Temporal variability patterns of stormwater concentrations in urban stormwater runoff

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ABSTRACT

Stormwater runoff is currently perceived as a major source of pollutants discharged to the coastal oceans of southern California, but the quality and quantity of stormwater runoff is highly variable. In this study, nearly 2,000 samples were collected at 15-min intervals during the 1997/98 wet season from the Santa Ana River, an urbanized watershed in Orange County, California, to assess the magnitude of "first flush" versus seasonal flushing, and to assess pollutant variability within and among storm events. All samples were analyzed for total suspended solids (TSS); and a selected subset was analyzed for total organic carbon (TOC), total nitrogen (TN), and trace metals (cadmium, chromium, copper, lead, nickel, and zinc). Flow ranged up to five orders of magnitude and constituent concentrations routinely varied among storms by two orders of magnitude. Flow was the largest factor that accounted for changes in TSS concentrations. The second largest factor was pollutant build-up and wash-off, but the "first flush" effect of concentrations (within-storm variance) appeared in only a limited number of storm events. However, significant seasonal flushing (among-storm variance) was observed. There were 220 non-rain days prior to the season's first event, and the first four storms had significantly higher concentrations of TSS and trace metals than the remaining storms of the season.

INTRODUCTION

Stormwater runoff is currently one of the largest sources of pollutants to coastal oceans and inland waterways (U.S. EPA 1995). Stormwater discharges currently contribute as much pollutants as, or more than, publicly owned treatment works (POTWs) in the Southern California Bight (SCB), a source that has long been perceived as the largest source of pollutants to the coastal oceans of this region (SCCWRP 1973, Schiff and Tiefenthaler 2001). Stormwater runoff rates and volumes increase in urban areas due to increased impervious surface areas. Urbanization also increases the number of sources, the types of constituents, and the amount of pollutants in surface runoff (Heaney *et al.* 1999).

Uncontrolled urban runoff can have adverse impacts on receiving waters. Between 1977 and 1981, Pitt and Bozeman (1982) investigated the effects of urban runoff on water quality, sediment quality, and biota in Coyote Creek in San Jose, California. These studies found a significant decrease in the abundance and diversity of biota in urban, compared to non-urban, creek reaches. The 1991 Santa Clara Valley Nonpoint Source Pollution Control Program (SCVNSS 1991) conducted toxicity tests at stream and land use stations including Coyote Creek. Results showed that during dry weather, only

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14% of the tests were toxic. During wet weather, however, the majority of samples from these sites were toxic. In 1996, Bay *et al*. (1996) conducted toxicity tests in southern California on discharges from an urbanized creek and an unurbanized creek in the Santa Monica Bay watershed. Results showed that urban creek stormwater toxicity was higher in magnitude and occurred more frequently than non-urban stormwater flows. Moreover, receiving water toxicity was directly correlated with the quantity and quality of stormwater it received.

Although stormwater discharges are currently perceived as one of the largest inputs of pollutants, and toxic effects are regularly measured in receiving waters, large variability and uncertainty remain associated with runoff mass emission estimates. Variability and uncertainty are the results of runoff loadings, which largely depend upon runoff amounts and precipitation. In the SCB, variability and uncertainty in runoff mass emission estimates are amplified by three factors: infrequent but intense rainfall patterns, differing watershed characteristics, and infrequent monitoring.

The first factor, infrequent but intense rainfall patterns, is characterized by long dry periods without rain (six months) followed by rain flow rates that can change by orders of magnitude in less than one hour. The second factor, differing watershed features, affects runoff quantity/quality and variability in pollutant concentrations. The third factor, lack of monitoring, limits the ability to perform regionwide estimates of stormwater inputs to the coastal ocean, compare watersheds, and assess the relative loading among different sources of inputs. The four coastal counties are home to over 17 million people; 25% of the nation's population within 50 km of the coastal zone reside in southern California (Culliton *et al*. 1990). There is relatively little coastal space that has not been subjected to construction and resource depletion. An estimated 5% of the watershed area and 2% of the total runoff volume were representatively sampled during the 1994/95 water year to make assessments of stormwater runoff water quality and mass emissions (Schiff and Stevenson 1996).

The goal of this study is to provide a census of runoff water quality to achieve an assessment of constituent variability within and among storm events. The objective is to comprehensively measure runoff from an urbanized southern California watershed and assess the magnitude of "first flush" versus seasonal flushing. This study was conducted during an El Nino year in which above-average precipitation occurred, allowing an opportunity to document extremes in variability of water quality and quantity.

