erica Kalve, Larry Guenther, Gregory O. Mendez, and Kenneth Belitz

Prepared in cooperation with the Orange County Water District

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Conversion Factors and Abbreviations

CONVERSION FACTORS

Multiply	By	To obtain
mile (mi)	1.609	kilometer (km)
square mile (mi^2)	2.590	square kilometer (km^2)

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

$$°F = (1.8 \times °C) + 32$$

ABBREVIATIONS

A	absorbance unit
A-L/mg	absorbance in liters per milligram
cm^2	square centimeter
µL	microliters
µM	micromoles
mg/L	milligrams per liter
mL	milliliters
nm	nanometers
QSU-L/mg	quinine sulfate units in liters per milligram
W	watt
cDOM	colored or chromophoric dissolved organic matter
DOC	dissolved organic carbon
DOM	dissolved organic material
EEM	excitation/emission matrix
FI	fluorescence intensity
PAH	polycyclic aromatic hydrocarbon
PCA	principal component analysis
SFI	carbon-specific fluorescence intensity
SUVA	specific ultra violet absorbance
UV	ultraviolet
UVA	ultraviolet absorbance at 254 nanometers
PCA	principal component analysis
N	nitrogen
EPA	U.S. Environmental Protection Agency
NAWQA	National Water Quality Assessment
USGS	U.S. Geological Survey

SITE ABBREVIATIONS

CML	Cucamonga Creek near Mira Loma
D1	Dairy Pond 1
D2	Dairy Pond 2
D3	Dairy Pond 3
D4	Dairy Pond 4
D5	Dairy Pond 5
H60	Cucamonga Creek at Highway 60
IMP	Santa Ana River at Imperial Highway
MEN	Mentone
MWD	Metropolitan Water District Crossing
PRD	Prado Reservoir
RP1	Inland Empire Utilities Agency Reclamation Plant 1
SDC	Mill Creek at Duck Club
SF	South Fork of the Santa Ana River
WC	Warm Creek

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Abstract

The ability to rapidly, reliably, and inexpensively characterize sources of dissolved organic material (DOM) in watersheds would allow water management agencies to more quickly identify problems in water sources, and to more efficiently allocate water resources by, for example, permitting real-time identification of high-quality water suitable for ground-water recharge, or poor-quality water in need of mitigation. This study examined the feasibility of using easily measurable intrinsic optical properties—absorbance and fluorescence spectra—as quantitative indicators of DOM sources and, thus, a predictor of water quality. The study focused on the Santa Ana River Basin, in southern California, USA, which comprises an area of dense urban development and an area of intense dairy production. Base flow in the Santa Ana Basin is primarily tertiary treated wastewater discharge. Available hydrologic data indicate that urban and agricultural runoff degrades water quality during storm events by introducing pathogens, nutrients, and other contaminants, including significant amounts of DOM. These conditions provide the basis for evaluating the use of DOM optical properties as a tracer of DOM from different sources.

Sample spectra representing four principal DOM sources were identified among all samples collected in 1999 on the basis of basin hydrology, and the distribution of spectral variability within all the sample data. A linear mixing model provided quantitative estimates of relative endmember contribution to sample spectra for monthly, storm, and diurnal samples. The spectral properties of the four sources (endmembers), Pristine Water, Wastewater, Urban Water, and Dairy Water, accounted for 94 percent of the variability in optical properties observed in the study, suggesting that all important DOM sources were represented. The scale and distribution of the residual spectra—that not explained by the endmembers— suggested that the endmember spectra selected did not adequately represent Urban Water base flow. However, model assignments of sources generally agreed well with those expected, based on sampling location and hydrology. The results suggest that with a fuller characterization of the endmember spectra, analysis of optical properties will provide rapid quantitative estimates of the relative contribution of DOM sources in the Santa Ana Basin.

Introduction

As water interacts with its environment, it accumulates dissolved organic material (DOM) through interaction with a wide variety of source materials, each with distinct chemical characteristics. Thus, the chemical characteristics of DOM contain information regarding the source of the organic material and, perhaps, the route the water in which it is dissolved has taken to a given location. One simple method often used to gather information about the chemical composition of DOM is to quantify interactions with light —its optical properties. Only a fraction of the DOM interacts with light, either by absorbing light through chromophores or by fluorescing, in response to light through fluorophores. The extent to which light of a particular wavelength interacts with the organic material is potentially characteristic of the intrinsic chemical composition of the organic material (Skoog, 1985), providing some information about its source and the source of the water that carries it.

A pilot study was done to assess whether chemical differences expressed in these optical properties (absorbance and fluorescence) are useful for quantifying the relative contribution of DOM sources and, by extension, the sources of Santa Ana Basin water in which the DOM is transported. This study was done in cooperation with the Orange County Water District (OCWD).

Purpose and Scope

This report describes an assessment of the optical properties of dissolved organic material as quantitative source indicators in the Santa Ana River Basin. A four-component mixing-model using optical properties representative of four endmembers (relatively Pristine Water, Wastewater, Urban Water runoff, and Dairy Water) was used to analyze spectra of samples from across the Santa Ana Basin and, thereby, to evaluate relative source contributions. The results of the mixing model were compared to expected results and hydrologic data, where available, and are presented in this report. The data, collected in 1999, also are presented.

Comparison of model results using the full spectrum of optical properties to model results using a selection of only

16 specific optical properties – a subset of the more than 2000 measurements made on each sample – revealed that source assignments using only a few measurements generally agreed with the full model estimates. This result suggests that more economical sensors and simpler analytical methodologies would be effective for similar source studies and routine monitoring.

Background

A variety of specific optical measurements commonly are used to quantify and understand environmental processes. Optical measurements, as distinct from optical properties analysis, can be defined broadly as measurements of the interaction of light with the suspended particulates and with dissolved or colloidal materials. An example of one routine use of optical measurements in the water-quality arena is measurement of suspended-sediment concentration using the backscatterance of light (for example, Schoellhamer, 1993). Backscatter is correlated through a series of calibration measurements to the suspended-sediment concentration. Also, chlorophyll fluorescence commonly is used to quantify total algal biomass, either in place or remotely, by relating it to chlorophyll-specific biomass (for example, Lavender and Groom, 2001).

Measurements of absorbance and fluorescence optical properties have been extensively employed to characterize the source and composition of DOM. A small subset of DOM, the colored or chromophoric dissolved organic matter (cDOM), comprising approximately 10 percent of the total DOM pool, is used to provide compositional information. In natural waters, cDOM is the primary dissolved constituent that absorbs ultraviolet (UV) light, with the spectral properties of this absorbance related to chemical composition and molecular size (Mopper and others, 1996; Stedmon and others, 2000). Spectral properties of fluorescence provide compositional information analogous to UV absorbance, but for a much smaller fraction of the DOM; only approximately 1 percent of DOM responds to visible or UV irradiation by emitting fluorescent light (Mobley, 1994).

Historically, the most common optical measurement used to characterize DOM has been the absorbance of UV at a single wavelength, typically 254 nanometers (nm). However, there is some confusion about why studies have focused on 254 nm as the wavelength of interest. Some sources suggest it was chosen because 254 nm is near one of the absorption maxima for aromatic structures within DOM (256 nm), while others suggest it is an artifact of using a mercury–argon lamp for early measurements, which has an output maximum of 253.7 nm (Skoog, 1985).

The UV absorbance at 254 nm (UVA) has been shown to correlate reasonably well with DOM content over a wide range of environmental samples (for example, see Fram and others, 1999), a result of the underlying general relationship between cDOM and DOM. Although the presence of interfering species such as iron (Weishaar and others, 2003) or nitrate (Ogura and Hanya, 1966; Skoog, 1985) may alter the correlation between UVA and DOM concentration, recent studies have shown that variations in the aromatic content of the DOM accounts for most of the variability observed between environmental samples (Fram and others, 1999; Weishaar and others, 2003). This is precisely the sort of chemical compositional indicator that may prove useful in source identification.

The U.S. Environmental Protection Agency (EPA) has promulgated regulations that capture variations in DOM chemical composition by normalizing the UVA value to separate measurements of DOM content. This parameter, usually referred to as specific UV absorbance, or SUVA, an expression of the cDOM:DOM ratio, is an indicator of compositional differences in samples, independent of concentration. The SUVA value can be a good indicator of the humic content of natural waters, and has been correlated in some instances with disinfectant by-product formation (Korshin and others, 1999; Barrett, 2000). However, compositional differences between source waters are frequently more complex than can be captured by the one-dimensional SUVA parameter. UV absorbance at wavelengths other than 254 nm provides additional information about the chemical moieties within DOM, as well as about inorganic species such as nitrate and sulfide (Skoog, 1985; Thurman, 1985).

Fluorescence measurements permit greater discrimination between chemical moieties because the wavelength of absorbed light (the excitation wavelength) and the wavelength of emitted light (the emission wavelength) are related to the chemical composition of the sample. This commonly is expressed as an excitation/emission matrix (EEM), wherein the intensity of fluorescence is arrayed against the irradiation, or excitation wavelength on one axis, and the wavelength of fluorescent emissions on the other. Although less common than UV absorbance as an analytical tool, several studies have used this sort of fluorescence spectroscopy to characterize DOM in natural waters. Goldberg and Weiner (1989) focused primarily on fluorescence measurements of natural fulvic acid from the Suwannee River in the southeastern United States, the standard aquatic fulvic acid of the International Humic Substances Society. Fulvic acids represent approximately 80 percent of the DOM in the Suwannee River, and typically are a large percentage of DOM in natural waters (Thurman, 1985). Goldberg and Weiner (1989) observed a 90-nm overlap between excitation/emission bands, attributing it to the contribution of multiple fluorophores within the pool of DOM.

Others have observed that EEM peak locations are characteristic of DOM source (Coble, 1996; Mobed and others, 1996). For example, Coble and others (1993) and Coble (1996) report that samples containing marine DOM consistently exhibit excitation/emission peaks at a lower wavelength than riverine or coastal water samples. They attribute these differences to differences in the underlying chemistry of the DOM, with the marine samples having a fluorescence pattern roughly similar to proteins and the river samples having a fluorescence pattern more similar to humic substances. Mobed and others (1996) compared the fluorescence spectrum of aquatic-

and soil-derived humic substances from the International Humic Substances Society and found differences sufficient to discriminate between these sources.

In addition to studying naturally occurring humic substances, fluorescence spectroscopy has proven effective at identifying polycyclic aromatic hydrocarbons (PAHs) from natural and anthropogenic source materials (Booksh and others, 1996; Ferrer and others, 1997; Beltran and others, 1998). Beltran and others (1998) demonstrated that fluorescence excitation/emission characteristics are sufficient to resolve mixtures of PAHs when combined with numerical analytical techniques such as chemometric analysis (Sharaf and others, 1986). The results were accurate to between 5 and 20 percent for synthetic mixtures of PAHs.

These and other studies demonstrate that absorbance and fluorescence optical properties respond to variations in DOM concentration and composition and suggest that source-specific information may be obtained from a broad suite of optical analyses.

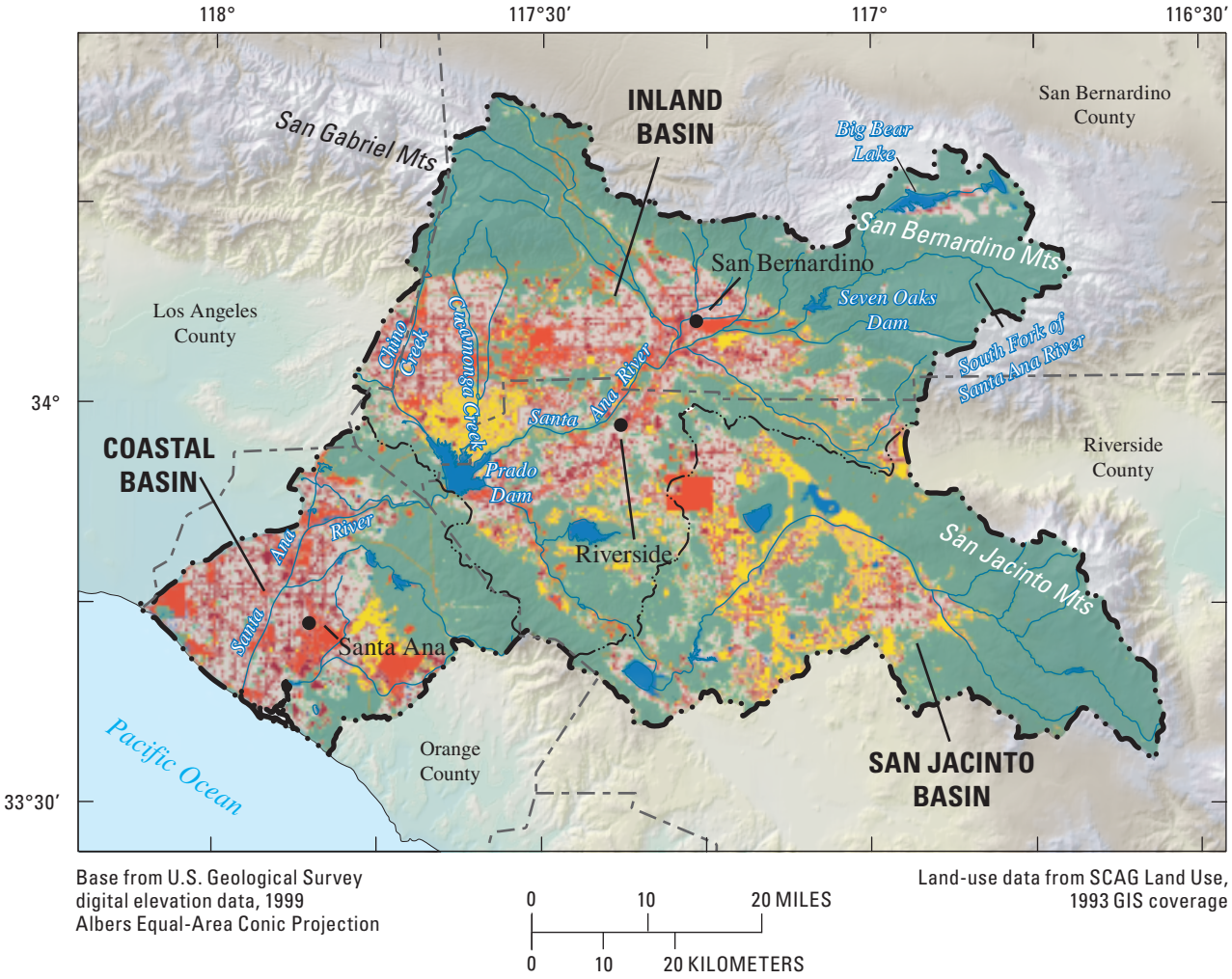
The goal of this study was to evaluate if variations in a broad suite of absorbance and fluorescence optical properties of DOM are useful as intrinsic tracers of the sources of DOM. Measurements were made on discrete samples collected within the Santa Ana watershed as part of another study (Burton and others, 1998; Izbicki and others, 2000; Belitz and others, 2004; Kent and Belitz, 2004). The suite of optical properties we analyzed encompassed the full spectrum of UV absorbance as well as a broad spectrum of UV and visible fluorescence. Variation in these spectra among the samples was used to identify the contributing sources of DOM. A linear mixing model then was used to quantitatively estimate the relative contribution of the sources to individual samples. Finally, these resulting estimates were evaluated against known DOM sources in the watershed, as well as quantitatively evaluated in relation to changes in the hydrograph.

Acknowledgments

This study would not have been possible without the generous assistance of the personnel on the USGS Santa Ana National Water Quality Assessment (NAWQA) program, who provided the means to collect and process these samples in a timely manner. Kathryn Crepeau, Susan Bird, Josh Berghouse, Kelley Paxton, Ellen Avery, and Miranda Fram expertly dispatched all necessary duties in the laboratory. This report benefited from careful reviews by John Izbicki, Lee Davisson, Greg Woodside, Roger Fujii, and Miranda Fram. The Orange County Water District and the USGS Drinking Water Initiative provided the funding to support this effort. The authors are grateful for this assistance.

Study Area Description

The Santa Ana Basin contains the largest stream system in southern California, draining an area of approximately 2,670 square miles (mi^2) of San Bernardino, Riverside, Los Angeles, and Orange Counties (*fig. 1*), and is divided into the Coastal, San Jacinto, and Inland sub-basins labeled as Basins on figure 1. This study examines the portion of the Santa Ana River main stem within the Inland sub-Basin and Cucamonga Creek, a major tributary.