METHODS

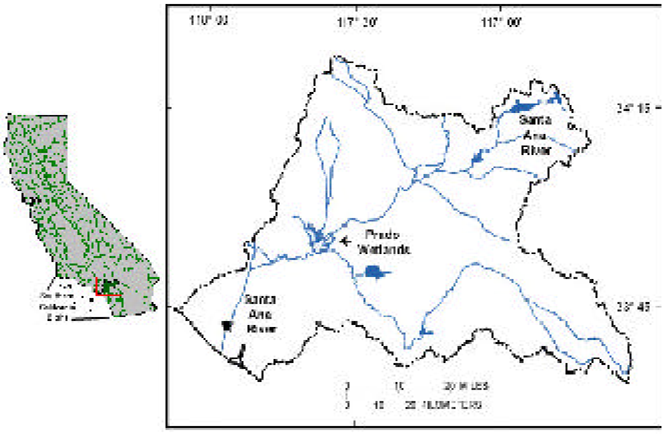
The Watershed

The Santa Ana River is a large coastal river system in southern California. The river originates in the San Bernardino Mountains and flows over 161 km southwesterly, where it discharges into the Pacific Ocean at Huntington Beach. Approximately 50% of the 6,863.5 km^2 watershed is comprised of urban and agricultural land uses (Figure 1). Long-term average annual rainfall is 33.02 cm (SAWPA 1998). Like many other channels in southern California, the Santa Ana River is a highly modified system. In the lower reaches, the trapezoidal, open channel measures over 76.25 m wide and is entirely concrete lined. Upstream uses, including Prado Dam (as flood control) and recharged groundwater (Orange County Water District) dramatically affect the hydrology of the Santa Ana River. As a result, the Santa Ana River is an intermittent stream with little or no flow during most of the year and with high runoff volumes reaching the ocean during storm events.

Stormwater Sampling

Stormwater flows were sampled for an entire water year (October 1, 1997, to September 30, 1998) on the Santa Ana River at W. 5th Street in Santa Ana, California, the last flow-gaging station before discharge to the ocean. Automated stormwater samplers were installed on the banks of the river with an intake pipe positioned on the channel bottom. Samplers were configured in a series capable of collecting forty-eight 500 to 1,000 mL individual samples. Samplers were activated when the flow

FIGURE 1. Map of the Santa Ana River watershed. The star represents the sampling site on the Santa Ana River.



rose above baseline conditions (0-0.7 cubic meters per second [m^3/s]). The samplers logged flow and sampling status. A modem enabled communication with the samplers over standard telephone lines. Samples were collected at 15-min intervals; sampling intervals were extended to 3 h for tailing flows during extremely large storms when flow and runoff concentrations were changing slowly.

Analytical Chemistry

Over 1,700 samples were collected during the 1998 water year. All samples were stored under refrigeration and analyzed for total suspended solids (TSS), which are widely viewed as an indicator of stormwater quality and are correlated with other stormwater quality constituents (Sansalone and Buchberger 1997, Thomson *et al.* 1997). One hundred seventy-five of the runoff samples (approximately 10%) were subsampled for total organic carbon (TOC)/total nitrogen (TN), and trace metals analysis. The samples for trace elements were acidified to a pH of less than 2 and held at room temperature until digested.

Suspended Solids

Total suspended solids were analyzed by filtering a 10 to 100 mL aliquot of stormwater through a tared 1.2 μm (micron) Whatman GF/C filter. The filters plus solids were dried at 60° C for 24 h, cooled, and weighed.

Total Organic Carbon and Total Nitrogen

Total organic carbon and total nitrogen (TOC/TN) analysis was performed using a Carlo Erba 1108 CHN Elemental Analyzer equipped with an AS/23 Autosampler in conjunction with Carlo Erba Data Systems software. After taring, an aliquot of each sample was digested with concentrated HCl vapors to remove inorganic carbon. The acidified sample was dried and weighed, then crimped in a tin boat. The Carlo Erba CHN Analyzer oxidizes each sample boat in a quartz combustion chamber. Reaction products were separated using a Poropak QS packed column, and then quantified using a thermal conductivity detector. Acetanilide was used as the external standard. Acetanilide and cyclohexanone were used for quality control check standards. The Certified Reference Material was PACS-1 (3.69% C, National Research Council 1990).

Trace Metal Analysis

Samples for trace metal analysis were prepared by digestion. A well-mixed, 25 mL aliquot of acidified sample was dispensed to a Teflon digestion vessel and 2 mL of ultra-pure HNO3 (Optima, Fisher Scientific) were added, and the vessel capped and sealed. The acidified samples were digested in a CEM MSP1000 Microwave Oven by ramping to 100 psi over 15 min and then holding at 100 psi for 10 min. After cooling, the digestate was centrifuged to remove any remaining residue from the sample. The supernatant with sample digest was transferred to a 15 mL test tube prior to analysis.

Inductively coupled plasma-mass spectroscopy (ICP-MS) was used to determine concentrations of inorganic constituents (aluminum, antimony, arsenic, beryllium, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, silver, and zinc) from sample digest solutions using a Hewlett Packard Model 4500 with Hewlett Packard Data Systems software and following protocols established by EPA Method 200.8 (U.S. EPA 1991). The internal standard solution included rhodium and thulium. Instrument blanks were processed to identify sample carry-over. A spiked sample of known concentration was used as the laboratory control material.