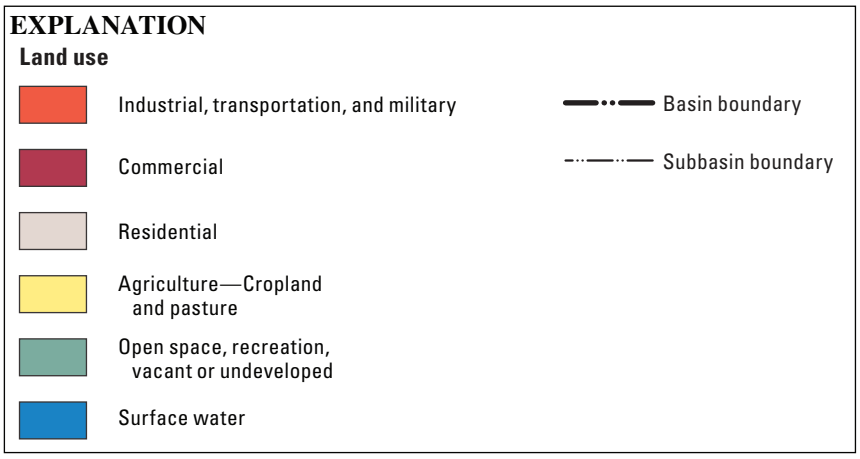
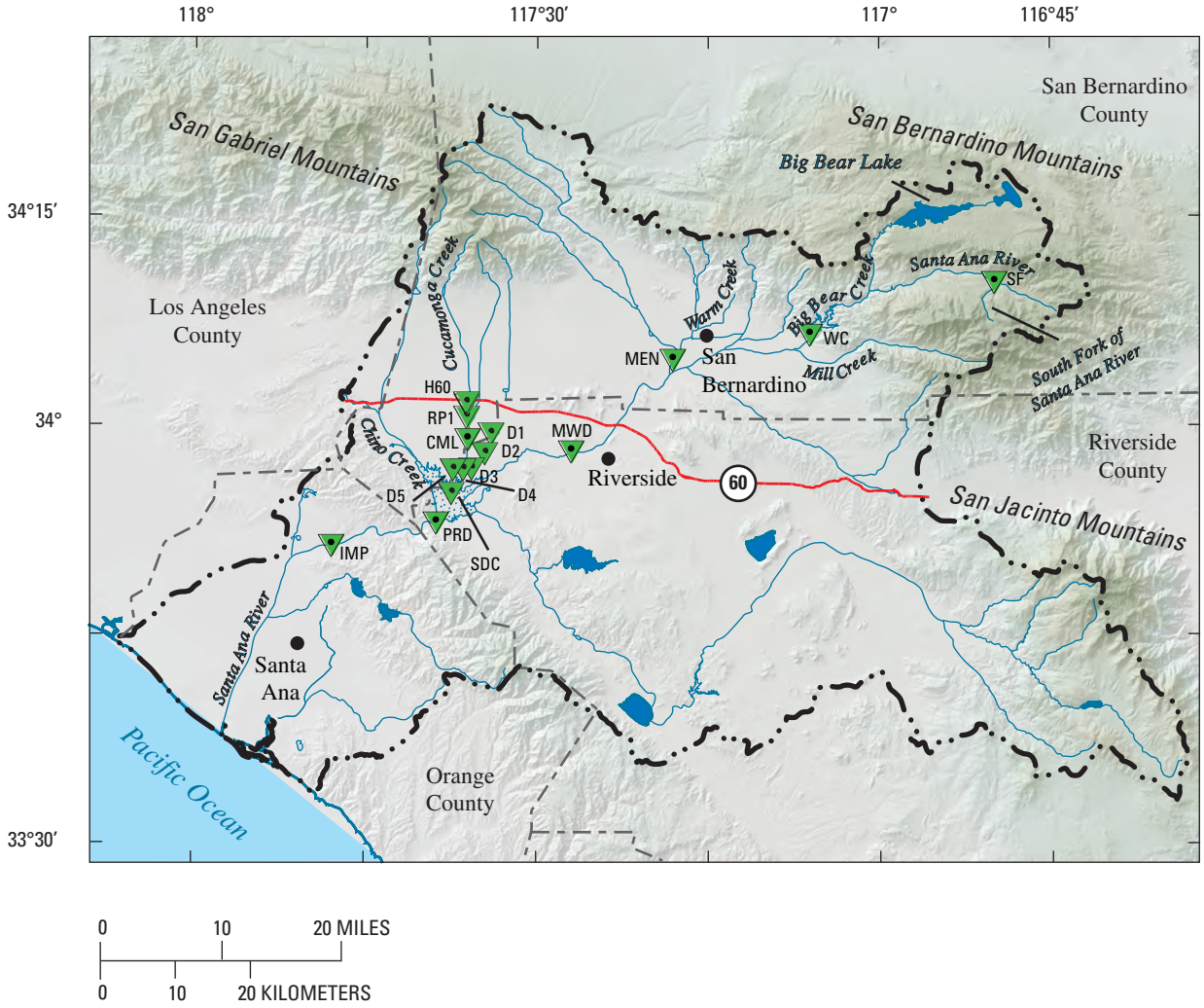


Figure 1. Location of study area and land use in the Santa Ana River Basin, southern California.

The Santa Ana River begins in the alpine areas of the San Bernardino Mountains, flows through a series of alluvial valleys, and eventually discharges into the Pacific Ocean near Huntington Beach, more than 100 miles away (*fig. 1*). Shortly after the Santa Ana River descends from the mountainous area, its flow is lost to stream-bed infiltration. Just below the mountain region, the river flow is derived from ground water seepage and from urban base flow. Further downstream, the river maintains a fairly continuous base flow during the year, with tertiary-treated wastewater comprising up to 80 percent of the base flow. Within this study area, we collected water samples from two alpine areas— from a small urban watershed at the base of the San Bernardino Mountains and from the Santa Ana River at the Metropolitan Water District Crossing (MWD) —effectively the first perennial Santa Ana River site supplying flow to the lower Santa Ana Basin (*fig. 2*).



EXPLANATION

Basin boundary

Sampling site

SF	South Fork	IMP	Imperial Highway
MEN	Mentone	D1	Dairy Pond 1
WC	Warm Creek	D2	Dairy Pond 2
MWD	MWD Crossing	D3	Dairy Pond 3
H60	Highway 60	D4	Dairy Pond 4
RP1	Inland Empire	D5	Dairy Pond 5
CML	Mira Loma	SDC	Mill Creek at Duck Club
PRD	Prado		

Figure 2. Locations of sites sampled in the Santa Ana River Basin, southern California.

Cucamonga Creek is a perennial tributary of the Santa Ana River that begins in the San Gabriel Mountains and flows through an urban landscape into an area of highly concentrated agricultural cropland, pasture and livestock production. Discharge from the Inland Empire Utility Agency Reclamation Plant 1 (RP1) (*fig. 2*), located near Highway 60, accounts for more than 90 percent of base flow below this location. From there, flow is contained in a concrete-lined channel past Mira Loma (CML) (*fig. 2*), and into Mill Creek at Duck Club (SDC) and Prado Reservoir (PRD). Upstream from site RP1, base flow is mostly surface runoff from urban areas. We collected samples from the urban area below site RP1 in a divided channel, and from downstream of both areas near Mira Loma on Cucamonga Creek (sites RP1 and CML, *fig. 2*).

Site PRD (*fig. 2*) integrates water from the three study areas within the Santa Ana River drainage. The primary inflow to the reservoir is water traversing site MWD (*fig. 2*) on the Santa Ana River main stem, with additional inputs from Cucamonga and Chino Creeks, as well as other sources not sampled as part of this study. We collected water from two Santa Ana River main stem sites downstream of Prado Reservoir; sites PRD and Santa Ana River at Imperial Highway (IMP), *fig. 2*.

Information about water use in the Santa Ana watershed is available in Burton and others, 1998; Izbicki and others, 2000; Belitz and others, 2004; and Kent and Belitz, 2004.

Sampling and Analytical Methods

Samples were collected simultaneously during a study by the U.S. Geological Survey (USGS) Santa Ana NAWQA program. This study includes different types of water samples collected between January and August 1999, comprising monthly samples that were collected at several sites to define baseflow conditions, storm samples that were collected at several sites to characterize the optical response to rapid increases in storm water flow, and time-series samples that were collected to characterize daily variability. Specific sample collection locations and times are presented in tables 1–3 and sampling locations are shown on *figure 2*.

All samples were filtered in the field as quickly as practical through precombusted glass fiber filters with a 0.3 micromoles (µM) nominal pore size, packed on ice and shipped overnight to the USGS laboratory in Sacramento, Calif. All samples were analyzed for DOM, UVA, and fluorescence.

Dissolved Organic Material

DOM measurements are expressed here as dissolved organic carbon (DOC) concentration, measured on filtered samples with a Shimadzu TOC-5000A total organic carbon analyzer according to the method of Bird and others (2003). The TOC-5000A was calibrated with potassium hydrogen phthalate standards prepared in "organic-free" water with standard concentrations bracketing the concentration of the samples. Each sample aliquot [4.5 milliliters (mL)] was acidified using 30 microliters (µL) 2 N hydrochloric acid and sparged with nitrogen for 3 minutes to remove inorganic carbon as carbon dioxide. The nonpurgeable organic carbon (NPOC) was measured by direct injection of liquid sample into a high-temperature (680ºC) combustion tube packed with Pt catalyst. The carbon dioxide produced by oxidation of the NPOC was detected with a nondispersive infrared photometric cell. Each analysis represents the mean of three or more injections. Accuracy and precision for this method are within 3 percent of the measured value (Bird and others, 2003).

Ultraviolet Absorbance

All ultraviolet absorbance was measured over the 190–310-nanometer wavelength range using a Perkin-Elmer Lambda 3B Double-Beam UV/Visible Spectrophotometer equipped with a deuterium lamp source. The reference cell is a 1-square-centimeter (cm^2) quartz cuvette that is kept filled with double deionized, "organic-free" water. The sample cell also is a 1-square centimeter quartz cuvette. Cuvettes are cleaned using an acid-base-acid treatment and rinsed thoroughly before use. The split beam design increases precision by simultaneously measuring the reference and sample cells. The wavelength output then is measured by a photomultiplier transducer and recorded in absorbance units, A (Skoog, 1985). The wavelength accuracy on the Lambda 3B is ±0.002 A. Data below 210 nm were not used in data analysis.

Aside from filtering, no further sample processing was performed before analysis, except that highly concentrated samples were analyzed at various dilutions to stay within the linear range of the UV instrument. All optical samples were analyzed after equilibration to 25ºC.

Fluorescence

All fluorescence data were collected using the SPEX FluoroMax-3 Spectrofluorometer. The FluoroMax-3 illuminates samples using a 150-watt (W) continuous-output, ozone-free Xenon arc lamp and is equipped with two Czerny-Turner monochromaters for controlling excitation/emission wavelengths measured. We used slit widths of 5 nm for excitation/emission, with an automatic shutter to protect the samples from photo bleaching. The signal is corrected by use of the reference detector, used to monitor and correct for wavelength response of the Xenon lamp and excitation monochromator as well as for fluctuations in the lamp power supply.

After the sample is given time to equilibrate to 25ºC, it was placed in a 1-square-centimeter quartz cuvette, then placed in the sample compartment. Excitation/emission spectra were generated by successive recording of the fluorescence emission wavelength using 40 fixed excitation wavelengths. We excited from 255 to 600 nm in equally spaced increments of 11 nm, and collect emission from 250 to 700 nm. The

resulting 5,700 excitation/emission pairs then were processed to remove Raman spectra that are common to all aqueous samples. This leaves 2,576 excitation/emission pairs that comprise the excitation/emission matrix (EEM) of fluorescence response for each sample. The total fluorescence intensity (FI) of a sample is the integrated value of the fluorescent response across the excitation and emission domains.

Data Analysis

Definitions

We used several empirical and derived parameters to assist in the evaluation of the absorbance and fluorescence spectral data. These are defined and explained below.

Excitation/Emission Pairs

Fluorescence data frequently are reported as excitation/emission maxima, meaning the excitation and emission wavelengths at which the maximum fluorescence intensity was observed. In this study, we use all such excitation/emission pairs to describe the fluorescent response of a sample, presenting the data as an EEM of the fluorescent emission observed at every excitation tested (see, for example, *fig. 3*). We express the result in quinine sulfate units (QSU)s. One QSU is equivalent to the fluorescence intensity of 1-micromolar solution of quinine sulfate in 0.1 molar sulfuric acid at an excitation wavelength of 350 nm and an emission wavelength of 450 nm (350/450).

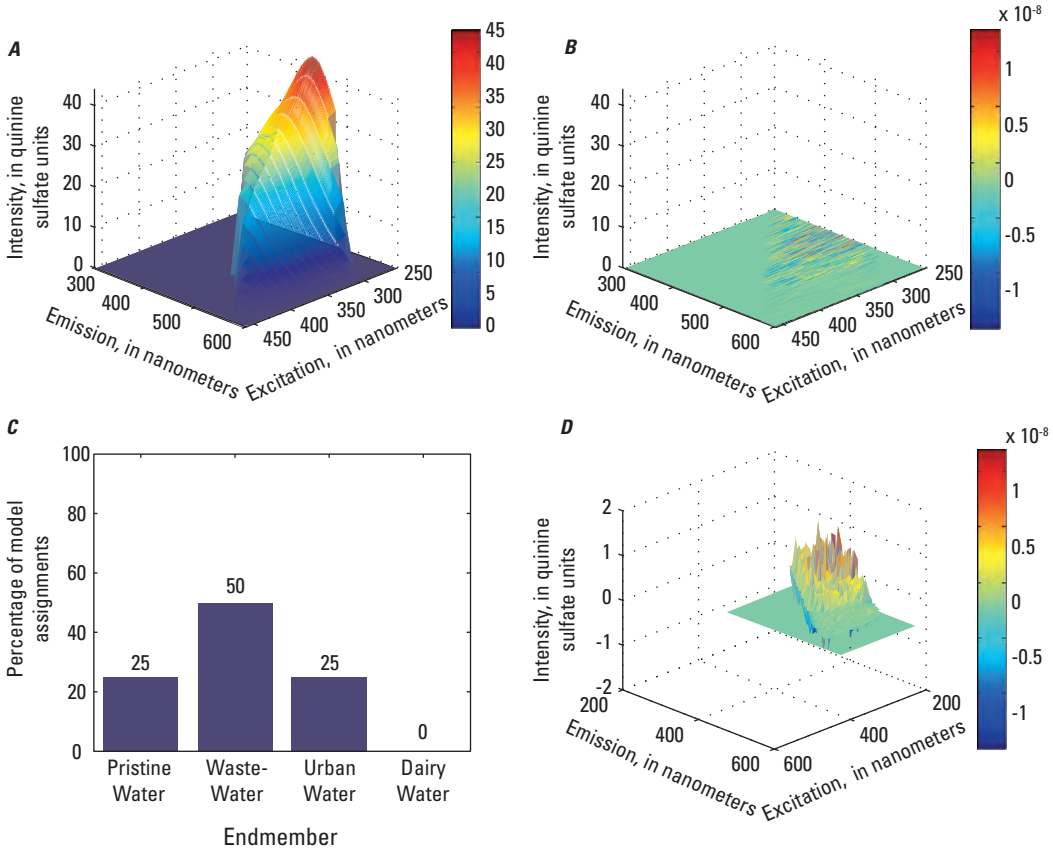


Figure 3. Results of model application to synthetic data. (A) synthetic spectra composed of endmember spectra, (B) residual of model results at same scale as full spectra, (C) model results for synthetic sample spectra, and (D) residual of model results; residual = 1.35e-8 percent of synthetic sample.

Three peaks often were prominent in the EEM of samples from this study. The first was at 255-nanometer excitation and 435-nanometer emission (255/435), and the remaining two at 323/435 and 255/350. When occurring together in relatively equal intensities, these peaks most often were associated with wastewater sources, but their presence or absence proved a useful tool for comparison of spectra. The intensity of fluorescence at characteristic wavelengths has been associated with terrestrial humic material and is useful for broad evaluation of contributions to samples. The excitation/emission pairs used for this purpose here are 255/435, 323/435, 335/445, and 350/430. We also used two excitation/emission pairs correlated with protein-like fluorescence, 255/350 and 277/340 (Coble and others, 1993).

Specific Ultraviolet Absorbance (SUVA)

The UV absorbance spectrum for most samples is a simple exponential function of wavelength, with higher absorption at lower wavelengths, and frequently represented by the absorption at a single wavelength, 254 nm (see Introduction section of this report). The carbon-specific UV absorption is reported as the SUVA, and is defined as the UVA normalized to the DOM. This value represents the concentration of chromophoric material within DOM. Thus, SUVA is a concentration-independent parameter that correlates with aromatic content of the dissolved constituents (Fram and others, 1999), although dissolved iron species, nitrate, and oxygen may interfere (Weishaar and others, 2003).

Specific Fluorescence Intensity

Unlike the UV spectrum, fluorescence intensity (FI) usually is not a smooth monotonic function, easily represented by a single excitation/emission pair. Therefore, we chose to use the FI integrated across all excitation/emission wavelengths as the one-dimensional expression of the content of fluorescent material, the analog to SUVA. This was accomplished by performing a trapezoidal integration of the full usable area of EEM fluorescence matrix. As for UV, it is useful to examine fluorescence efficiency per unit carbon, so we divide the FI by the sample DOM to generate the carbon-specific fluorescence intensity (SFI). SFI represents the concentration of fluorophores within the DOM, and is a concentration-independent parameter related to the quantum fluorescent efficiency of the dissolved constituents.

Modeling

A simple linear mixing model was constructed such that the matrix of measured optical responses of any sample was taken to be the sum of the contributions of each of the possible "endmember" sources. We refer to contributing sources as "endmembers" in this report because they were selected from among the samples as representative of responses associated with specific sources, and are not strictly representative of pure source contributors. A description of the endmembers and justification for their selection is presented in the "Model endmember selection" section of this report. To identify the contribution of each endmember, the model simply assumes that the spectral response of each sample is the product of the fractional contribution of each of the endmembers and the optical response of the endmember for each individual excitation/emission value in the matrix. Thus, in matrix notation, the model is simply

$$S = m * C \quad (1)$$

where 'S' is the sample matrix, 'm' is the matrix of the fractional contribution of endmembers, and 'C' is a matrix of the endmember spectra. We solve for m by multiplying the inverted endmember spectra matrix so that

$$\langle m \rangle = S * C^{-1} \quad (2)$$

where 'C^{-1}' is the inverse of the endmember spectra matrix and $\langle m \rangle$ is the matrix of estimated endmember contributions, the best nonnegative least-squares fit to the sample spectrum.

The difference between the composite endmember matrix and the sample matrix, termed the residual spectrum, R, provides a measure of how well the model reproduces the actual data, as well as a means to examine the properties of missing endmembers. The residual matrix is calculated as

$$R = S - (m * C) \quad (3)$$

To test the model, we generated synthetic sample spectra from linear combinations of the endmembers and compared the model results to the known endmember fraction in the synthetic mixture. This test was performed to determine the ability of the model to the discriminate between endmembers. These synthetic data sets were composed of a wide variety of endmember fractions, including several that contained, for example, order-of-magnitude differences between endmember fractions.

In the test data, differences between input and estimated endmember fractions typically differed by order 10^{-14}, which is the precision of the computer (*fig. 3 B,D*). Additionally, integrated values of residual spectra typically were of order 10^{-14} percent of the input data spectrum. We, therefore, concluded that the model was capable of deconvolving noise-free synthetic spectra representative of those found within the Santa Ana River Basin with a high degree of precision.

Results and Discussion

The goal of this study was to evaluate the extent to which optical properties of dissolved materials may be used as quantitative tracers for DOM from different sources, and, thereby, to elucidate hydrologic processes in the Santa Ana watershed. Because samples were collected on an empirical basis, we evaluated the approach using several subsets of samples to assess performance, first by using empirical relationships to verify quality and constancy of the optical properties, and then by using a simple linear mixing model to quantitatively estimate the contribution of DOM sources that produced them. Again, due to the empirical sampling, DOM sources were represented in the model by endmember spectra selected from among the samples. We used the following criteria to assist our assessment and tested each criterion separately:

Are the differences in optical properties among model endmembers greater than the random variation observed in blanks and replicates? To make this assessment, we applied the model to field blank and replicate samples to determine if random noise confounded interpretation.

Are the differences in optical properties among model endmembers greater than any changes that result from photo-exposure, degradation, or other reaction? To make this assessment, we examined diurnal changes to determine if these effects were of sufficient magnitude to confound model results.

Are the observed differences in optical properties between and among sampling sites consistent with the published relationships between specific optical properties and source? To make this assessment, we examined variations in empirical parameters in monthly, storm, and grab samples to assess if they were consistent with what is known about the hydrology and chemistry of the site, and the published information about selected DOM sources.

Are the model apportionments of DOM source consistent with what is known about sampling locations, inputs, chemistry, and hydrology? To make this assessment, we qualitatively examined variations in model assignments for monthly, storm, and grab samples to assess consistency with the sources and hydrology. In a few cases, it was possible to test model assignments quantitatively.

Do the variations in the contribution of endmembers account for the majority of variation in the full data set? This criterion requires that all major sources be represented in the endmember set. To make this assessment, we monitored the residual of the model fit to the sample data.