Data Analysis

Rainfall data, summarized from the National Weather Service (Nationwide Climatic Data Center, Ashville NC), were used to complement flow data and to assess the relative amount and intensity of precipitation during storm events. Mean daily runoff volumes and 15-min instantaneous flow were obtained from the United States Geological Survey (USGS 1998) from five instrumented stream flow gaging stations installed on the Santa Ana River. These data were used to evaluate storm flows and calculate runoff volumes; volumes of runoff could be attributed to upstream sources (i.e., dam releases versus local runoff) based upon these gage measurements. Additional stream flow information came from the Orange County Water District (OCWD) Imperial Highway groundwater diversion gages. The OCWD captures low flow and storm flow for recharge in spreading basins of the Orange County groundwater basin. These data were used to calculate the amount of runoff diverted for groundwater infiltration. A combination of flow measurements from USGS and from the samplers in the present study were used to estimate the fraction of runoff volumes representatively sampled during the study.

Stormwater concentrations among storms were compared using an estimate of the central tendency called the event mean concentration (EMC) (U.S. EPA 1983)

(Equation 1). The EMC method weights concentrations by instantaneous flow at the time of sampling and is reported in units of mg/L.

Equation 1:

$$\mathrm{EMC} = \frac{\sum_{i=1}^{n} C_{(t)} Q_{(t)}}{\sum_{i=1}^{n} Q_{(t)}}$$

where:

EMC = Event mean concentration for a storm
$C_{(t)}$ = Individual runoff sample concentration at time t
$Q_{(t)}$ = Instantaneous flow rate at time t of sampling
i = First sample of storm event
n = Last sample of storm event

A related statistic, but calculated to estimate the annual mean rather than by individual storm event, is the flow-weighted mean (FWM) concentration (Equation 2).

Equation 2:

$$\mathrm{FWM} = \frac{\sum_{p=1}^{z} C_{(t)} Q_{(t)}}{\sum_{p=1}^{z} Q_{(t)}}$$

where:

FWM = Flow-weighted mean concentration for the year
$C_{(t)}$ = Individual runoff sample concentration at time t
$Q_{(t)}$ = Instantaneous flow rate at time t of sampling
p = First sample of year
z = Last sample of year

Seasonal Flush and First Flush Analysis

We evaluated two types of pollutant build-up and wash-off phenomena, “seasonal flush” and “first flush.” Seasonal flushing examines among-storm variance to assess whether initial storms of the season have substantially higher pollutant concentrations than storms occurring later in the season. “First flush” examines within-storm variance to assess whether initial flows during a storm have substantially higher concentrations than flows later in the storm.

Seasonal flushing was evaluated in this study for near-continuous sampling of TSS by creating a cumulative FWM curve. The curve was examined for the point at which individual storms no longer affected the slope and baseline FWM conditions had been achieved. Using the cumulative FWM curve as a guide for seasonal break points, seasonal flushing for trace metals was evaluated by comparing EMCs among storms.

First flush was evaluated using both a concentration and mass emissions approach. The concentration approach compared TSS concentrations during a fixed time interval (first hour of storm flow) or initial proportion of storm volume (10, 20, or 30%) relative to concentrations during the remainder of the storm. Concentration ratios for the two portions of each event were calculated with values greater than unity indicating higher first flush concentrations. The second approach examined the cumulative mass emissions throughout a single event. Based upon Bertrand-Krajewski *et al.* (1998), it was assumed that the first flush was significant if at least 80% of the total pollutant load was transported in the first 30% of the volume discharged during a storm event.

RESULTS

Variability of Rainfall, Hydrologic Changes, and Sampling Success

The average volume of rainfall in the lower portions of the Santa Ana River was double the long-term average during the study period. Between October 1, 1997, and September 30, 1998, the average rainfall was 77.8 cm compared to an annual average of 30.0 cm between 1966 and 1967. Of the 22 storms that occurred during this period, 17 had precipitation higher than 0.6 cm (Table 1). All 17 of these storms resulted in significantly elevated stream flows above baseline conditions of < 0.7 m^3/s. The smallest sampleable storm of the season occurred on January 19, 1998, with 0.9 cm of rainfall and a runoff volume of 248.2 x 10^6 L. The largest rain event of the season occurred on December 6-8, 1997, with 11.6 cm of rainfall. The event had a peak intensity of 2.6 cm/h and its longest continuous duration of rainfall lasted approximately 27 h. The next largest runoff events of the season occurred during the following storms: February 6-11, February 14-18, and February 22-March 2, 1998, which resulted in storm volumes ranging from approximately 28.4 to 104.4 x 10^9 L. Total cumulative storm runoff for the year was 264.4 x 10^{12} L.