Note that the application of the model used in this study is independent of DOM concentration. Rather, it depends only on the spectral response. This approach ensures that similar sources contributing at different concentrations do not confound interpretation, but may limit the ability of the model to discriminate between sources with similar spectral properties.

DOM concentration was the dominant factor controlling this optical response for these samples from the Santa Ana Basin. The observed variation in FI was near three orders of magnitude, and the variation in UVA was near one order of magnitude (*fig. 4*). Variability in DOM concentration accounted for 89 percent of the variability in UVA, and 83 percent of the variability in FI (*fig. 4A,B*). This result agrees with previous studies of UVA and FI (Fram and others, 1999), which found that the total chromophore and fluorophore content was strongly related to the DOM concentration.

Much of the published information regarding optical properties of DOM sources relies on the carbon-specific chromophore (SUVA) or fluorophore (SFI) content (for example, Thurman, 1985). In this study, there was no clear relationship between the DOM-normalized parameter, SUVA, and its fluorescence analog, SFI (*fig. 4C*), indicating that variability in DOM controlled variability in total absorbance and total fluorescence. This lack of relationship is consistent with other studies and was expected because the chemical constituents absorbing UV light are much more abundant and diverse than those exhibiting fluorescence (Skoog, 1985; Thurman, 1985). However, qualitative examination of these parameters was useful for assessing the consistency of our observations with published data.

One of the observations made during this study was that deconvolution of the sources using the UV absorbance spectra did not provide reasonable source assessment, or agree with those using fluorescence data alone. Other fields routinely use spectral deconvolution for this purpose. For example, the spectral slope of the attenuation in the UV spectrum is used to deduce the algal distribution in marine systems (Roesler and Boss, 2003). In this study, however, the UV spectral slope did not contain useful information that was diagnostic of source. This likely was because much of the base flow within the system is sustained by waters that have been chlorinated; either because of tertiary wastewater treatment or because the water originates from the drinking water-supply system. The sample SUVA values generally were higher in the Pristine Water sites and lower in the Urban Water sites. This suggests that the Urban Water sites are depleted in chromophores, probably due to the reaction of chlorine with the UV absorbent aromatic chemical moieties, which preferentially react with chlorine in comparison to aliphatic and heteroatomic moieties (Rook, 1977). In contrast, SFI values of samples from the relative Pristine Water sites were similar to samples from Urban Water sites and storm samples. This observation supports the use of fluorescence properties for source identification rather than the more commonly employed UV spectra.

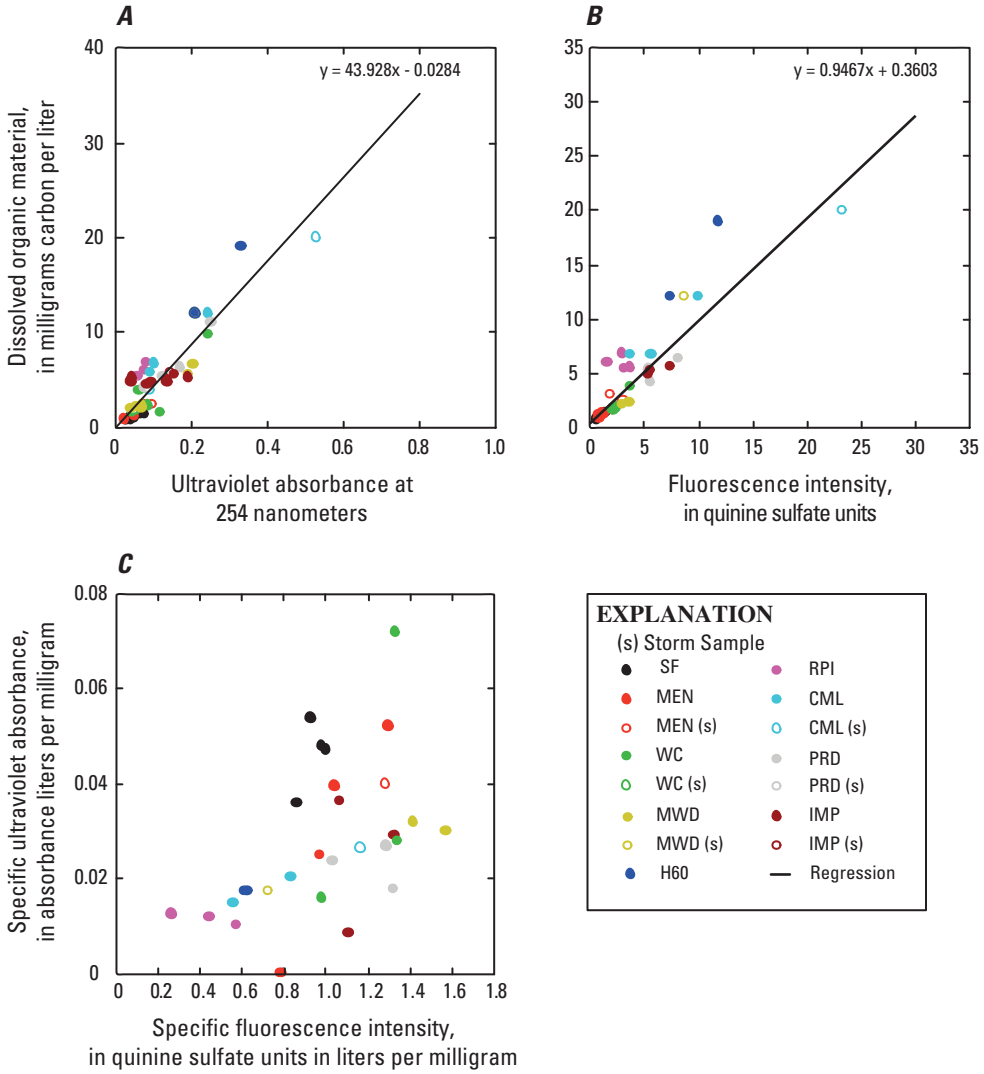


Figure 4. Comparison of (A) ultraviolet absorbance and dissolved organic material (DOM) concentration content, (B) fluorescence intensity and DOM, and (C) specific fluorescence intensity and specific ultraviolet absorbance for samples collected in the Santa Ana River Basin, southern California.

Model Endmember Selection

Candidate endmember spectra were chosen to represent DOM sources, based on the hydrology within the Santa Ana Basin, principal component analysis of the entire data set, and iterative application of the model. This approach identified samples within the study that contained reasonably pure endmember DOM, based on hydrologic and spectral data. Four endmembers were chosen:

Pristine Water – The Pristine Water endmember represents water that has interacted minimally with the environment and, thus, contains insignificant input from, for example, Wastewater, Urban Water, or Dairy Water discharge. Ground water or water that has flowed quickly from the mountainous areas as surface water are examples of Pristine Water. This endmember is indicative of water that has escaped anthropogenic inputs, such as are characteristic of wastewater and runoff. Therefore, the sample from site SF on the south fork of the Santa Ana River in the San Bernardino Mountains, which has little anthropogenic input, was chosen as the sample representing the Pristine Water endmember (*fig. 5A*).

Wastewater – The Wastewater endmember represents the municipal discharge from treatment plants located within the Santa Ana Basin, and comprises the majority of the base flow in the lower Santa Ana system. The Wastewater endmember was selected from among samples collected on Cucamonga Creek immediately downstream of site RP1. Spectra from samples gathered at this site always exhibited three well-defined peaks with similar maximum intensity values (*fig. 5B*). It should be noted that all chlorinated waters, even runoff from domestic sprinklers, will likely resemble the Wastewater endmember because chlorination for any purpose will have an effect on chromophores and fluorophores similar to Wastewater treatment.

Urban Water – The Urban Water endmember represents the nonstorm-related, low-volume urban runoff from urban areas and the high-volume runoff generated during storms. Two separate optical property endmember spectra were used to constrain the contributions of this endmember, one representing urban storm runoff and one representing urban base-flow runoff. The results were aggregated for reporting.

The Urban storm-flow endmember was a sample collected at site CML (*fig. 2*) during the first flush at the onset of the March 15, 1999, storm. We assumed that the first flush sample at this site would represent nearly 100-percent urban runoff, on the basis of the total flow from the nearby Wastewater discharge facility and the total river flow at the time the sample was taken. The Urban storm runoff endmember has very high FI at 255/435 and very little definition around 323/435 or 255/350 (*fig. 5C*).

Urban base-flow runoff is represented in the model by a sample collected at H60 (*fig. 2*), draining an area heavily influenced by Urban Water inputs, but lacking upstream wastewater treatment facilities. The Cucamonga Creek channel in this area is divided into two channels, one receiving Wastewater, and one receiving Urban Water runoff. The samples from the Urban base-flow site are unique due to the increase from near zero to about 20 QSU at 275/375 (*fig. 5D*). This endmember was added after the model failed to resolve urban contributions solely using the storm endmember.

Dairy Water – The Dairy Water endmember represents the potential runoff from confined animal feeding operations that may occur if dairy manure treatment lagoons are breached or overland flow from the dairies exceeds the infiltration rate. Most of the dairies in the Santa Ana Basin are located near Cucamonga Creek and Chino Creek in the northwestern section of the Inland Basin, and five different dairy manure treatment lagoons in this area were sampled for this study in July 1999 (*fig. 2*). The dairy samples generally exhibited the highest FI, ranging in value from 21.5 to 31.7 QSU, the latter value being the maximum FI found in the entire study. The maximum intensities are located near 295/405 and (or) 360/440, resulting in spectral topologies comparatively unique among the endmember spectra (*fig. 5E*). Because the model can fit an unlimited number of endmembers, to ensure maximum sensitivity to dairy influences, all dairy samples were used as endmembers, and the results aggregated for reporting.

The spectra from these representative endmembers all exhibit fluorescence excitation/emission maxima in distinct locations, with the exception of the Pristine Water endmember and urban storm runoff component of the Urban Water endmember. The Pristine Water and urban storm runoff endmembers have spectral topologies that are similar, though their maximum values differ by up to two orders of magnitude, and specific fluorescence differ by a factor of two. However, testing the model with synthetic mixtures of these two endmembers demonstrated that the model could resolve them with greater than 99 percent accuracy. Therefore, the assumption that all endmembers are resolvable proves to be valid, with the caveat that natural variability in endmember compositions may result in erroneous assignment of endmember composition, particularly in the case of Urban Water and Pristine Water endmembers. In this case, application of the model may be improved by using the total fluorescence parameter to inform the model assignment prior to spectral deconvolution.

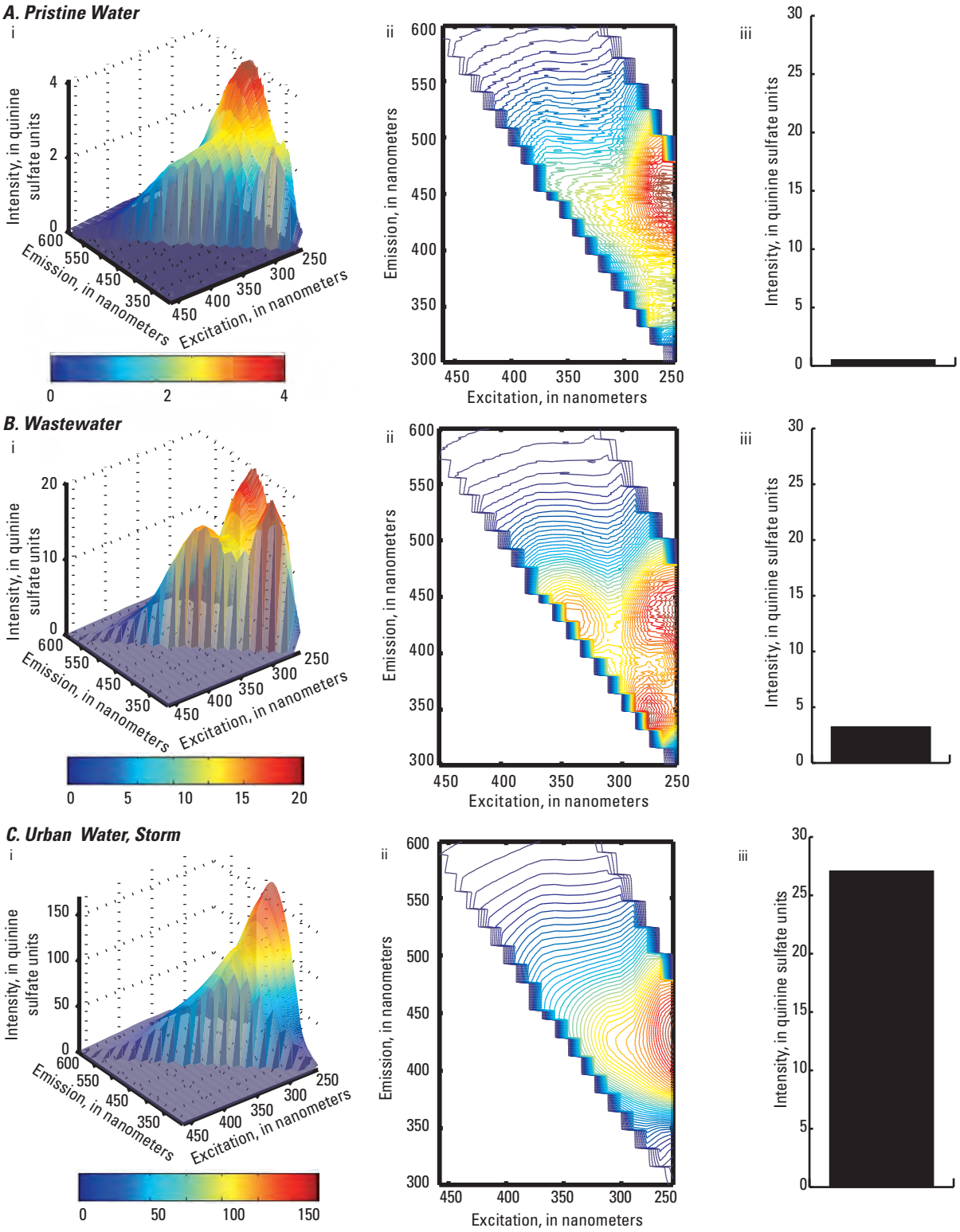


Figure 5. Fluorescence spectral response of representative endmember components used for the optical modeling of samples from the Santa Ana River Basin, southern California. (i) full scale spectral response, (ii) contour map of the spectral response, and (iii) spectral response scaled to the highest observed fluorescence intensity.

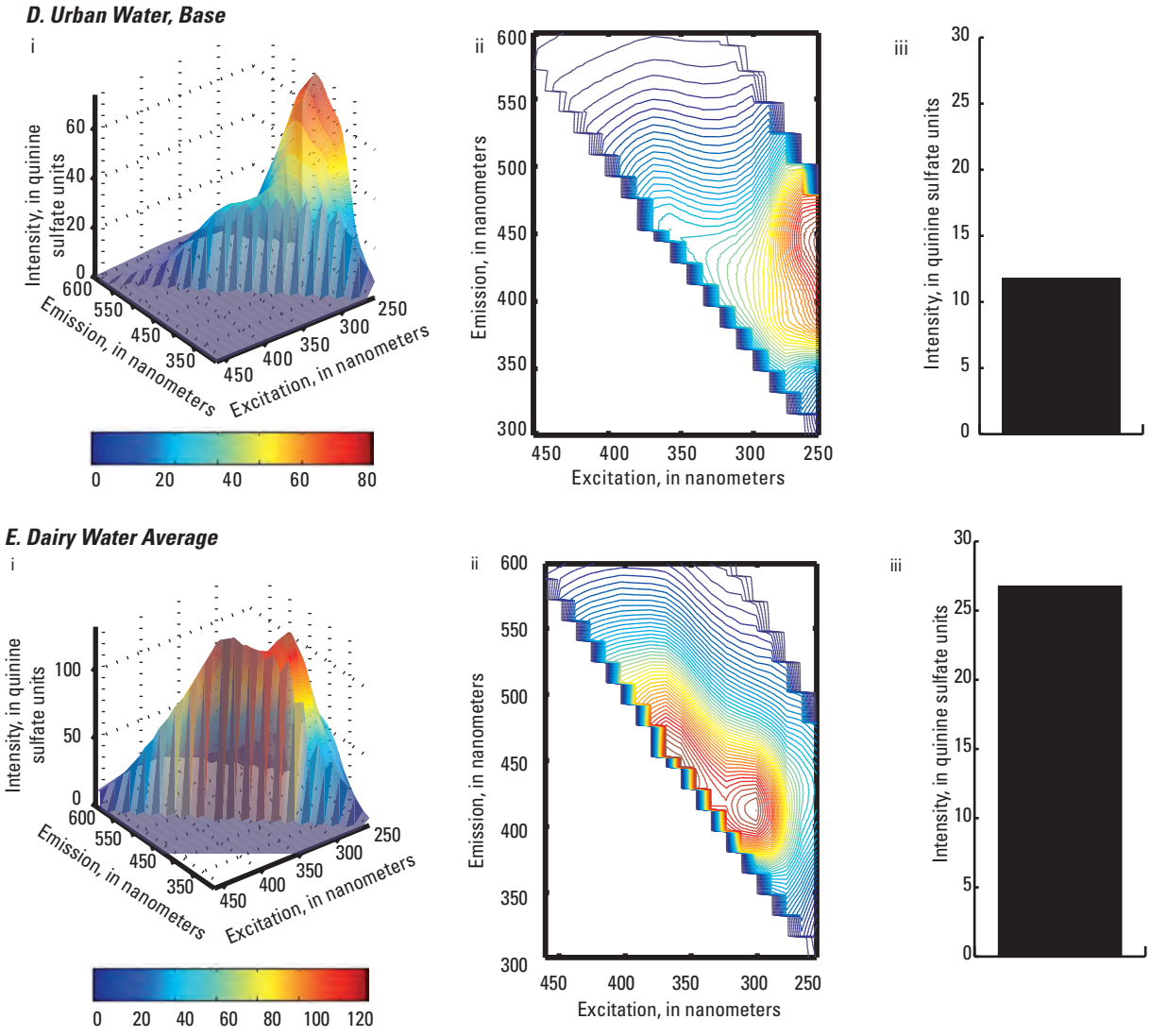


Figure 5.—*Continued.*

Model Response to Blank and Replicate Samples

Field blank samples were generated by processing "organic-free" water through the entire field collection process as samples. Model results from analysis of blank sample spectra generate a large residual, with only small positive assignments for any endmember (*fig. 6*), indicating that the model has a low probability of generating false positive source assignments from essentially what is essentially noise spectra.

In three cases, duplicate samples were collected sequentially from a sampling location. The intent of the duplicate sampling was to assess the cumulative error in the entire process of collection, filtration, storage and analysis, and generation of model endmember assignments. Modelling of duplicate samples using fluorescence data yielded nearly identical results for two of the three replicate samples (*fig. 7A,B*). For the third replicate sample, the model reversed the Pristine Water and the Urban Water assignments (*fig. 7C*). However, the high FI value clearly identifies this sample as predominantly impacted by urban inputs. Small spectral differences between the Pristine Water and the Urban Water endmembers account for the misassignment. Better characterization of the Urban Water base-flow endmember should improve the reproducibility of endmember assignment at this location.

Diurnal Variation

There are several reasons why diurnal variability in optical properties may be significant. For example, algal production of optically active material during daylight hours may contribute to changes in the optical characteristics of the DOM. Also, it is generally recognized that photo exposure may bleach the chromophores and fluorophores (Zafiriou, 2002), thereby altering the optical properties. However, for a diurnal change in optical properties to interfere with the source assignments made by the model, the magnitude of the change must be on the same scale as the differences observed through the watershed.

We collected samples every 3 hours at a single site (SDC) during a diurnal cycle on July 29 and 30, 1999, to assess whether diurnal changes in optical properties reduce the source resolution of the model (*table 1*). If the source of the DOM was constant during this period, variation in optical properties only should be due to bleaching of chromophores, degradation, or algal additions of DOM. Mill Creek is channelized with a natural bottom; surface water from this area is composed primarily of Wastewater discharge. It should be noted that treated Wastewater likely is relatively depleted in highly photosensitive and biodegradable materials.

The DOM varied somewhat during the sampling period, ranging from 5.9 to 7.6 milligrams per liter (mg/L) (*fig. 8A*), suggesting potential changes in DOM sources during the sampling period. Consequently, there was a large variation in FI during this sampling period, with the total FI varying from 4.27 to 6.27 QSU (*fig. 8B*). The majority of change, however, was related to the change in DOM concentration, as indicated by the relative stability of SFI (*fig. 8C*). The range of variability of the optical parameters (*table 1*) during the diurnal cycle suggests that environmental processes such as photo bleaching, algal production, microbial degradation, and sorption do not obscure source-related optical properties during time scales similar to river transit times.

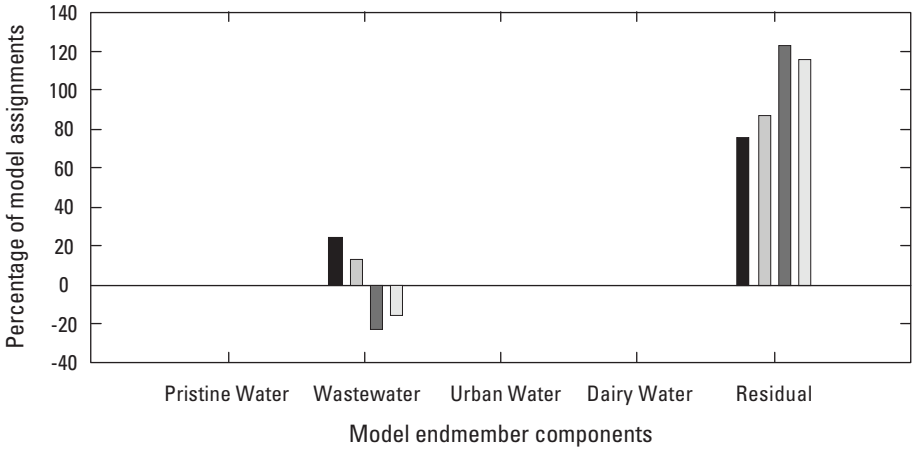


Figure 6. Comparison of model-derived endmember assignments for blank samples. Each bar represents results for a separate blank sample.

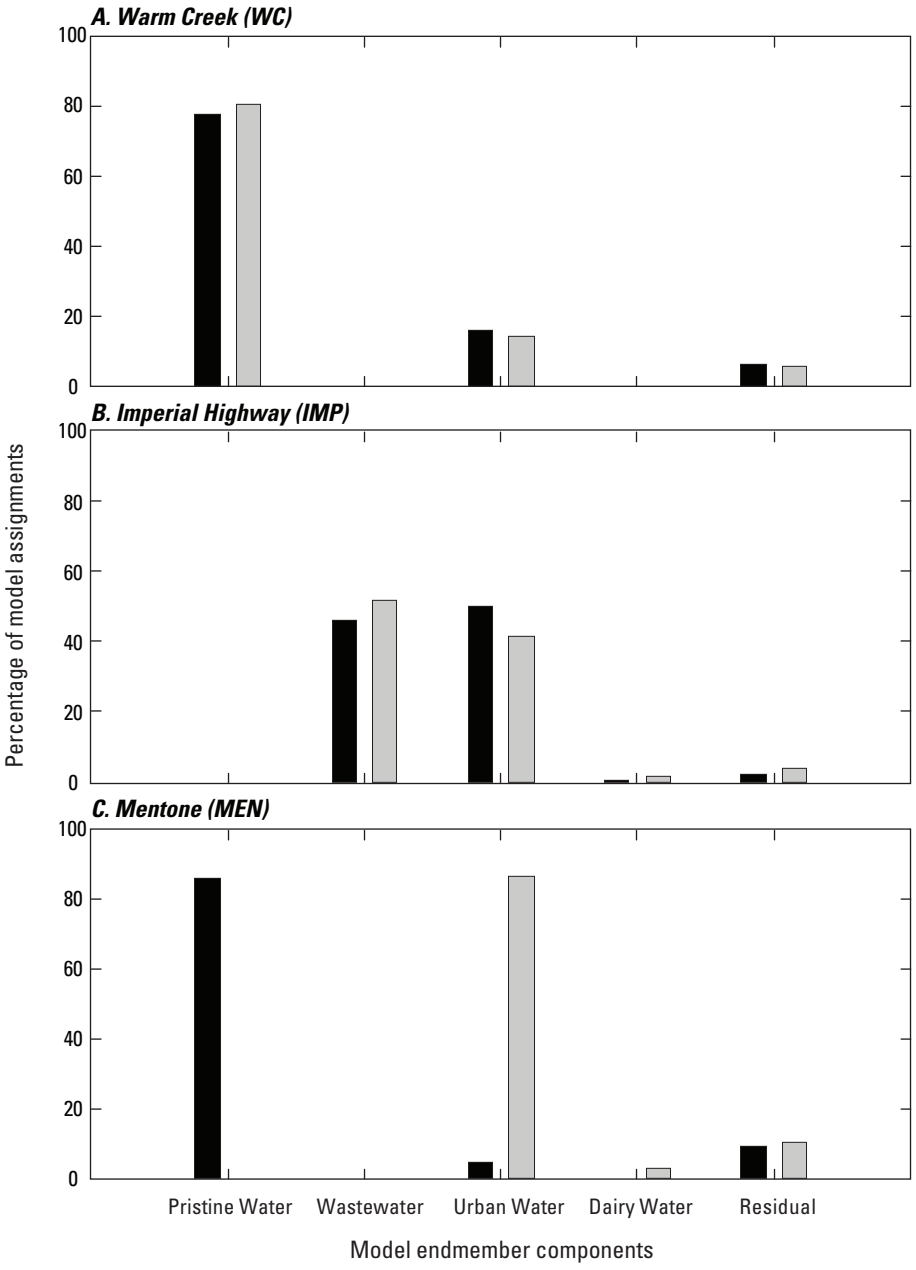


Figure 7. Comparison of model-derived endmember assignments between duplicate samples collected in the Santa Ana River Basin, southern California.

Table 1. Concentrations of dissolved organic material, associated optical properties, and normalized parameters of surface-water samples from the Santa Ana River Basin, southern California.

[DOM, dissolved organic material; mg C/L, milligrams of carbon per liter; UVA, ultraviolet absorbance; A, absorbance units; FI, fluorescence intensity; QSU, quinine sulfate units; SUVA, specific ultraviolet absorbance; A-L/mg, absorbance in liters per milligram; SFI, specific fluorescence intensity; QSU-L/mg, quinine sulfate units in liters per milligram; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	DOM (mg C/L)	Optical values		Normalized parameters	
						UVA (A)	FI (QSU)	SUVA (A-L/mg)	SFI (QSU-L/mg)
			Monthly and storm sampling						
South Fork of the Santa Ana River	SF	Monthly	3/8/1999	1530	0.7	0.03	0.6	0.036	0.9
		Monthly	4/13/1999	1700	1.4	0.06	1.4	0.046	1.0
		Monthly	5/17/1999	1340	1.4	0.08	1.3	0.054	0.9
		Monthly	6/15/1999	1540	0.8	0.04	0.8	0.048	1.0
Mentone	MEN	Monthly	1/12/1999	920	0.9	0.02	na	0.023	na
		Monthly	2/10/1999	910	2.3	0.07	na	0.032	na
		Monthly	3/9/1999	930	0.9	0.02	0.8	0.025	1.0
		Monthly	4/11/1999	1950	1.2	0.05	1.3	0.039	1.0
		Monthly	5/18/1999	930	1.1	na	0.9	na	0.8
		Monthly	6/16/1999	1000	1.4	na	1.1	na	0.8
		Storm	4/7/1999	1420	1.6	0.08	2.1	0.052	1.3
		Storm	4/12/1999	1250	2.4	0.10	3.1	0.040	1.3
		Storm recessional	4/14/1999	1000	1.8	0.07	1.7	0.037	1.0
		Storm	6/2/1999	1300	3.0	na	1.8	na	0.6
Warm Creek	WC	Monthly	1/12/1999	1300	1.4	0.03	na	0.024	na
		Monthly	2/10/1999	1620	1.9	0.05	na	0.028	na
		Monthly	3/9/1999	1510	1.5	0.04	na	0.029	na
		Monthly	4/14/1999	1450	2.3	0.08	3.3	0.036	1.4
		Monthly	5/18/1999	1430	1.6	0.12	2.1	0.072	1.3
		Monthly	6/16/1999	1620	1.8	0.05	2.4	0.027	1.3
		Monthly	8/10/1999	1500	3.8	0.06	3.7	0.016	1.0
		Storm	1/27/1999	115	3.7	0.10	na	0.027	na
		Storm	2/9/1999	1900	9.7	0.24	na	0.025	na
		Storm	3/15/1999	1340	32.0	0.74	na	0.023	na
Metropolitan Water District Crossing	MWD	Monthly	1/13/1999	1210	1.8	0.05	na	0.027	na
		Monthly	2/11/1999	1050	2.0	0.18	3.8	0.089	1.9
		Monthly	3/10/1999	1020	1.9	0.04	3.5	0.021	1.9
		Monthly	4/15/1999	1050	2.3	0.07	3.6	0.030	1.6
		Monthly	5/19/1999	1140	2.1	0.07	3.0	0.032	1.4
		Monthly	6/17/1999	1210	2.4	0.03	3.6	0.014	1.5
		Monthly	8/11/1999	1100	2.2	0.05	na	0.024	na
		Storm	1/25/1999	1545	6.6	0.20	na	0.031	na
		Storm	3/15/1999	1800	3.6	0.10	6.2	0.028	1.7
		Storm	4/7/1999	1220	5.5	0.19	10.7	0.035	1.9
Cucamonga Creek at Highway 60	H60	Grab	3/10/1999	1530	12.0	0.21	8.7	0.017	0.7
		Grab	2/11/1999	1600	4.9	0.17	9.0	0.034	1.8
		Grab	4/15/1999	1630	19.0	0.33	11.8	0.017	0.6
		Grab	5/19/1999	1610	12.0	0.21	7.4	0.017	0.6
		Grab	8/11/1999	1820	na	0.43	14.2	na	na

Table 1. Concentrations of dissolved organic material, associated optical properties, and normalized parameters of surface-water samples from the Santa Ana River Basin, southern California—*Continued*.

[DOM, dissolved organic material; mg C/L, milligrams of carbon per liter; UVA, ultraviolet absorbance; A, absorbance units; FI, fluorescence intensity; QSU, quinine sulfate units; SUVA, specific ultraviolet absorbance; A-L/mg, absorbance in liters per milligram; SFI, specific fluorescence intensity; QSU-L/mg, quinine sulfate units in liters per milligram; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	DOM (mg C/L)	Optical values		Normalized parameters	
						UVA (A)	FI (QSU)	SUVA (A-L/mg)	SFI (QSU-L/mg)
Monthly and storm sampling—Continued									
Inland Empire Utilities Agency Reclamation Plant 1	RP1	Monthly	2/11/1999	1630	6.0	0.08	3.4	0.013	0.6
		Monthly	3/10/1999	1540	6.3	0.06	3.1	0.010	0.5
		Monthly	4/15/1999	1700	6.8	0.08	3.0	0.012	0.4
		Monthly	5/19/1999	1720	6.0	0.07	1.6	0.012	0.3
		Monthly	6/17/1999	1840	5.5	na	3.7	na	0.7
		Monthly	8/11/1999	1830	5.4	0.06	3.1	0.010	0.6
Cucamonga Creek near Mira Loma	CML	Monthly	2/11/1999	1600	5.9	0.10	4.1	0.017	0.7
		Monthly	3/10/1999	1750	6.1	0.07	3.5	0.012	0.6
		Monthly	4/15/1999	1620	6.7	0.10	3.7	0.015	0.6
		Monthly	5/19/1999	1600	12.0	0.24	10.0	0.020	0.8
		Monthly	6/17/1999	1720	7.1	na	5.6	na	0.8
		Monthly	7/29/1999	1900	6.7	na	5.7	na	0.8
		Monthly	8/11/1999	1640	5.8	0.09	na	0.015	na
		Storm	3/15/1999	1030	32.0	0.64	27.6	0.020	0.9
		Storm	3/15/1999	1100	18.0	na	21.0	na	1.2
		Storm	4/1/1999	1500	20.0	0.53	23.3	0.026	1.2
		Storm	4/6/1999	1610	na	0.58	27.2	na	na
Prado	PRD	Monthly	1/14/1999	1530	4.0	0.09	na	0.022	na
		Monthly	2/12/1999	1500	5.5	0.17	7.7	0.030	1.4
		Monthly	3/11/1999	1700	4.2	0.08	na	0.019	na
		Monthly	4/16/1999	1500	6.3	0.17	8.1	0.027	1.3
		Monthly	5/20/1999	1410	5.3	0.13	5.5	0.024	1.0
		Monthly	8/12/1999	1150	4.2	0.08	5.6	0.018	1.3
		Storm	1/25/1999	1315	11.0	0.25	na	0.023	na
		Storm	3/15/1999	1520	14.0	0.29	16.7	0.021	1.2
		Storm	4/6/1999	1930	4.9	0.13	5.7	0.027	1.2
Santa Ana River at Imperial Highway	IMP	Monthly	1/14/1999	1100	4.1	0.08	na	0.020	na
		Monthly	2/12/1999	1100	5.2	0.14	7.4	0.027	1.4
		Monthly	3/11/1999	1120	4.7	0.09	6.4	0.020	1.4
		Monthly	4/16/1999	1030	5.6	0.15	7.4	0.027	1.3
		Monthly	5/20/1999	1200	5.2	0.19	5.5	0.036	1.1
		Monthly	6/18/1999	930	4.8	0.04	5.3	0.008	1.1
		Monthly	8/12/1999	1040	4.5	0.08	na	0.018	na
		Storm	1/25/1999	1140	4.8	0.13	na	0.028	na
		Storm	2/9/1999	2000	4.4	0.13	na	0.029	na
		Storm	3/15/1999	1350	5.8	0.14	9.0	0.024	1.5

Table 1. Concentrations of dissolved organic material, associated optical properties, and normalized parameters of surface-water samples from the Santa Ana River Basin, southern California—*Continued*.

[DOM, dissolved organic material; mg C/L, milligrams of carbon per liter; UVA, ultraviolet absorbance; A, absorbance units; FI, fluorescence intensity; QSU, quinine sulfate units; SUVA, specific ultraviolet absorbance; A-L/mg, absorbance in liters per milligram; SFI, specific fluorescence intensity; QSU-L/mg, quinine sulfate units in liters per milligram; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	DOM (mg C/L)	Optical values		Normalized parameters	
						UVA (A)	FI (QSU)	SUVA (A-L/mg)	SFI (QSU-L/mg)
			Diurnal study element						
Mill Creek at Duck Club	SDC	Time-series grab	7/29/1999	1520	7.4	na	6.3	na	0.8
		Time-series grab	7/29/1999	1730	7.6	na	6.0	na	0.8
		Time-series grab	7/29/1999	2030	7.5	na	5.2	na	0.7
		Time-series grab	7/29/1999	2330	6.6	na	4.5	na	0.7
		Time-series grab	7/30/1999	230	6.2	na	4.3	na	0.7
		Time-series grab	7/30/1999	530	5.9	na	4.9	na	0.8
		Time-series grab	7/30/1999	830	6.3	na	5.2	na	0.8
			Dairy ponds						
Dairy pond 1	D1	Grab	7/29/1999	1150	400	3.09	28.3	0.008	0.1
Dairy pond 2	D2	Grab	7/29/1999	1120	110	na	28.6	na	0.3
Dairy pond 3	D3	Grab	7/29/1999	1040	1,000	3.09	21.5	0.003	0.0
Dairy pond 4	D4	Grab	7/29/1999	1010	170	na	24.8	na	0.1
Dairy pond 5	D5	Grab	7/29/1999	1140	40	na	31.7	na	0.8
			Study averages						
Average values					5.9	0.15	6.4	0.026	1.1
Standard deviation					5.5	0.15	6.0	0.013	0.4
Maximum value					32.0	0.74	27.6	0.089	1.9
Minimum value					0.7	0.01	0.6	0.008	0.3

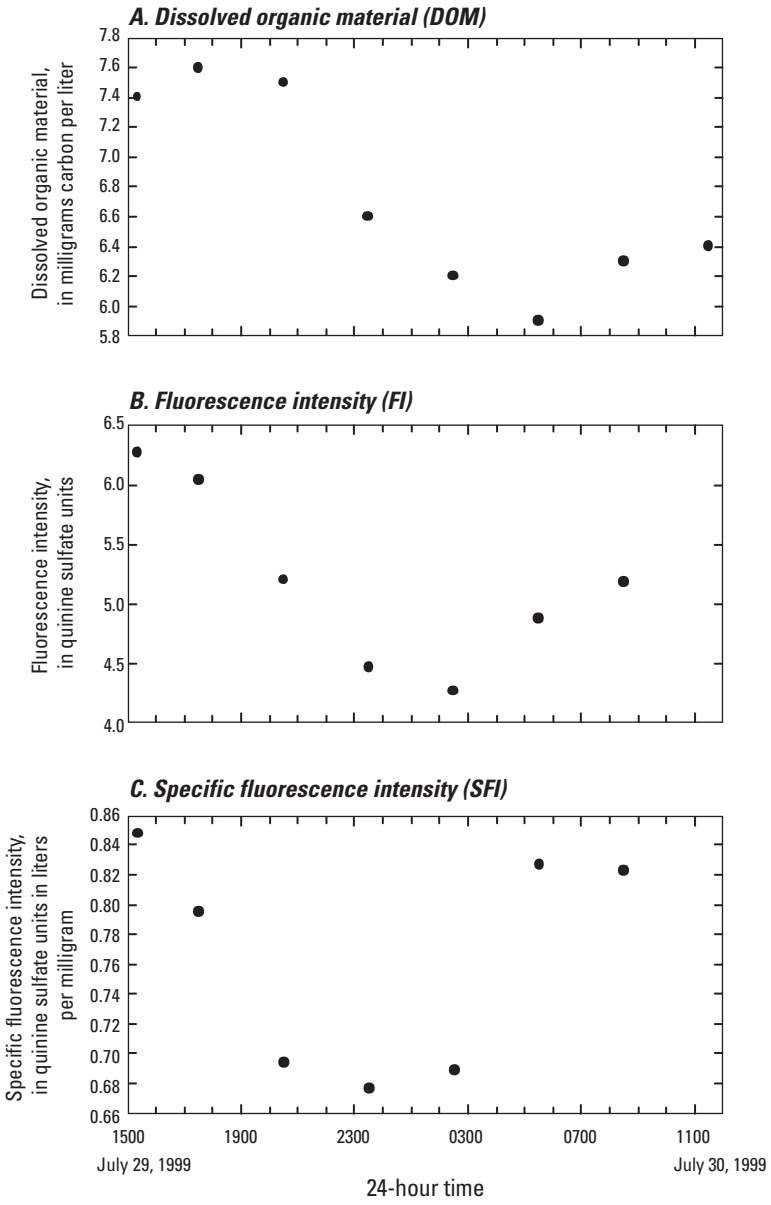


Figure 8. Diurnal changes in properties for samples collected between 1530 on July 29 and 0830 on July 30, 1999, Santa Ana River Basin, southern California.