The main source of the annual discharge volume originated from overflows at Prado Dam (74%), while only 9% of the volume was attributable to local runoff (Table 1). The remaining 17% was a mixture of local runoff and Prado Dam release. The contributions of Prado Dam overflows were exemplified during the February 14-18, 1998, storm (Figure 2). Rainfall intensi-

TABLE 1. Summary of individual storm event characteristics on the Santa Ana River including total rainfall, peak flow for each storm event (peak), total storm volume, percent of total storm volume sampled (percent capture), and percent of volume attributable to upstream sources such as local urban runoff (local), releases from Prado Dam (Prado), or a mix of both between October 1997 – July 1998.

Storm		Total Rainfall	Peak	Volume (L X 10^6)	Percent	Volume (%)		
No.	Date	(cm)	(m^3/s)	Total	Capture	Local	Mix	Prado
1	1997 Sept. 25-27	0.0	3.8	63.2	NA	0.0	100.0	0.0
2	Nov. 13-14	0.9	6.5	229.2	NA	0.0	100.0	0.0
3	Nov. 26-27	1.5	43.1	580.6	55.5	24.8	16.8	58.4
4	Nov. 30 - Dec. 1	1.4	5.6	133.5	NA	0.0	100.0	0.0
5	Dec. 6-8	11.6	270.8	10,698.1	96.8	43.7	26.4	29.9
6	Dec. 18-19	1.6	47.9	824.9	82.2	0.0	100.0	0.0
7	1998 Jan. 9-11	2.0	91.2	4,938.2	79.1	28.3	0.0	71.7
8	Jan. 19	0.1	1.4	17.9	NA	0.0	100.0	0.0
9	Jan. 29	0.9	18.8	248.2	30.3	47.0	0.0	52.9
10	Feb. 3-5	4.7	134.6	6,910.4	89.2	41.1	27.4	31.5
11	Feb. 6-11	6.6	328.9	58,730.0	90.8	2.1	38.2	59.7
12	Feb. 14-18	6.5	211.0	28,389.6	77.4	16.1	5.3	78.6
13	Feb. 19-21	1.7	46.7	3,207.0	81.9	0.0	27.0	73.0
14	Feb. 22 - Mar. 2	5.2	328.9	104,381.2	98.6	2.7	9.0	88.4
15	Mar. 6-11	0.7	43.1	19,158.6	12.03	0.0	3.7	96.3
16	Mar. 13-14	1.6	26.8	606.4	76.5	100.0	0.0	0.0
17	Mar. 25-26	3.6	219.3	3,089.8	90.9	68.2	0.0	31.8
18	Mar. 27-29	0.7	105.5	3,668.7	96.4	0.0	14.9	85.1
19	Mar. 31 - Apr. 2	1.7	47.9	2,960.7	92.7	32.0	11.4	56.7
20	Apr. 11-12	0.5	6.9	359.9	NA	0.0	100.0	0.0
21	May 5-7	3.2	102.9	8,230.6	57.1	18.2	25.2	56.6
22	May 12-15	4.9	189.2	19,478.3	91.2	7.1	21.8	71.2
	Season	77.8	328.9	264,386.4	89.5	9.0	17.3	73.7

ties of approximately 0.8 cm/h generated peak flows in local runoff within 3 h of the beginning of the storm. These flows increased from < 0.7 m^3/s to > 113.3 m^3/s during this time period. Due to a flow lag associated with dam releases, a rapid increase in flow rate occurred 6 h after the cessation of rain. Flow associated with dam releases nearly doubled, climbing to approximately 212.4 m^3/s. Dam releases also ended abruptly, as opposed to tailing storm flows, as weirs were raised and discharges were cut off.

Seasonal Flushing and Among-Storm Variance

Individual storm event mean concentrations from the Santa Ana River varied widely during the 1998 water year and typically followed a log-normal distribution. Concentrations of TSS, TOC, TN, and six trace metals varied between one and two orders of magnitude among all storms of the year (Table 2). The median EMC, which is often used as a measure of the central tendency for programs that do not sample every storm, was consistently biased low relative to the FWM concentration for the entire year (Table 3). The bias ranged from 24 to 44% lower. The only exception was TOC; the median TOC value was 12% higher than the annual FWM concentration.

A portion of the variability associated with among-storm variance was attributable to seasonal flushing (Figure 3, Table 2). Initial storms of the water year generated much higher TSS concentrations, presumably as a result of the extended build-up of this constituent on urban surfaces. Moreover, each of the first four sampleable storms of the season significantly affected the slope of the cumulative FWM curve. Although the inflection point of the curve is located somewhere after the seventh sampleable storm, the last three storms did not impact the curve other than to dilute the seasonal flushing. The antecedent rainfall period between the first storm of the year and the last storm of the previous year had been 220 d.