Large-Scale Trends

Several systematic differences in DOM concentrations and optical properties were observed across the Santa Ana Basin. DOM concentrations generally increased with decreasing elevation and increasing urbanization in the Santa Ana Basin for monthly samplings in this study, even though flow is not continuous among the sites on the Santa Ana River. DOM values ranged from an average of near 1 mg/L at site SF, to 4.9 mg/L at sites PRD and IMP. Higher values were observed on Cucamonga Creek than on the Santa Ana River main stem, averaging 7.0 mg/L at site CML. This water is a mixture of an average DOM of 6.1 mg/L from the Wastewater inputs at site RP1, and 12.0 mg/L from the urban inputs captured at site H60. Variation in UVA and FI values closely tracked the variation in DOM concentration, with site H60 samples having the highest average UVA and FI values observed in the study (*fig. 9A–C*).

The optical properties and DOM concentrations of Pristine Water sites, as well as those receiving predominantly Wastewater discharge, were much less variable than those with more urban influence. Specifically, sites SF, MEN, MWD and the Wastewater discharge samples at site RP1 had much less variability in DOM, UVA and fluorescence yield analyses compared to sites WC, PRD, IMP, H60, and CML, which had more variable signals on a monthly basis (*fig. 9A–E*).

The compositional parameters were more characteristic of source. The maximum average SUVA value was from site SF, consistent with terrestrial runoff values seen elsewhere (Thurman, 1985). In contrast, the maximum average SFI value for base-flow conditions was from site MWD, with lower values observed on samples from the Cucamonga drainage. The addition of Wastewater-derived DOM to Cucamonga Creek after it passes Cucamonga Creek at Highway 60 (site H60) is a likely explanation for these low values because of the depleted levels of chromophores and fluorophores in chlorinated Wastewater. In contrast, the nonchlorinated Wastewater from site RP1 supplies a large fraction of the flow at site MWD during base-flow conditions. The wastewater treatment facility infiltrates secondary-treated wastewater, then extracts and UV oxidizes it by UV extraction for disinfection (City of San Bernardino Municipal Water Department, 2001). Although this treatment scheme differs considerably from that of site RP1 and there are large differences in SFI, this site exhibits low overall fluorescence, and the model recognizes this as largely of Wastewater origin.

The model-assigned endmember contributions for monthly samples generally agreed with the expected sources. The highest average Urban Water contributions were found at the urban sites, H60 (60 percent), IMP (53 percent), while the lowest were found at sites South Fork of the Santa Ana River (SF) (2 percent) and RP1 (1 percent). In contrast, the highest average model-assigned Wastewater contributions were found at sites RP1 (92 percent) and MWD (74 percent). The model-derived average contribution of Pristine Water was highest for

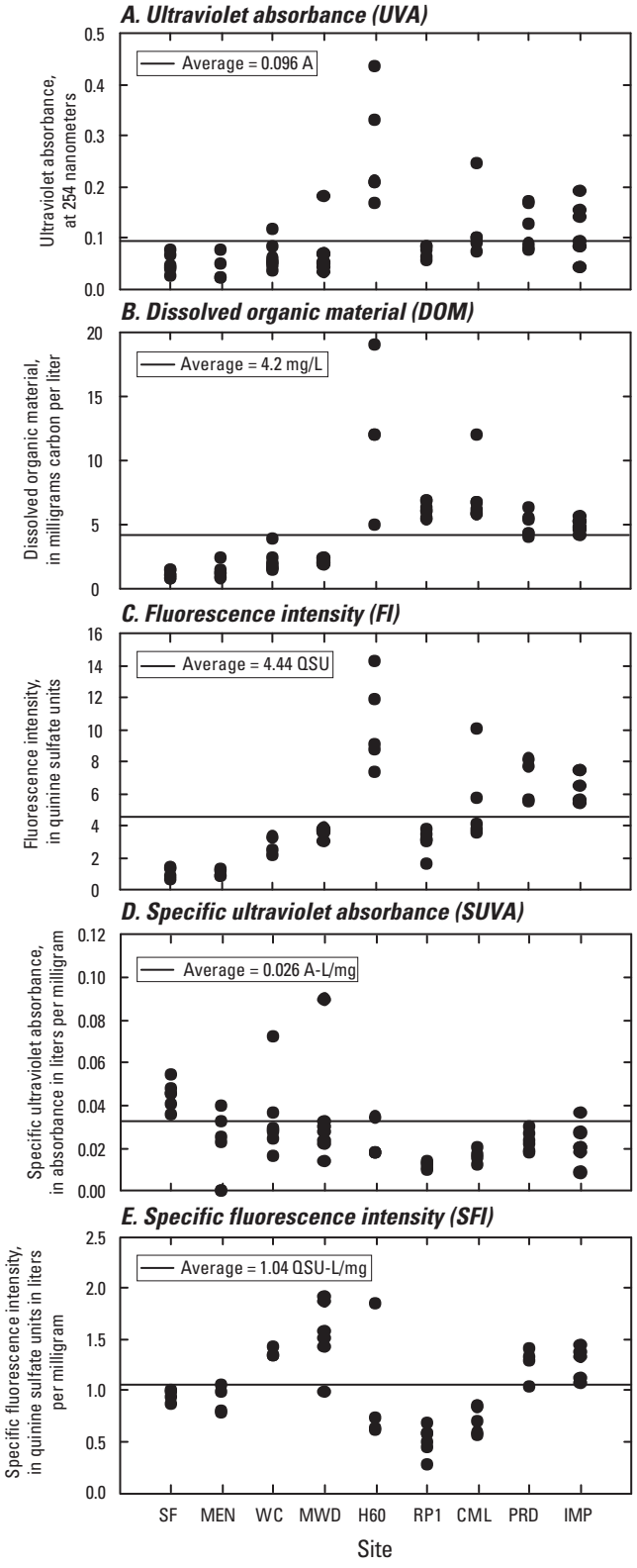


Figure 9. Comparison of properties measured in samples collected monthly in the Santa Ana River Basin, southern California.

site SF samples (90 percent), reflecting a relatively pristine upstream environment.

Results from Monthly Sampling

Analysis of the response of optical properties to changing seasons or hydrologic conditions, and assessment of the accuracy of source assignments provide a basis for understanding dominant processes responsible for signal variation. These factors were evaluated by examining the change in optical properties and source assignments evident in monthly time-series samples as presented below.

South Fork of the Santa Ana River

Site SF is on the Santa Ana River near the headwaters of the Santa Ana watershed in the San Bernardino Mountains, with little agricultural or urban influence. Therefore, samples collected from this site may be expected to represent relatively pristine source water, unaffected by addition of natural or urban material.

The DOM measurements at site SF ranged from 0.7 to 1.4 mg/L during the sampling period, averaging 1.1 mg/L (*fig. 9B*)—the lowest average of the sites in the study. The UVA measurements at site SF ranged from 0.025 to 0.075 A, with an average value of 0.051 A (*fig. 9A*). Similarly, the FI of samples from site SF were extremely low, averaging 1.02 QSU, and ranging from 0.60 to 1.40 QSU (*fig. 9C*). The fluorescence spectral distribution was dominated by a peak at 255/435, with the peak at 323/435 half or less in intensity. The abundance of humic-like fluorescence in the fluorescence spectra was near the average for the study, but the protein-like fluorescence was at the low end. This is consistent with predominantly natural DOM contributions to water at this site and the lack of a protein-rich Wastewater input.

Table 2. Values for representative fluorescence excitation/emission pairs of surface-water samples from the Santa Ana River Basin, southern California.

[QSU, quinine sulfate units; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	Values for representative fluorescence excitation/emission pairs, in QSU x 1000								
					255/435	323/435	255/350	277/340	334/445	346/430	346/450	370/453	370/500
Monthly and storm sampling													
South Fork of the Santa Ana River	SF	Monthly	3/8/1999	1530	0.06	0.03	0.01	0.01	0.03	0.03	0.03	0.03	0.02
		Monthly	4/13/1999	1700	0.13	0.08	0.03	0.04	0.07	0.07	0.07	0.06	0.05
		Monthly	5/17/1999	1340	0.13	0.07	0.03	0.02	0.07	0.06	0.07	0.06	0.04
		Monthly	6/15/1999	1540	0.07	0.04	0.04	0.04	0.04	0.03	0.04	0.03	0.03
Mentone	MEN	Monthly	1/12/1999	920	na	na	na	na	na	na	na	na	na
		Monthly	2/10/1999	910	na	na	na	na	na	na	na	na	na
		Monthly	3/9/1999	930	0.09	0.05	0.02	0.02	0.05	0.04	0.04	0.04	0.03
		Monthly	4/11/1999	1950	0.11	0.07	0.04	0.07	0.07	0.06	0.06	0.06	0.04
		Monthly	5/18/1999	930	0.09	0.05	0.02	0.02	0.05	0.05	0.04	0.04	0.03
		Monthly	6/16/1999	1000	0.10	0.06	0.04	0.05	0.06	0.05	0.05	0.05	0.04
		Storm	4/7/1999	1420	0.18	0.11	0.09	0.14	0.10	0.10	0.10	0.09	0.07
		Storm	4/12/1999	1250	0.28	0.17	0.08	0.08	0.16	0.15	0.16	0.15	0.11
		Storm recessional	4/14/1999	1000	0.17	0.10	0.03	0.03	0.10	0.09	0.10	0.09	0.06
		Storm	6/2/1999	1300	0.16	0.11	0.10	0.09	0.10	0.08	0.09	0.08	0.06
Warm Creek	WC	Monthly	1/12/1999	1300	na	na	na	na	na	na	na	na	na
		Monthly	2/10/1999	1620	na	na	na	na	na	na	na	na	na
		Monthly	3/9/1999	1510	na	na	na	na	na	na	na	na	na
		Monthly	4/14/1999	1450	0.35	0.17	0.10	0.09	0.16	0.15	0.15	0.13	0.09
		Monthly	5/18/1999	1430	0.24	0.11	0.08	0.08	0.11	0.10	0.10	0.08	0.05
		Monthly	6/16/1999	1620	0.24	0.12	0.08	0.10	0.12	0.11	0.11	0.10	0.07
		Monthly	8/10/1999	1500	0.40	0.20	0.18	0.13	0.19	0.17	0.18	0.17	0.11
		Storm	1/27/1999	115	na	na	na	na	na	na	na	na	na
		Storm	2/9/1999	1900	na	na	na	na	na	na	na	na	na
		Storm	3/15/1999	1340	na	na	na	na	na	na	na	na	na
Metropolitan Water District Crossing	MWD	Monthly	1/13/1999	1210	na	na	na	na	na	na	na	na	na
		Monthly	2/11/1999	1050	0.39	0.23	0.14	0.18	0.23	0.22	0.21	0.17	0.10
		Monthly	3/10/1999	1020	0.36	0.22	0.14	0.19	0.22	0.22	0.20	0.17	0.10
		Monthly	4/15/1999	1050	0.37	0.21	0.14	0.19	0.22	0.21	0.20	0.17	0.10
		Monthly	5/19/1999	1140	0.31	0.17	0.13	0.18	0.18	0.18	0.15	0.14	0.07
		Monthly	6/17/1999	1210	0.33	0.19	0.35	0.29	0.19	0.19	0.17	0.15	0.09
		Monthly	8/11/1999	1100	na	na	na	na	na	na	na	na	na
		Storm	1/25/1999	1545	na	na	na	na	na	na	na	na	na
		Storm	3/15/1999	1800	0.69	0.36	0.19	0.20	0.34	0.31	0.30	0.24	0.16
		Storm	4/7/1999	1220	1.18	0.57	0.36	0.32	0.53	0.47	0.46	0.38	0.26
Cucamonga Creek at Highway 60	H60	Grab	3/10/1999	1530	0.84	0.43	0.37	0.52	0.41	0.37	0.37	0.33	0.24
		Grab	2/11/1999	1600	1.07	0.45	0.39	0.32	0.40	0.35	0.34	0.26	0.19
		Grab	4/15/1999	1630	1.20	0.59	0.42	0.49	0.56	0.53	0.54	0.51	0.36
		Grab	5/19/1999	1610	0.77	0.32	0.31	0.40	0.34	0.34	0.35	0.40	0.25
		Grab	8/11/1999	1820	1.33	0.73	0.47	0.59	0.70	0.65	0.67	0.66	0.48
Inland Empire Utilties Agency Reclamation Plant 1	RP1	Monthly	2/11/1999	1630	0.30	0.23	0.16	0.27	0.24	0.23	0.21	0.17	0.09
		Monthly	3/10/1999	1540	0.27	0.21	0.16	0.26	0.22	0.21	0.19	0.15	0.09
		Monthly	4/15/1999	1700	0.28	0.21	0.14	0.22	0.22	0.21	0.19	0.15	0.08
		Monthly	5/19/1999	1720	0.15	0.11	0.08	0.12	0.12	0.12	0.10	0.08	0.04
		Monthly	6/17/1999	1840	0.33	0.23	0.25	0.32	0.25	0.25	0.23	0.19	0.10
		Monthly	8/11/1999	1830	0.29	0.20	0.14	0.23	0.21	0.20	0.19	0.16	0.09

Table 2. Values for representative fluorescence excitation/emission pairs of surface-water samples from the Santa Ana River Basin, southern California—*Continued*.

[QSU, quinine sulfate units; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	Values for representative fluorescence excitation/emission pairs, in QSU x 1000								
					255/435	323/435	255/350	277/340	334/445	346/430	346/450	370/453	370/500
Monthly and storm sampling—Continued													
Cucamonga Creek near Mira Loma	CML	Monthly	2/11/1999	1600	0.40	0.24	0.18	0.25	0.24	0.23	0.22	0.19	0.11
		Monthly	3/10/1999	1750	0.32	0.21	0.17	0.27	0.22	0.22	0.21	0.18	0.11
		Monthly	4/15/1999	1620	0.35	0.22	0.17	0.25	0.24	0.23	0.22	0.20	0.12
		Monthly	5/19/1999	1600	0.99	0.54	0.41	0.66	0.58	0.58	0.56	0.57	0.32
		Monthly	6/17/1999	1720	0.48	0.25	0.81	0.57	0.26	0.25	0.24	0.21	0.13
		Monthly	7/29/1999	1900	0.58	0.31	0.30	0.32	0.32	0.32	0.32	0.35	0.20
		Monthly	8/11/1999	1640	na	na	na	na	na	na	na	na	na
		Storm	3/15/1999	1030	2.77	1.69	0.58	0.53	1.49	1.28	1.29	1.01	0.77
		Storm	3/15/1999	1100	2.25	1.22	0.54	0.51	1.05	0.87	0.90	0.68	0.53
		Storm	4/1/1999	1500	2.53	1.27	0.66	0.50	1.15	1.00	1.00	0.78	0.58
		Storm	4/6/1999	1610	2.78	1.47	0.65	0.51	1.31	1.12	1.16	0.92	0.74
Prado	PRD	Monthly	1/14/1999	1530	na	na	na	na	na	na	na	na	na
		Monthly	2/12/1999	1500	0.78	0.44	0.26	0.30	0.42	0.40	0.38	0.32	0.21
		Monthly	3/11/1999	1700	na	na	na	na	na	na	na	na	na
		Monthly	4/16/1999	1500	0.85	0.45	0.25	0.27	0.43	0.40	0.39	0.33	0.22
		Monthly	5/20/1999	1410	0.56	0.31	0.20	0.27	0.31	0.30	0.28	0.24	0.15
		Monthly	8/12/1999	1150	0.54	0.32	0.22	0.31	0.32	0.30	0.28	0.24	0.15
		Storm	1/25/1999	1315	na	na	na	na	na	na	na	na	na
		Storm	3/15/1999	1520	1.82	0.97	0.45	0.47	0.85	0.73	0.73	0.57	0.42
		Storm	4/6/1999	1930	0.59	0.31	0.24	0.33	0.31	0.29	0.28	0.25	0.16
Santa Ana River at Imperial Highway	IMP	Monthly	1/14/1999	1100	na	na	na	na	na	na	na	na	na
		Monthly	2/12/1999	1100	0.77	0.42	0.24	0.28	0.41	0.39	0.37	0.31	0.21
		Monthly	3/11/1999	1120	0.67	0.37	0.23	0.27	0.35	0.32	0.31	0.26	0.17
		Monthly	4/16/1999	1030	0.78	0.41	0.24	0.26	0.39	0.37	0.36	0.30	0.20
		Monthly	5/20/1999	1200	0.56	0.32	0.20	0.26	0.31	0.30	0.28	0.27	0.15
		Monthly	6/18/1999	930	0.52	0.29	0.33	0.36	0.28	0.27	0.25	0.22	0.14
		Monthly	8/12/1999	1040	na	na	na	na	na	na	na	na	na
		Storm	1/25/1999	1140	na	na	na	na	na	na	na	na	na
		Storm	2/9/1999	2000	na	na	na	na	na	na	na	na	na
		Storm	3/15/1999	1350	0.98	0.49	0.28	0.28	0.45	0.40	0.40	0.33	0.23
Diurnal study element													
Mill Creek at Duck Club	SDC	Time-series grab	7/29/1999	1520	0.58	0.32	0.32	0.47	0.32	0.31	0.30	0.28	0.18
		Time-series grab	7/29/1999	1730	0.57	0.32	0.27	0.41	0.33	0.31	0.31	0.29	0.19
		Time-series grab	7/29/1999	2030	0.49	0.29	0.21	0.32	0.29	0.28	0.28	0.27	0.16
		Time-series grab	7/29/1999	2330	0.42	0.25	0.19	0.29	0.26	0.25	0.24	0.23	0.14
		Time-series grab	7/30/1999	230	0.40	0.24	0.20	0.30	0.25	0.25	0.23	0.21	0.13
		Time-series grab	7/30/1999	530	0.44	0.27	0.23	0.36	0.28	0.27	0.25	0.24	0.15
		Time-series grab	7/30/1999	830	0.47	0.27	0.25	0.39	0.28	0.27	0.26	0.25	0.16

Table 2. Values for representative fluorescence excitation/emission pairs of surface-water samples from the Santa Ana River Basin, southern California—*Continued*.