The seasonal flushing was observed not only for TSS, but for every trace metal examined (Table 2). The EMCs for all constituents were much higher in early season

FIGURE 2. Measured characteristics of rainfall and runoff flow recorded on the Santa Ana River during a February 1998 storm event. The peak discharge for this storm was approximately 212 m^3/s.

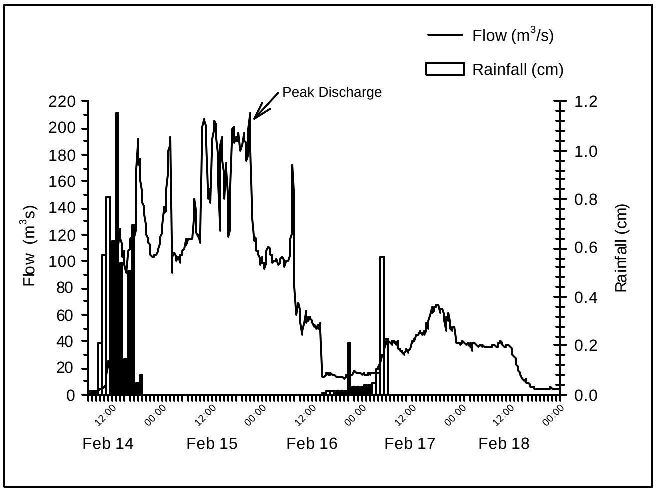


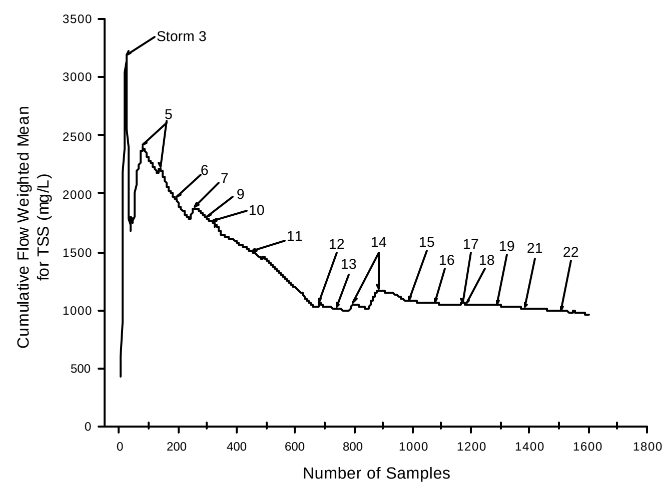
TABLE 2. Event mean concentrations (EMC) of total suspended solids (TSS), total organic carbon (TOC), total nitrogen (TN), and various trace metals for every storm on the Santa Ana River. A dash (—) represents no sampleable flows for this event.

		Event Mean Concentration (EMC)									
Storm Number	Date	TSS (mg/L)	TOC (%)	TN (%)	Cadmium (mg/L)	Chromium (mg/L)	Copper (mg/L)	Iron (%)	Lead (mg/L)	Nickel (mg/L)	Zinc (mg/L)
	1997										
1	Sept. 25-27	—	—	—	—	—	—	—	—	—	—
2	Nov. 13-14	—	—	—	—	—	—	—	—	—	—
3	Nov. 26-27	2,936.7	7.2	0.6	8.6	169.2	223.6	12.5	163.1	124.3	1,048.9
4	Nov. 30-Dec. 1	—	—	—	—	—	—	—	—	—	—
5	Dec. 6-8	1,780.0	3.1	0.4	2.9	131.7	116.0	11.7	66.0	75.8	432.3
6	Dec. 18-19	1,150.8	5.6	0.5	2.1	85.9	91.0	6.2	56.6	52.4	235.3
	1998										
7	Jan. 9-11	1,460.0	4.3	0.5	1.9	73.2	77.0	5.7	52.5	45.9	272.4
9	Jan. 29	278.6	8.0	0.8	1.0	19.6	28.5	1.2	24.3	15.8	144.3
10	Feb. 3-5	856.2	3.5	0.4	1.3	54.7	57.1	4.5	34.1	153.3	200.2
11	Feb. 6-11	596.8	3.3	0.4	0.8	41.7	44.4	3.3	24.4	26.1	136.4
12	Feb. 14-18	817.4	3.9	0.5	0.8	40.0	40.6	3.3	21.1	25.4	132.3
13	Feb. 19-21	329.7	8.3	1.0	0.7	23.3	27.3	1.6	12.4	16.2	95.9
14	Feb. 22-Mar2	890.6	33.1	5.1	1.6	84.7	70.9	6.9	31.3	50.8	212.5
15	Mar. 6-11	409.1	7.4	1.0	1.4	35.4	36.3	2.1	15.4	23.9	119.2
16	Mar. 13-14	174.6	8.1	1.1	0.6	14.3	17.3	0.8	8.2	11.0	65.4
17	Mar. 25-26	1,100.3	3.4	0.5	1.5	60.9	56.0	5.0	33.6	40.4	231.3
18	Mar. 27-29	440.1	2.3	0.4	0.9	44.2	39.9	3.7	16.7	27.3	125.4
19	Mar. 31-Apr. 2	227.1	4.6	0.7	0.2	12.2	12.0	0.8	6.6	8.2	43.3
20	Apr. 11-12	—	—	—	—	—	—	—	—	—	—
21	May 5-7	448.0	4.1	0.5	0.8	33.6	29.1	2.7	16.1	20.0	122.6
22	May 12-15	534.7	2.7	0.4	0.9	51.1	38.7	4.8	17.2	28.9	140.6
	Season	722.1	3.7	0.4	1.6	72.4	65.9	6.0	35.1	43.8	229.9