[QSU, quinine sulfate units; na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	Values for representative fluorescence excitation/emission pairs, in QSU x 1000								
					255/435	323/435	255/350	277/340	334/445	346/430	346/450	370/453	370/500
Dairy ponds													
Dairy pond 1	D1	Grab	7/29/1999	1150	0.36	2.22	0.11	0.28	2.29	2.33	2.25	2.42	1.84
Dairy pond 2	D2	Grab	7/29/1999	1120	1.12	1.84	0.35	0.79	2.00	2.19	2.04	2.25	1.45
Dairy pond 3	D3	Grab	7/29/1999	1040	0.07	1.05	0.01	0.01	1.32	1.69	1.83	2.54	2.25
Dairy pond 4	D4	Grab	7/29/1999	1010	0.49	2.14	0.07	0.15	2.30	2.36	2.29	1.33	0.83
Dairy pond 5	D5	Grab	7/29/1999	1140	2.48	2.02	1.08	1.89	1.86	1.69	1.51	2.25	1.66
Study averages													
Average values					0.65	0.35	0.25	0.28	0.34	0.31	0.30	0.26	0.17
Standard deviation					0.63	0.34	0.18	0.16	0.30	0.25	0.26	0.20	0.16
Maximum value					2.78	1.69	0.81	0.66	1.49	1.28	1.29	1.01	0.77
Minimum value					0.06	0.03	0.01	0.01	0.03	0.03	0.03	0.03	0.02

The model endmember assignments suggest, on average, 90 percent Pristine Water with 8 percent residual for samples collected at site SF, indicating that there were some fluctuations in optical properties even though only Pristine Water should be observed (*fig. 10A*). A small amount of Urban Water (0–4 percent) was detected in most samples from this site, likely because the model has had difficulty discriminating between Pristine Water and Urban Water.

Mentone

Site Mentone (MEN) is on the Santa Ana River just upstream of where it enters the San Bernardino Valley, upstream of most Urban Water influence (*fig. 2*). Water from this site represents typical "mountain front" Pristine Water that enters the San Bernardino Valley, though most of the base flow passing this site is lost to streambed infiltration. Water at site MEN probably contains some flow from site SF, but a larger component was from Big Bear Creek. Water quality in Big Bear Creek almost certainly was affected by development at Big Bear, but there were no Wastewater treatment facilities, dairies, or significant agricultural operations upstream of this site. Seven Oaks Dam was under construction at the time of this study.

The DOM content of samples collected at site MEN (*fig. 2*) ranged from 0.9 to 2.3 mg/L during normal flow conditions, averaging 1.3 mg/L (*fig. 9B*). These values were only slightly above those at the Pristine site SF, and much lower than those at sites farther down the San Bernardino Valley. Similarly, the UVA and fluorescence yield averaged 0.041 A (*fig. 9A*), and 1.10 QSU (*fig. 9C*), respectively, lower than sites farther down the valley.

The appearance of fluorescence spectra of site MEN samples was similar to those from site SF, with the peak at 255/435 prominent in the regular monthly samples of March, April, and May, and a prominent ridge in the direction of 323/435 (*table 2*). The June sample also possessed these features, but was distinguished by a relative increase in intensity at 255/350 (*table 2*). Similar to samples from site SF, the humic-like fluorescence of the monthly and storm samples was near average, and the protein-like fluorescence was low for site MEN samples.

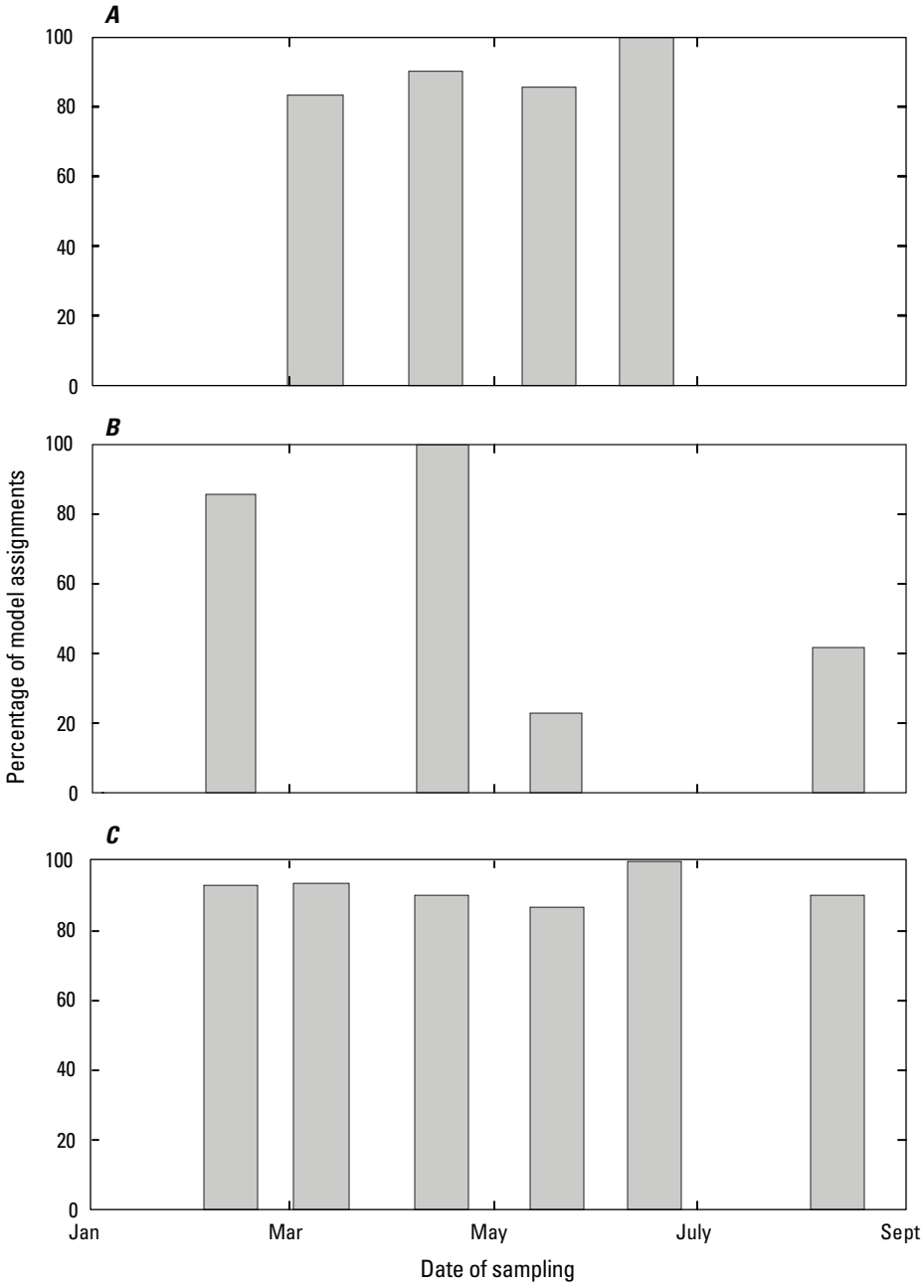


Figure 10. Model-derived endmember assignments for all samples collected at sites from which representative endmembers samples were selected. (A) South Fork, Pristine Water endmember; (B) Cucamonga Creek at Highway 60 Urban Water endmember; and (C) Inland Empire Utility Agency Reclamation Plant 1 Wastewater endmember.

Application of the model resulted in assignment of an endmember contribution averaging 88 percent Pristine Water for monthly samples and a 6 percent residual, with the exception of the monthly sample in May, collected following a storm in the area (*table 3*). For the May sample, the model assigned 90 percent of the spectral properties to the Urban Water endmember. However, as for the misassignment previously discussed in the replicate samples, the low FI value for the May sample at site MEN clearly indicates that it was not affected by Urban storm water. As discussed previously, addition of a threshold trigger based on FI values, will ameliorate this and similar misassignments. Except for this misassignment, the results for site MEN are consistent with the predominantly Pristine Water inputs.

Table 3. Model results for endmembers of surface-water samples from the Santa Ana River Basin, southern California.

[na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	Model results, percentage of each endmenber				
					Pristine Water	Wastewater	Urban Water, total	Dairy Water, total	Residual
			Monthly and storm sampling						
South Fork of the Santa Ana River	SF	Monthly	3/8/1999	1530	83.5	0.0	2.8	0.4	13.3
		Monthly	4/13/1999	1700	89.8	0.0	1.7	0.3	8.2
		Monthly	5/17/1999	1340	85.4	0.0	4.2	0.3	10.1
		Monthly	6/15/1999	1540	100.0	0.0	0.0	0.0	0.0
Mentone	MEN	Monthly	1/12/1999	920	na	na	na	na	na
		Monthly	2/10/1999	910	na	na	na	na	na
		Monthly	3/9/1999	930	85.8	0.0	4.6	0.2	9.3
		Monthly	4/11/1999	1950	86.2	4.6	5.8	0.2	3.2
		Monthly	5/18/1999	930	0.0	0.0	89.8	3.1	7.1
		Monthly	6/16/1999	1000	92.3	0.0	3.5	0.0	4.2
		Storm	4/7/1999	1420	78.3	12.6	3.6	0.1	5.4
		Storm	4/12/1999	1250	89.1	0.0	1.7	0.3	8.9
		Storm recessional	4/14/1999	1000	83.9	0.0	4.0	0.7	11.4
		Storm	6/2/1999	1300	88.5	6.8	0.6	0.1	4.1
Warm Creek	WC	Monthly	1/12/1999	1300	na	na	na	na	na
		Monthly	2/10/1999	1620	na	na	na	na	na
		Monthly	3/9/1999	1510	na	na	na	na	na
		Monthly	4/14/1999	1450	55.0	0.0	39.8	0.0	5.2
		Monthly	5/18/1999	1430	0.0	0.0	93.3	0.0	6.7
		Monthly	6/16/1999	1620	77.5	0.0	16.1	0.0	6.3
		Monthly	8/10/1999	1500	68.3	0.0	26.0	0.0	5.7
		Storm	1/27/1999	115	na	na	na	na	na
		Storm	2/9/1999	1900	na	na	na	na	na
		Storm	3/15/1999	1340	na	na	na	na	na
Metropolitan Water District Crossing	MWD	Monthly	1/13/1999	1210	na	na	na	na	na
		Monthly	2/11/1999	1050	0.0	69.6	26.1	0.0	4.3
		Monthly	3/10/1999	1020	0.0	75.9	19.1	0.0	5.0
		Monthly	4/15/1999	1050	0.0	71.7	24.3	0.0	4.0
		Monthly	5/19/1999	1140	0.0	65.1	25.6	2.8	6.5
		Monthly	6/17/1999	1210	0.0	88.2	0.0	0.0	11.8
		Monthly	8/11/1999	1100	na	na	na	na	na
		Storm	1/25/1999	1545	na	na	na	na	na
		Storm	3/15/1999	1800	0.0	12.3	81.8	0.0	5.9
		Storm	4/7/1999	1220	0.0	0.0	92.4	0.0	7.6
Cucamonga Creek at Highway 60	H60	Grab	3/10/1999	1530	0.0	41.8	51.1	2.3	4.9
		Grab	2/11/1999	1600	0.0	0.0	85.7	0.7	13.6
		Grab	4/15/1999	1630	0.0	0.0	100.0	0.0	0.0
		Grab	5/19/1999	1610	64.5	1.8	23.1	0.0	10.6
		Grab	8/11/1999	1820	55.0	0.0	41.4	1.5	2.1

Table 3. Model results for endmembers of surface-water samples from the Santa Ana River Basin, southern California—*Continued*.

[na, data not available]

Site name	Site name abbreviation	Sample type	Sampling date	Sampling time	Model results, percentage of each endmember				
					Pristine Water	Wastewater	Urban Water, total	Dairy Water, total	Residual
Inland Empire Utilities Agency Reclamation Plant 1									
	RP1	Monthly	2/11/1999	1630	0.0	92.8	0.4	1.9	5.0
		Monthly	3/10/1999	1540	0.0	93.3	0.0	1.8	4.9
		Monthly	4/15/1999	1700	0.0	90.2	1.9	1.2	6.6
		Monthly	5/19/1999	1720	0.0	86.6	0.9	4.1	8.3
		Monthly	6/17/1999	1840	0.0	100.0			0.0
		Monthly	8/11/1999	1830	0.0	90.2	4.0	0.6	5.2
Cucamonga Creek near Mira Loma									
	CML	Monthly	2/11/1999	1600	0.0	73.0	23.0	0.6	3.4
		Monthly	3/10/1999	1750	14.1	75.5	5.7	0.6	4.1
		Monthly	4/15/1999	1620	32.7	50.5	9.5	0.6	6.6
		Monthly	5/19/1999	1600	0.0	65.8	26.2	0.1	7.9
		Monthly	6/17/1999	1720	0.0	76.3	0.0	0.0	23.7
		Monthly	7/29/1999	1900	68.6	12.7	6.4	0.1	12.2
		Monthly	8/11/1999	1640	na	na	na	na	na
		Storm	3/15/1999	1030	0.0	0.0	100.0	0.0	0.0
		Storm	3/15/1999	1100	0.0	0.0	95.7	0.0	4.3
		Storm	4/1/1999	1500	0.0	0.0	93.4	0.0	6.7
		Storm	4/6/1999	1610	0.0	0.0	94.8	0.0	5.2
Prado	PRD	Monthly	1/14/1999	1530	na	na	na	na	na
		Monthly	2/12/1999	1500	0.0	35.6	60.9	0.9	2.7
		Monthly	3/11/1999	1700	na	na	na	na	na
		Monthly	4/16/1999	1500	0.0	9.0	87.9	0.0	3.1
		Monthly	5/20/1999	1410	0.0	55.9	38.3	1.6	4.3
		Monthly	8/12/1999	1150	0.3	66.3	28.9	1.0	3.5
		Storm	1/25/1999	1315	na	na	na	na	na
		Storm	3/15/1999	1520	0.0	0.0	95.3	0.0	4.7
		Storm	4/6/1999	1930	14.7	47.2	34.5	0.0	3.6
Santa Ana River at Imperial Highway	IMP	Monthly	1/14/1999	1100	na	na	na	na	na
		Monthly	2/12/1999	1100	0.0	32.6	63.8	0.6	3.0
		Monthly	3/11/1999	1120	0.0	44.5	51.6	0.0	3.8
		Monthly	4/16/1999	1030	0.0	8.2	88.1	0.0	3.6
		Monthly	5/20/1999	1200	0.0	52.2	41.8	1.7	4.3
		Monthly	6/18/1999	930	0.0	76.3	17.8	0.0	5.9
		Monthly	8/12/1999	1040	na	na	na	na	na
		Storm	1/25/1999	1140	na	na	na	na	na
		Storm	2/9/1999	2000	na	na	na	na	na
		Storm	3/15/1999	1350	0.0	0.0	95.3	0.0	4.7
				Diurnal study element					
Mill Creek at Duck Club	SDC	Time-series grab	7/29/1999	1520	52.6	34.8	6.6	0.0	6.0
		Time-series grab	7/29/1999	1730	51.1	32.7	11.5	0.0	4.8
		Time-series grab	7/29/1999	2030	52.0	28.7	13.9	0.1	5.4
		Time-series grab	7/29/1999	2330	36.4	44.3	14.0	0.3	4.9
		Time-series grab	7/30/1999	230	31.8	54.1	10.2	0.2	3.7
		Time-series grab	7/30/1999	530	52.9	36.7	5.8	0.0	4.6
		Time-series grab	7/30/1999	830	49.4	40.2	5.1	0.0	5.3
				Dairy ponds					
Dairy pond 1	D1	Grab	7/29/1999	1150	0.0	0.0	0.0	100.0	0.0
Dairy pond 2	D2	Grab	7/29/1999	1120	0.0	0.0	0.0	100.0	0.0
Dairy pond 3	D3	Grab	7/29/1999	1040	0.0	0.0	0.0	100.0	0.0
Dairy pond 4	D4	Grab	7/29/1999	1010	0.0	0.0	0.0	100.0	0.0
Dairy pond 5	D5	Grab	7/29/1999	1140	0.0	0.0	0.0	100.0	0.0

Warm Creek

Site Warm Creek (WC) is located high in the lower Santa Ana River Basin, and the most urbanized of all the sites in this study. This site receives little or no mountain water. Rather, the base flow in this reach is mostly ground water discharged to the river channel, with some addition of Urban Water runoff. The DOM concentrations at site WC ranged in value from 1.4 mg/L to 3.8 mg/L (*fig. 9B*), with an average value of 2.0 mg/L, near the middle of the range of samples in this study. The UVA averaged 0.063 A, ranging from 0.034 to 0.115 A (*fig. 9A*), and the FI averaged 2.79 QSU with a range from 2.13 to 3.73 QSU (*fig. 9C*).

The FI of site WC (*fig. 2*) samples were greater than the upstream sites, although the general shape of the spectra were similar to the upstream sites. The major feature of the site WC fluorescence spectra was a maximum near 255/435 with an extension toward the area of 323/435. The height of the peak at 255/435, in relation to that at 323/435, was consistently higher at site WC than was seen in samples lower in the Santa Ana Basin (*fig. 9*, *table 2*). On the basis of the indicator excitation/emission pairs, humic-like fluorescence was elevated in comparison to sites at higher elevations, following the general pattern of increasing humic-like fluorescence with increasing DOM content. The protein-like fluorescence of samples from this site was similar to study averages.

The model apportionment of sample spectral properties to endmembers was more variable at this site than at most other sites in the study. The apportionments averaged 51 percent Pristine Water and 44 percent Urban Water, with the remainder captured by the residual. However, the endmember apportionment ranged from 0–79 percent Pristine Water, and from 15–93 percent Urban Water. Although these values may be realistic on the basis of known sources within the watershed, the relative apportionment between Pristine Water and Urban Water in samples of intermediate fluorescence is questionable.

Metropolitan Water District Crossing

Site MWD is located in the center of the valley between the San Bernardino Mountains and Prado Dam; the highest site located on the main stem of the Santa Ana River (*fig. 2*). This site is a few miles downstream of two major wastewater-treatment facilities. A tracer-discharge experiment conducted at the same time as this study showed that Wastewater discharge comprised 75 percent to 80 percent of base flow, with 20 percent to 25 percent from non-Wastewater sources (Mendez and Belitz, 2002).