TABLE 3. Annual flow-weighted mean (FWM) concentrations for all data is compared with the mean and median event mean concentration (EMC) from individual storm events for the 1997/98 water year.

Parameter	EMC Mean	EMC Median	FWM / Year
TSS (mg/L)	722.1	534.7	809.0
TOC / TN (µg/L)	148.9 / 22.2	42.2 / 4.8	29.2 / 3.5
Cadmium (µg/L)	1.6	1.0	1.6
Chromium (µg/L)	72.4	41.7	71.8
Copper (µg/L)	65.9	39.9	65.6
Iron (µg/L)	60.0	32.8	60.1
Lead (µg/L)	35.1	24.3	34.9
Nickel (µg/L)	43.8	26.1	43.6
Zinc (µg/L)	229.9	140.6	228.5

FIGURE 3. Cumulative flow-weighted mean (FWM) concentrations (mg/L) for total suspended solids (TSS) on the Santa Ana River for the entire wet season. The arrow indicates peak TSS concentrations for each storm.



storms (the first four storms) relative to late season storms (the last 13 storms). The first sampleable storm, November 26-27, 1998, had the highest EMC for all trace metal constituents and TOC. For example, the range of EMCs between the first four storms for copper was 77 to 224 µg/L while the EMCs for zinc ranged from 272 to 1,049 µg/L. In contrast, the highest EMC during the last 13 storms of the 1997-98 season for copper and zinc was 57 and 231 µg/L, respectively.

Within-Storm Variance and First Flush Phenomenon

Concentrations of TSS as well as the trace metals and TOC ranged over an order of magnitude within a single event (Figure 4). This finding was largely a result of flow, of which TSS and trace metal concentrations were

FIGURE 4. The relationship between total suspended solids (TSS) concentrations and flow illustrating both "first flush" and effects of TSS associated with releases from Prado Dam during a February 1998 storm event on the Santa Ana River.

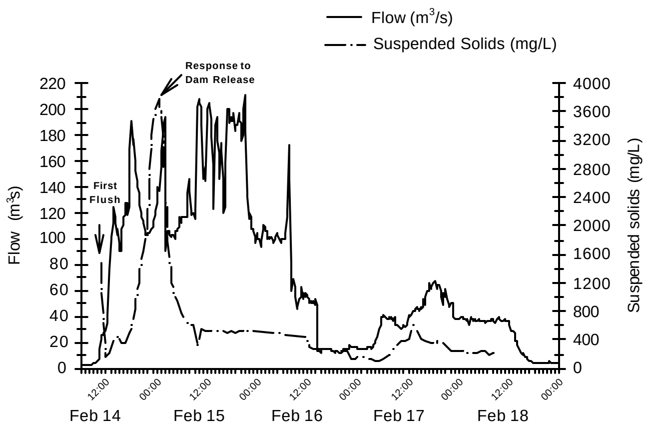


TABLE 4. The relationship between flow, total suspended solids (TSS), total organic carbon (TOC), and selected trace metals from the Santa Ana River during the 1997/98 wet season. All parameters are significant at (p<0.01).

Parameter	Correlation Coefficient Flow (cf/s)	TSS
TSS	0.38	
TOC/TN	-0.37	-0.72
Cadmium (Cd)	0.23	0.76
Chromium (Cr)	0.32	0.94
Copper (Cu)	0.35	0.91
Iron (Fe)	0.39	0.97
Lead (Pb)	0.24	0.83
Nickel (Ni)	0.37	0.94
Zinc (Zi)	0.26	0.85

covariates (Table 4). A stronger correlation existed between TSS and trace metals. The concentration of TSS accounted for 58 to 94% of the variability in trace metal concentrations, depending upon the metal. The only exceptions were relationships between flow or TSS and TOC. These relationships were also significant, but negatively correlated (Table 4) as a result of the shift in grain size as flows increased. The TOC is associated with the fine-grained fraction of TSS. As flows increased, more coarse-grained sediments were mobilized and the result was a dilution effect for fines.

Peak suspended-sediment concentration preceded the peak in discharge for the Santa Ana River in approximately 40% of the storms monitored. For example, a slight increase in TSS concentrations was observed as flows climbed following the onset of rainfall during the February 14-18, 1998, storm (Figure 4). Other variables, however, elicited stronger within-storm bias. In the present study, the highest TSS concentrations were associated with releases from Prado Dam during individual storm events. On February 15, dam releases generated an additional 113 m^3/s in less than 2 h which resulted in a seven-fold increase in flow over baseline conditions and doubled the suspended solids concentration beyond the first flush concentration.

No trend was found between the first flush effect and the other rainfall and runoff characteristics (Table 5). Calculating the relative increase in TSS concentrations as a function of time (first hour) and initial proportion (i.e., 30%) of storm volume did not produce significantly higher or lower concentrations compared to the remaining storm event. No storm events exhibited a first flush effect during the initial hour of rainfall. The first hour of rainfall generally coincided with the first 0.6 cm of precipitation. Two storm events showed a first flush effect in the initial 10% of storm volume. When the initial 20 and 30% of storm volume were isolated, the number of storm events exhibiting a first flush effect increased to 6 and 8, respectively.

A first flush effect from the Santa Ana River was not observed using a mass emissions approach (Table 5). On average, the first 30% of event runoff volume washed off 35% of the event suspended solids load from the Santa Ana River. The February 6-11, 1998, storm comprised the best first flush agreement between the concentration ratios using percent of volume (3.43) and the proportion of load (60%) transported in the first 30% of storm volume. The relationship between the values of all three estimators of first flush effect (first hour, concentration ratios for 30% of volume, and proportional mass emissions) indicated that the February 19-21, 1998, storm was the best first flush of TSS.

Evaluation of trace metals also demonstrated that first flush effects are limited on the Santa Ana River (Table 6). On average, every trace metal was less concentrated during early storm flows than at peak flows; the mean concentration ratio ranged from 0.41 (copper) to 0.81 (chromium). Only five of the seven metals concentration ratios exceeded unity. Of those five metals, concentration ratios only exceeded unity from one (for cadmium and nickel) to five (for chromium) out of 17 events. Only three storms had more than one metal with concentration ratios that exceeded unity; only the December 18-19, 1998, event exceeded unity for three metals.

TABLE 5. Assessment of the first flush phenomenon by storm event using time (first hour of flow) and percent of storm volume. Data are expressed as a ratio of the total suspended solids (TSS) flow weighted mean concentration in the first flush divided by the flow weighted mean concentration in the remainder of the storm. First flush was also assessed by calculating the proportion of TSS load discharged during the first 30% of the total storm volume.

		Concentration Ratio				Proportion
		Fixed Time	Percent of Volume			of Load in First
Storm No.	Date	First Hour	10	20	30	30% of Volume
	1997					
1	Sept. 25-27	—	—	—	—	—
2	Nov. 13-14	—	—	—	—	—
3	Nov. 26-27	0.83	0.12	0.12	0.12	5
4	Nov. 30-Dec. 1	—	—	—	—	—
5	Dec. 6-8	0.73	0.72	0.78	0.87	28
6	Dec. 18-19	0.61	0.69	0.55	0.40	15
	1998					
7	Jan. 9-11	0.79	0.31	0.66	0.83	43
9	Jan. 19	0.59	0.00	0.72	0.99	38
10	Jan. 29	0.72	1.21	1.21	1.18	31
11	Feb. 3-5	0.71	0.99	1.11	1.39	39
12	Feb. 6-11	0.28	0.87	2.36	3.43	60
13	Feb. 14-18	0.81	0.30	0.57	0.71	38
14	Feb. 19-21	0.90	1.66	2.04	2.62	56
15	Feb. 22- Mar. 2	0.82	0.82	0.35	0.00	26
16	Mar. 6-11	0.76	0.63	0.57	0.51	19
17	Mar. 13-14	0.42	0.00	0.25	0.50	17
18	Mar. 25-26	0.38	0.00	1.28	2.30	53
19	Mar. 27-29	0.39	0.85	0.95	1.44	40
20	Apr. 11-12	—	—	—	—	—
21	May 5-7	0.8	0	1.25	2.20	52
22	May 12-15	0.9	0.36	0.83	1.12	34

DISCUSSION

Pollutant build-up and wash-off is a common assumption in semi-arid environments, but has not been quantified in southern California previously. We observed significant seasonal flushing during the 1997-98 water year. Seasonal flushing occurred when early-season storms discharged significantly higher concentrations than storms of a similar size or larger later in the season. Contaminant concentrations in runoff tend to be higher during the first few storms of the season compared to later storms, possibly due to the resuspension of bottom sediment which contains contaminants deposited during the extended summer dry-weather period. In the present study, 220 non-rain days were noted prior to the season's first event. The first four storms, accounting for a cumulative 16.7 cm (21%) of

TABLE 6. Concentration ratios of trace metals from samples collected during initial storm flows divided by the concentration in samples collected at peak flows. A dash (—) represents no sampleable flow from this storm.