DOM concentrations and variability in samples from this site were low, varying over a small range between 1.8 and 2.4 mg/L (*fig. 9B*); nearly one-half of the study average. The UVA was more variable, ranging from 0.033 to 0.179 A (*fig. 9A*), with an average value of 0.070 A. FI was much less variable, ranging from 2.97 to 3.81 QSU (*fig. 9C*) with an average value of 3.51 QSU. SUVA and SFI were notably high at this site (*fig. 9D,E*), however, averaging 0.034 A-L/mg and 1.65 QSU-L/mg, respectively, much higher than the study averages of 0.026 A-L/mg for SUVA and 1.04 QSU-L/mg for SFI (*fig. 9D,E*). These values indicate there was a relatively high concentration of chromophores and fluorophores in the DOM pool at this site. All humic-like and one of the two protein-like excitation/emission pairs were elevated at this site, suggesting a complex origin for the DOM.

The fluorescence spectra of samples from site MWD were similar to that of the Wastewater endmember, having prominent maxima in the regions of 255/435, 323/435, and 255/350. However, the peak at 255/350 was not as topologically defined as that at 323/435 in the site MWD samples as it was in other Wastewater-impacted sites such as site RP1 (*tables 2, 3*).

Deconvolution of endmember contributions using the model found an average of 74 percent Wastewater endmember contribution to the spectral properties of individual samples, varying between 65 and 88 percent. Urban Water accounted for an average of 19 percent of the mixture, and there was an average of 6 percent residual. The Wastewater contribution derived by the spectral deconvolution was similar to that found in the tracer study, a totally different and unrelated method, by Mendez and Belitz (2002), and generally corresponds to known sources in this reach of Santa Ana River.

Cucamonga Creek at Highway 60

Site H60 is located on Cucamonga Creek, a tributary to the Santa Ana system that drains a lower and more westerly part of the Santa Ana Basin. The watershed above site H60 is a small urban watershed, similar to site WC. The difference between the two sites is that the flow at site WC is mostly ground water, whereas site H60 is mostly Urban Water surface runoff.

DOM concentrations in samples from this site averaged 12.0 mg/L and ranged from 4.9 to 19.0 mg/L (*fig. 9B*). These were much higher than the average value of 4.2 mg/L in the study, and near values observed in storm samples. Consequently, UVA and FI values also were elevated, averaging 0.270 A (*fig. 9A*) and 10.24 QSU (*fig. 9C*), respectively. DOC-normalized values of SUVA and SFI, however, were below the study averages, indicating that the relative abundance of chromophores and fluorophores in the DOM pool was low, in comparison to most other sites. This result is consistent with inputs of chlorinated source waters such as Wastewater or treated drinking-water. Site H60 samples have a low response in the humic-like fluorescence region, but were in the mid-range of response in the region of protein-like fluorescence.

The fluorescence spectra from this site were different than those found at the other sites. Like many other sites, site H60 spectra have a high FI located at 255/435, and an arm reaching in the direction of 323/435, but there also was an arm that reached in the direction of 275/375 (*table 2*). These differences were likely the expression of the chromophores and fluorophores characteristic of urban settings.

Application of the model to samples from this site produced mixed results. The model assigned an average contribution of 60 percent Urban Water to the monthly samples, but the variability was high, ranging from 23–100 percent of the total (*fig. 10B*). The model estimated a contribution of 64 and 55 percent Pristine Water in the May and August samples, respectively—an unlikely result in view of the elevated fluorescence values. Also, the model assigned a 42-percent endmember contribution to Wastewater in the March sample. This assignment may reflect a large fraction of treated drinking water such as runoff from domestic sprinklers, but no evidence of such inputs is available. The relatively poor model assignments at this site may result from poor characterization of the Urban Water nonstorm endmember; it was not adequately sampled and characterized as part of this study. This may, in part, account for the high variability for the Urban Water contributions.

Inland Empire Utilities Agency Reclamation Plant 1

Monthly water samples were collected immediately downstream of the reclamation plant, located on Cucamonga Creek. During base flow periods, discharge from this facility comprises more than 90 percent of the flow in Cucamonga Creek.

The DOM concentrations ranged from 5.4 to 6.8 mg/L (*fig. 9B*) with an average value of 6.1 mg/L, near the study average of 4.2 mg/L. The UVA and FI were much lower than study average values, averaging 0.071 A (*fig. 9A*) and 2.99 QSU (*fig. 9C*), respectively, in comparison to study means of 0.096 A and 4.45 QSU. Consequently, SUVA and SFI values similarly were lower, averaging 0.012 A-L/mg (*fig. 9D*) and 0.50 QSU-L/mg (*fig. 9E*), respectively, in comparison to study mean values of 0.026 A-L/mg and 1.04 QSU-L/mg.

The fluorescence spectra of the Wastewater discharge were stable, relative to other sites, with peaks at 255/435, 323/435, and 275/375 present in all samples at relatively equal intensities (*table 2*). As might be expected, fluorescence indicators indicative of humic materials were low in the spectra of samples from this site, but indicators of protein-like fluorescence were elevated. The model endmember assignments based on the spectra of samples collected at this site were consistent with a Wastewater endmember source (*fig. 10C*), averaging a 92-percent Wastewater assignment, with a 5-percent residual.

Cucamonga Creek near Mira Loma

Site CML is located on Cucamonga Creek downstream of site RP1, below the confluence of the drainage represented by site H60, and below a storm-water-diversion system (*fig. 2*). Flow at site CML is confined in a concrete-lined channel. During base-flow conditions, the majority of the flow is Wastewater discharge from site RP1 (*fig. 2*); although there are additional inputs from various other sources, including Urban Water runoff. Site CML also is located within an area of intense dairy production, wherein several confined animal feeding operations and associated manure treatment lagoons are located adjacent to the channel.

At site CML, DOM concentrations ranged from 5.8 to 12.0 mg/L (*fig. 9B*) (average 7.0 mg/L) and were above the monthly system average of 4.2 mg/L for the Santa Ana River Basin. The UVA and FI were lower than expected, based on these DOM values, and were below the monthly average for the system. Accordingly, SUVA averaged 0.016 A-L/mg (*fig. 9D*) and SFI averaged 0.70 QSU-L/mg (*fig. 9E*), lower than average. The lower-than-average concentration of chromophores and fluorophores within the DOM pool corresponds to samples known to be high in Wastewater inputs.

The fluorescence spectra generally were similar in appearance to site RP1 samples. The overall FI had an average value of 5.41 QSU (*fig. 9C*), but peaks at 255/435, 323/435, and 255/350 were well defined, and relatively equal in prominence. The intensities at 255/435 in site CML samples were higher than those found in site RP1 samples, although intensities at 323/435 generally maintained similar FI values, suggesting that fluorophores responsible for fluorescence at 255/435 are concentrated by environmental processes. Within the site CML samples, there was a low abundance of humic-like fluorophores, and a high abundance of protein-like fluorescence, similar to samples at sites MWD and RP1 (*fig. 2*).

Model assignments of endmember contributions at site CML were problematic, probably due to the previously described poor characterization of the Urban Water base flow endmember. Nevertheless, the model apportioned the sources an average value of 55 percent for Wastewater, 23 percent for Pristine Water, and 14 percent for Urban Water for the monthly data in *table 3*. The variability within these averages was high, however, with the assignment of Wastewater ranging from 13 to 76 percent, Pristine Water ranging from 0 to 69 percent, and Urban Water ranging from 6 to 26 percent. Similar to results for other sites, the summer samples most poorly fit the conceptual model of sources, suggesting a seasonal calibration of model endmembers would improve the model assignments (*table 3*).

Prado

The Prado site (site 7, *fig. 2*) is located on the main stem of the Santa Ana River downstream of the Prado Dam. The dam was erected primarily for flood control, and the reservoir behind it received inputs from the upper Santa Ana system, Cucamonga Creek, Chino Creek, and other minor tributaries. Within the confines of the reservoir, Orange County Water District maintains a series of wetlands that receive a portion of the flow of the Santa Ana River and are operated to mitigate nutrient concentrations in base flow. The flow at the Prado sampling site is derived principally from dam release of reservoir water during and immediately after storms. The reservoir is operated for flood control and typically detains water for

1 week or less before releasing the mixture into the Santa Ana River. Thus, samples collected at this site represent a contemporaneous mixture of upstream sources. Given the complex mosaic of sources and the possibility that DOM concentration, composition, and fluorescence structure may change while water is impounded behind the dam, the system downstream of Prado Dam provides an opportunity to test whether optical properties are a robust indicator of source.

Santa Ana River at Imperial Highway

Site IMP is located 11 miles downstream of Prado Dam, where Imperial Highway crosses the mainstem of the Santa Ana River (*fig. 2*). During base flow, most of the flow at site IMP is water passing site PRD, although there are some additional sources of water as well as transformations in water quality between these two sites. During storms, however, there may be substantial changes in DOM sources to this site, due to flood-control operation of the dam and runoff from the surrounding urban landscape. This site is immediately upstream of the system of diversion structures that captures Santa Ana River water for ground-water recharge.

Monthly samples from IMP were similar to those from site PRD, in most respects. The DOM concentrations ranged in value from 4.1 to 5.6 mg/L (*fig. 9B*), with an average value of 4.9 mg/L. SUVA values averaged 0.022, ranging from 0.008 to 0.036 A-L/mg (*fig. 9D*). SFI values averaged 1.26 QSU-L/mg, ranging from 1.07 to 1.43 QSU-L/mg (*fig. 9E*). As for the site PRD samples, concentrations of humic-like fluorophores were higher than average, and concentrations of protein-like fluorophores were lower than average. The appearance of fluorescence spectra in samples from site IMP was very similar to those obtained from monthly samples at site PRD, although the area surrounding 255/435 was broader and, on average, slightly more intense (*table 2*). Model apportionment of endmember contributions also were similar, averaging 53 percent Urban Water (range: 18–88 percent), 43 percent Wastewater (range: 8–76 percent), and 0 percent for Pristine Water and Dairy Water, and a 4-percent residual.

The similarity and consistency of the results for sites PRD and IMP, given their direct hydrologic connection during base-flow conditions, provides additional evidence that the optical properties were robust.

Results from Storm Sampling

Analysis of samples collected during storms at selected sites provided the opportunity to examine the response of the optical signals to changes in sources of DOM associated with storm runoff. Considerable change in the hydrograph was observed at these sites during storms, presumably causing changes in the sources of DOM in comparison to base-flow conditions. The analysis of the optical properties of monthly samples indicated that the source assignments generally were robust based on the limited number of source samples used for this study. But, in most cases, storm samples represent a dramatic change in DOM source when compared to base-flow conditions (see, for example, *fig. 5C,D*). Stormflow samples from different areas in the Santa Ana Basin were examined and compared to base flow results to see if changes in optical properties and model source assignments corresponded to changes in the hydrograph, as well as any expected changes in the source of water at the sample sites. The stormflow samples were collected at sites MEN, WC, MWD, CML, PRD, and IMP (*fig. 2*).

Storm samples generally were higher in DOM concentration than monthly base-flow samples from the same location, ranging up to 32.0 mg/L at site WC. The storm sample averages of DOM concentrations from all sites roughly doubled in comparison to monthly averages of base-flow conditions. The considerable variability in base flow DOM concentrations also was reflected in the doubling during storm flows. For example, samples from site MEN increased from a monthly average of 1.3–2.2 mg/L DOM during storms, while samples from CML increased from a monthly average of 7.0–16.4 mg/L DOM during storms.

The optical properties of storm samples changed considerably in comparison to properties during base flows. Storm samples generally were elevated in chromophore and fluorophore content, relative to DOM. The SUVA of storm samples from the relatively pristine site MEN were nearly 50 percent greater than monthly averages, and the SFI increased by 14 percent. In comparison, chromophore and fluorophore content in samples from the predominantly urban site H60 elevated to a greater degree; the SUVA of storm samples were elevated by 70 percent and the SFI by 66 percent. The difference between these two sites illustrates that DOM optical properties respond differently to storm flows, likely reflecting different DOM sources within the drainages.

Although the differences in SUVA and SFI were sizeable, for optical measurements to be an effective indicator of changing sources within the Santa Ana Basin, the model assignments of endmember source should reflect sources within the drainage related to storm water runoff. In the case of the relatively pristine site MEN, model assignments of endmember contributions changed little in storm samples from site MEN even though the DOM nearly doubled; 85 percent was allocated to the Pristine Water endmember, consistent with the upland undeveloped watershed above site MEN. In contrast, samples from sites MWD and CML, both of which had majority Wastewater source assignments during monthly sampling, shifted in source assignment during storm samples to more than 85 percent Urban Water, consistent with the properties of their drainages.

The model also provided reasonable source assignments for apparently conflicting results from site PRD, where the two storm samples analyzed gave dissimilar results, with one identified as principally composed of Urban Water, and the other a mixture of Pristine Water, Wastewater, and Urban Water, similar to the monthly sample assignments. The storm sample receiving the Urban Water assignment was collected

during a period when water was being impounded behind Prado Dam and, thus, represents a period of predominantly Urban Water inputs. The sample that received the mixed source assignment was collected during a period when water was being released from Prado Dam and, thus, represents a mixture of water from upstream of the Dam (California Data Exchange Center, 2000) rather than local stormflow inputs. This source assignment was similar to monthly samples during base-flow conditions, which generally receive water from the same mixture of sources.

Finally, we quantitatively assessed the performance of the model by comparing model source assignments to changes in the hydrograph during storms at sites MWD and CML (*fig. 11*). The measured discharge at each site can be decomposed into base flow and storm flow. Thus, the relative contribution of stormflow sources can be calculated throughout the hydrograph, assuming base flow remains constant. At sites MWD and CML, the base flow primarily was composed of Wastewater discharge, and the model results can be decomposed into the base-flow Wastewater endmember, and the stormflow sources. The results from these two analyses agree well (*fig. 11A,B*), indicating that model deconvolution of optical spectral data provides a reasonable approximation of the proportional contributions from DOM sources, as related to the hydrology.

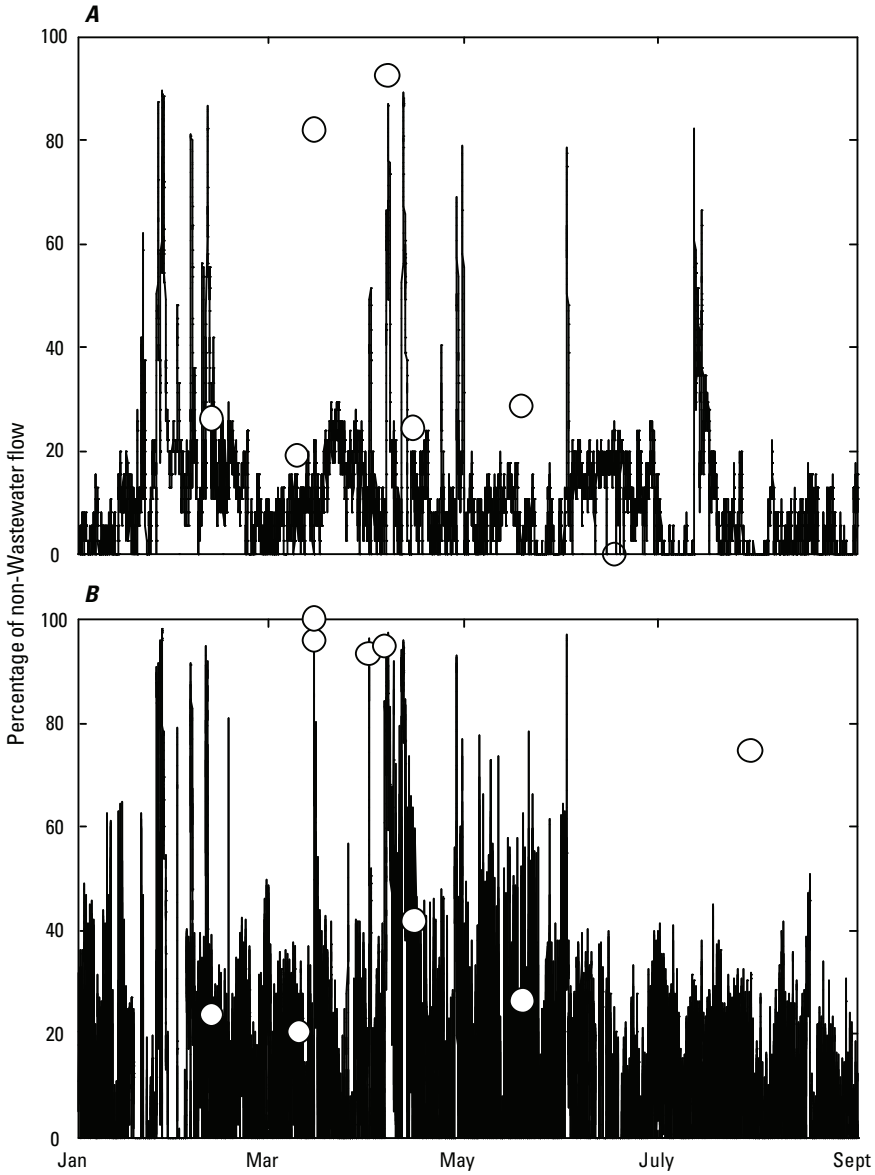


Figure 11. Comparison of hydrologic and model-derived endmember assignments for two sites in the Santa Ana River Basin, southern California. (A) Metropolitan Water District Crossing, and (B) Cucamonga Creek near Mira Loma. Solid line represents fraction of non-Wastewater flow derived from hydrograph separation. Open symbols represent optical properties apportioned by the model to non-Wastewater endmembers.

Results from Comparison to Common Materials

Water extracts of a few common materials likely to be present in urban surface-water runoff were analyzed to test whether the optical properties were similar to those observed in the samples or whether their presence confounded the discrimination of the model. Our hypothesis was that the similarities between the spectra of common materials and environmental samples would be small because organic material in runoff is dominated by natural sources, even in urban settings. Conversely, if we found that the presence of one or a small suite of common materials dominated the observed variation in optical properties, the effectiveness of using optical properties would be diminished to those cases where the substance was intimately associated with the endmember. We examined extracts of antifreeze, gasoline, motor oil, shampoo, and laundry detergent as representative common materials that might be found in urban systems.

The antifreeze exhibited four prominent fluorescence peaks, including one at 260/350, another at 260/510, another at 340/510, and another at 380/510. The principal peak for the gasoline extract was located at approximately 275/335. Motor oil also had only one prominent peak located at approximately 260/350. Shampoo had one peak located at 260/325. The laundry detergent exhibited peaks on fluorescence at approximately 260/430 and 320/430.

To investigate if the presence of these common materials in water samples affected the observed variance in the optical spectra of the study samples, we ran the model using the spectra obtained from the common materials in place of the original model endmembers. Using common materials as endmembers did not explain the variability among the water samples. The average model residual using the common materials as endmembers was 28 percent. This value is similar to the 35-percent average residual fit for "organic-free" blank water, which has no spectral structure. Treated Wastewater discharge consistently exhibited a residual of 26–28 percent. The high residual for fits of common material spectra to sample data suggests that common substances tested do not control or confound the optical signals or model fits in this study.