Storm Number	Date	First Flush Concentration Ratios Cadmium	Chromium	Copper	Iron	Lead	Nickel	Zinc
	1997							
1	Sept. 25-27	—	—	—	—	—	—	—
2	Nov. 13-14	—	—	—	—	—	—	—
3	Nov. 26-27	0.15	0.18	0.26	0.18	0.57	0.17	0.25
4	Nov. 30-Dec. 1	—	—	—	—	—	—	—
5	Dec. 6-8	1.00	1.00	1.00	1.00	1.00	1.00	1.00
6	Dec. 18-19	1.09	0.48	0.77	0.42	1.34	0.61	1.38
	1998							
7	Jan. 9-11	0.30	0.46	0.28	0.06	0.44	0.11	0.38
9	Jan. 29	1.00	1.00	1.00	1.00	1.00	1.00	1.00
10	Feb. 3-5	0.24	1.42	0.21	0.17	0.41	0.21	0.37
11	Feb. 6-11	0.17	0.56	0.19	0.16	0.39	0.18	0.28
12	Feb. 14-18	0.60	1.64	0.37	0.28	0.34	1.44	0.68
13	Feb. 19-21	0.25	1.97	0.60	0.32	0.25	0.44	0.33
14	Feb. 22-Mar. 2	0.11	0.26	0.14	0.06	0.16	0.65	0.17
15	Mar. 6-11	0.14	0.84	0.25	0.12	0.53	0.20	0.38
16	Mar. 13-14	0.32	1.00	0.54	0.32	0.49	0.77	0.74
17	Mar. 25-26	0.24	1.07	0.26	0.13	0.22	0.13	0.30
18	Mar. 27-29	0.48	0.54	0.34	0.54	0.44	0.23	0.46
19	Mar. 31-Apr. 2	0.62	1.06	0.55	0.69	0.57	1.19	0.70
20	Apr. 11-12	—	—	—	—	—	—	—
21	May 5-7	0.15	0.32	0.17	0.15	0.83	0.28	0.13
22	May 12-15	0.43	0.03	0.06	0.02	0.25	0.06	0.04
Mean		0.43	0.81	0.41	0.33	0.54	0.51	0.50

precipitation, had significantly higher concentrations of TSS and every trace metal examined than the remaining storms of the season. Other studies have indicated a potential for seasonal flushing in toxicity (Bay *et al.* 1997, Schiff and Stevenson 1996).

We observed two factors that influenced within-storm variability. First and foremost, flow was the largest factor that accounted for changes in TSS concentrations. The influence that flow has over concentrations has been documented in other southern California channels (SCCWRP 1990). The second factor that influenced within-storm variability was first flush. The first flush concept assumes that contaminant concentrations are higher at the beginning of a storm compared to similar flows later in the storm event (Chang *et al.* 1990). Although first flush was observed in less than half of all storms during the 1997/98 water year, the concentrations we observed were not dramatically higher and isolating these portions of the storms did not produce significantly higher results. It is clear that the first flush of suspended solids is not very distinctive on the Santa Ana River. However, we did not examine dissolved components that could be mobilized faster than particulate-bound constituents; the dissolved components may be more susceptible to initial storm flows.

The magnitude of within- and among-storm variability that we observed in our frequent sampling of stormwater runoff demonstrated that representative concentrations cannot be characterized by a limited number of samples. Storms that are characterized by a single grab sample, or wet seasons that are characterized by a single storm event, are clearly inadequate. In many monitoring programs around the country, multiple grab samples during a single event are often taken and composited prior to chemical analysis. While the compositing technique can be cost-effective, it does not provide an assessment of the variability around the mean average. This limits scientific investigation due to the uncertainty of the relationship of the sampled result to the true mean. In the end, many storms are required to generate the variability estimate one desires to assess differences among watersheds or over time. What scientists truly need is an assessment of how many samples are needed to accurately characterize a storm and how many storms are needed to characterize a season with an adequate amount of confidence (Leecaster *et al.* 2000).

If many samples are required to capture not only representative central tendencies (i.e., means), but also within- and among-storm variance, a cost-effective strategy is required for accomplishing this goal. Relationships among correlated constituents, such as suspended solids and trace metals, can be utilized to increase sample loading while at the same time keeping costs at a minimum. The TSS measurements are one-tenth the cost of trace metal analyses. However, TSS concentrations accounted for up to 95% of the variability in some trace metal concentrations. In fact, runoff contaminants tend to be highly correlated with suspended solids in large rivers and creeks throughout southern California (SCCWRP 1992). If sufficient samples are collected to verify contaminant:TSS relationships, numerous samples can be collected and analyzed for the same cost as ongoing monitoring programs. Stormwater scientists or managers can then collect more samples per storm or more storms per season to address the issues raised in this study.

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