Results from Data Reduction

An ancillary goal of this study was to identify the most discriminating subset of data useful for source assignment, and to test if the model assignments using the reduced subset were accurate. Using a subset of targeted wavelengths, samples may be analyzed more rapidly. Also, in-place monitoring devices could be manufactured more inexpensively if fewer measurements were required. We chose to optimize the model for 16 excitation/emission wavelengths as a reasonable goal. This represents less than 1 percent of the information in the full optical spectra.

We identified the most discriminatory excitation/emission pairs within the data set using principal component analysis (PCA). Sixteen excitation/emission pairs with large loadings were chosen by picking the peaks of the PCA spectra that collectively describe more than 99 percent of the variance in the data. The 16 excitation/emission pairs identified in this way then were modeled using the same modeling technique we used for the full EEM data. The model assignments and residual of the full EEM model were then compared to those obtained from the reduced data model to establish the relative accuracy.

Model assignments using only the most discriminating 16 excitation/emission pairs agreed well with model results using the full fluorescence spectra (*fig. 12*). Of the 88 samples used for this study, the reduced data model assignments for only 17 samples (20 percent) are more than 15 percent different than the model assignments of the full EEM model. Thus, 80 percent of the samples (71 samples) had results using the 16 excitation/emission pairs that were greater than 85 percent similar to those obtained with the full EEM model. There was no discernible pattern for samples exceeding the 15-percent threshold; deviations from the full EEM model results were found in one or more samples for most sites in the study, including sites WC, PRD, IMP, SDC, H60, and CML. All the reduced data model results from the Dairy areas are identical to the output from the full EEM model.

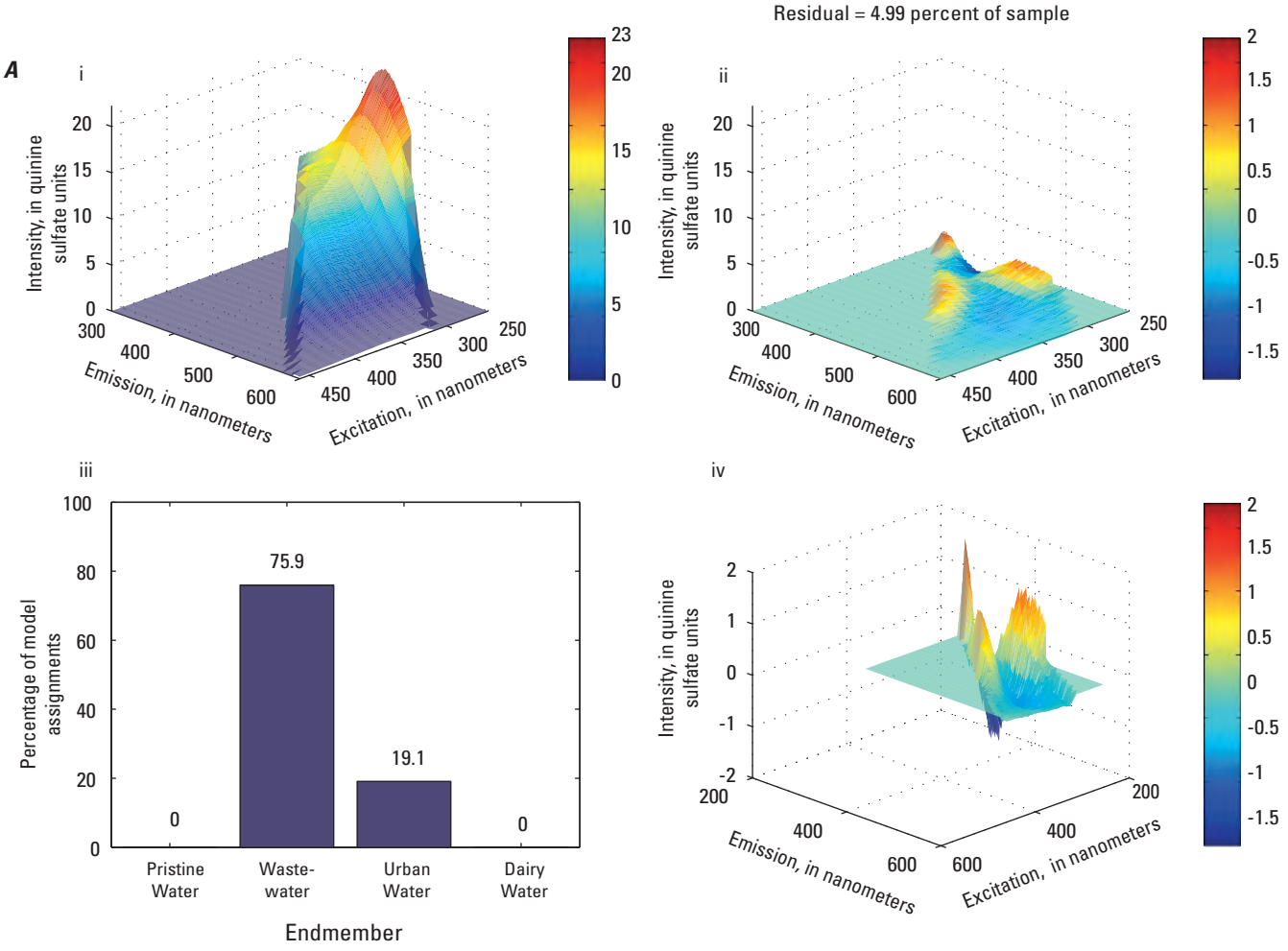


Figure 12. Representative example of model-derived assignments using the full and reduced data sets. (A) Full data set; (i) full-scale spectral response, (ii) spectral response set to the scale of maximum intensity in the whole data set, (iii) component fraction estimates, and (iv) spectral response of the residual. (B) Reduced data set; (i) component fraction estimates, (ii) full-scale response for the selected excitation/emission pairs, and (iii) reduced data set residual.

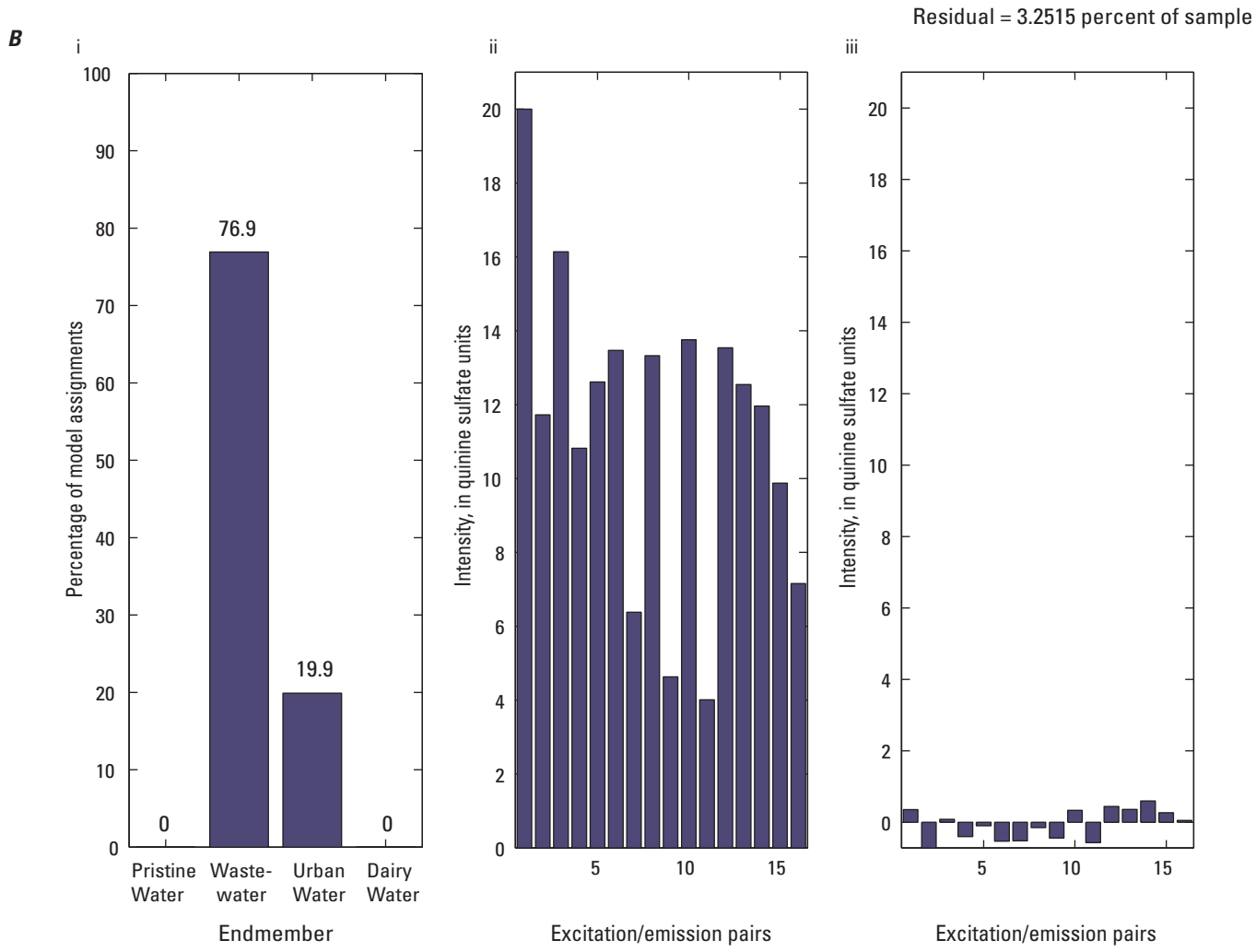


Figure 12.—*Continued.*

These results suggest that it is feasible to reduce the number of wavelengths monitored, although it seems clear that some of the discriminatory potential is lost. There is likely a trade off between discriminatory ability and number of wavelengths measured, but the reduction from more than 2,000 wavelengths to 16 wavelengths retained the major discriminatory elements in the data.

Evaluation of Results

The analysis of the optical properties of selected samples from the Santa Ana Basin indicate that there was a substantial amount of discriminatory, source-related information available in the optical properties of the water samples in this study. The results provide good empirical evidence that deconvolution of optical data using a simple linear mixing model provides reasonable identification of the DOM from different sources in the Santa Ana Basin. Variations in sample spectra were in general agreement with probable contributions from major DOM sources. For example, the variation in humic and protein indicators followed trends that can be explained through the fundamental organic geochemical processes that are controlling the distribution and occurrence of DOM chromophores and fluorophores in the Santa Ana Basin, rather than the occurrence of simple common materials. Explicit examination of the potential contribution of common materials in urban environments found that they did not obscure optical spectra or source assignments. Also, several potentially confounding effects, such as changing DOM concentrations and photo alteration during time-series samplings did not interfere with endmember source assignments. Together, these empirical observations indicate that the optical data are sufficiently discriminatory, and the DOM sufficiently chemically robust to function as a tracer of source.

The four principal endmembers used in this study, Pristine Water, Wastewater, Urban Water, and Dairy Water, account for 94 percent of the variability in optical properties of the samples in this study. These endmember spectra were sufficient to explain the vast majority of variability in the optical properties within the samples tested, and indeed provide reasonable and plausible explanations for the variation in DOM from different sources in the system. Pristine Water accounted for an average of 25 percent, Wastewater accounted for 32 percent, and Urban Water accounted for 37 percent of the model source assignments.

Most often, the optical properties of individual samples were best explained as a simple mixture of two endmembers, either Urban Water and Wastewater spectra or Urban Water and Pristine Water. Most of the samples in a ternary plot of Pristine Water, Wastewater, and Urban Water contributions appear at the edge of the plot rather than in the interior field, indicating the samples generally represent a simple mixture of two endmembers (*fig. 13*). Samples integrating watershed areas receiving mostly unadulterated rain water reflect a mixture with Urban Water sources during storms. Samples from regions where base flow is largely reclaimed water exhibit a mixture of Urban Water and Wastewater source spectra.

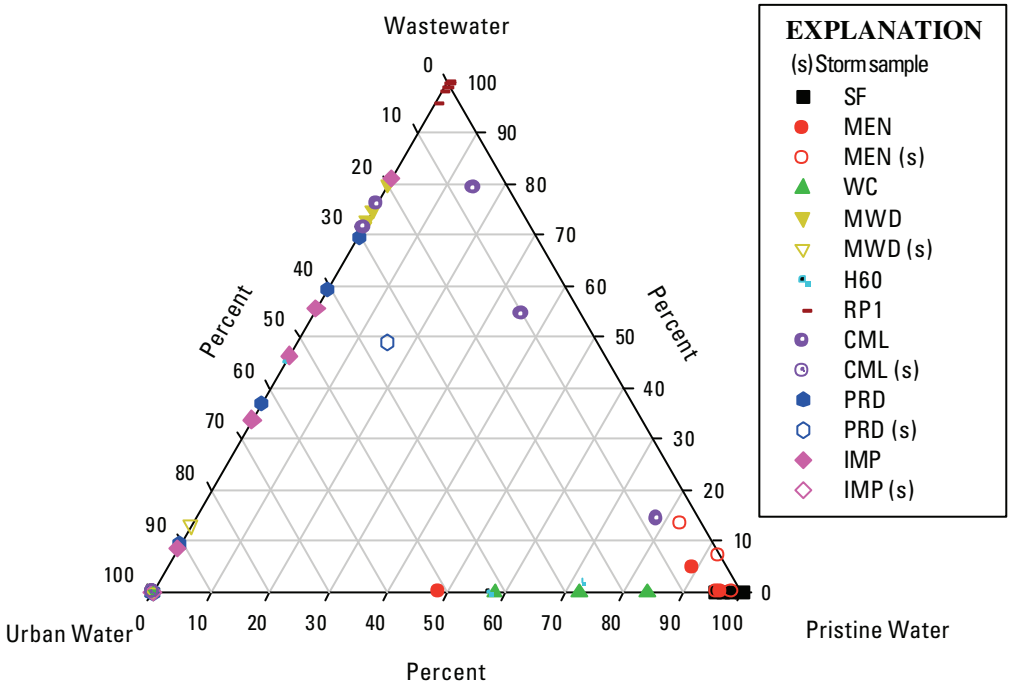


Figure 13. Ternary diagram showing model apportionment of endmember contributions for fluorescence spectral data in samples collected monthly in the Santa Ana River Basin, southern California.

Model assignments of source generally agreed with known sources at most sites. For example, the model endmember assignments for sites CML and MWD were predominantly Wastewater during base-flow conditions and Urban Water during storms, whereas samples from the relatively undeveloped site MEN are assigned to the Pristine Water endmember. The spectral properties of source were robust even in relatively complicated mixtures where the retention times are long. For example, samples from site PRD reflect the mixture of Pristine Water, Wastewater, and Urban Water endmembers that exists when water is released from the Prado Dam during and following storms.

The Dairy Water endmember was included in the model but appeared to be a vanishingly minor contributor to the spectra of the watershed samples. This was true even though all available examples of dairy pond spectra were used in the model to maximize the sensitivity of the model to optical properties related to dairy manure treatment lagoons. Dairy endmember model assignments were reported as the aggregated value of the fit to each of the available dairy samples, but the average model-derived dairy source assignment for the samples in this study was less than 0.01 percent, and the high value was slightly more than 4 percent.

The residual of the model endmember assignments averaged 6 percent of the whole, indicating that the modeled endmembers described the fundamental variability in the spectra of watershed samples, but not all of the variability within the data was captured. Residuals could be caused by either a missing endmember or by variation within the optical spectra of the endmembers during the course of the study. The properties of an endmember may be more variable than was captured in this study or the properties may change systematically with time. For example, seasonal changes in the optical spectra of urban runoff may occur due to seasonal variability in rates and extents of decomposition of natural organic matter.

The observation that the residuals within this dataset are distributed equally between the base flow samples (when endmember variability is expected to be high) and storm samples (when endmember variability is expected to be low) suggests that poor constraints on endmember optical properties, rather than a missing endmember, is the best explanation for the residual. Monthly samples at sites of known source, such as sites MWD and H60, exhibit model residuals near the system average, indicating variability in the optical properties of sources. In some cases, such as at site CML, the model residual increased during the course of the study, suggesting that seasonal changes affected endmember properties.

The patterns of residual occurrence and source misassignments suggest potentially useful changes to the model approach. For example, if a study using a system-wide optical-monitoring program were undertaken, the effects of changes in the source spectra with time could be mitigated by sampling the sources frequently during the period of the study, and recalibrating the model as frequently as is practical. Another approach would be to acquire a library of source spectra with time, representing the possible variation in the endmember. Each element of this library of source spectra could be tested as an individual model endmember, but aggregated into the source assignment for reporting, as was done for the Dairy Water endmember in this study. This would provide a much broader representation of endmember variability. Another potential improvement to the modeling approach is to use a simple parameter such as FI to identify the endmembers to be used in the model. This approach would ameliorate the model confusion between Pristine Water and Urban Water sources, since samples with a low FI always are Pristine, and samples with a high FI always are Urban. This approach also would permit separation of samples with similar spectra.

Despite the confounding effects and inherent imprecision in using optical properties for source assignment, the differences in the signals seem to be sufficient to provide reasonable estimated source assignments, in most cases. This, in turn, suggests that resolution of optical properties using field or lab-based instrumentation is a potentially useful tool for understanding hydrologic and DOM variability in watersheds. Given the results of this pilot study, further development seems warranted.

Conclusions

The results of the study support the following conclusions:

(1) There was significant source-related variability in the optical spectra of water samples collected across the Santa Ana Basin during the period of the study.

(2) Substantial, robust differences were present in the optical spectra of sources of dissolved organic material (DOM) to the Santa Ana Basin.

(3) A four-component model using optical properties representative of relatively Pristine water, Wastewater, Dairy Water, and Urban Water runoff explained 93 percent of the variability in optical properties among samples collected during the course of the study, indicating: (a) the primary DOM sources were represented in the study; and (b) the optical characteristics of endmember sources were persistent during surface-water residence times in the Santa Ana Basin.

(4) Model decomposition of spectra obtained from blank water and other test water samples resulted in unattributed source assignments greater than 90 percent, indicating the model responded well to source related optical signatures, and that those signatures were sufficient to differentiate the sources from random or background signatures.

(5) Dairy (waste) Water was a trivial contributor to the optical properties of water samples collected in the Santa Ana Basin.

(6) Model estimates of endmember contributions agreed within 15 percent with physical hydrologic estimates, such as hydrograph separation and tracer studies.

(7) Model estimates using a selection of 16 fluorescence excitation/emission pairs agreed with full excita-

tion/emission matrix model estimates more than 80 percent of the time within a tolerance of 10 percent, suggesting that more economical sensors and simpler analytical methodologies would be effective for similar source studies and routine monitoring.

(8) Significant improvement to the model assignments would likely result from two minor modifications: (a) improved characterization of the base flow urban endmember; and (b) use of total fluorescence intensity to discriminate between Pristine Water and Urban Water endmember spectra prior to spectral deconvolution.

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