

Anthropogenic versus natural mass emission from an urban watershed

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ABSTRACT

Accounting for naturally occurring constituents of concern, such as trace metals, is a problem that frequently occurs when trying to estimate stormwater mass emissions. The objective of this study was to comprehensively measure runoff from an urban watershed to assess the total pollutant load, then estimate what proportion of the total load was attributable to natural versus anthropogenic sources.

Over 1,700 samples were collected approximately every 15 min during every sampleable storm during the 1997/98 water year from the last gaging station on the Santa Ana River. Every sample was analyzed for total suspended solids (TSS) and approximately 10% of the samples were analyzed for total organic carbon, total nitrogen, cadmium, chromium, copper, iron, lead, nickel, and zinc. We used iron as a conservative tracer of natural contributions and to assess anthropogenic enrichment.

Every trace metal showed some level of anthropogenic enrichment. Cadmium, copper, lead, and zinc showed the greatest levels of enrichment (33-63% of total concentration), while chromium and nickel showed the least (<1% of total concentration). Trace metal enrichment was also found during every storm.

Over 90% of the total annual load occurred during less than 10% of the water year. The loading was disproportionate among sources of runoff discharge. For example, 74% of the runoff volume occurred as a result of dam releases, but these discharges accounted for less than 40% of the trace metal emissions. In contrast, runoff from the local urban surfaces below the dam accounted for 9% of the discharge volume, but accounted for 34 to 41% of the trace metal emissions, depending upon the metal. Nearly all of the nickel and chromium emissions and approximately two-thirds of the copper, lead, and zinc emission, were of natural origin.

INTRODUCTION

Stormwater runoff is currently perceived as one of the largest sources of pollutants discharged to coastal oceans and inland waterways (U.S. EPA 1995). This is because stormwater runoff from urban areas has the potential to transport contaminants that accumulate from multiple sources within the watershed. The build-up of contaminants in southern California urban areas is of particular concern because the region is extensively developed and precipitation is infrequent. The result is increased densities of non-point pollutant sources that magnify build-up coupled with extensive impermeability (e.g., cement) that efficiently transports these pollutants to the ocean when rain events occur. Moreover, storm sewer and sanitary sewer systems are separate in southern California so runoff is discharged directly into creeks, rivers, bays, and the ocean without treatment.

Not only is urban runoff a large source of potential pollutants, but discharges have been shown to impact water and sediment quality in receiving water bodies. Increased imperviousness (development) was directly correlated with decreased water quality on the eastern coast of the U.S. (Schueler 1994). Moreover, aquatic toxicity is routinely found in wet-weather discharges from urbanized watersheds. In southern California, reduced water clarity and aquatic toxicity were observed in discharge plumes offshore urban watersheds near Los Angeles (Bay and Schiff 1997). Increased sediment contamination was found offshore of the 12 largest river and creek mouths from San Diego to Santa Barbara (Schiff and Weisberg 1999). Impacts to benthic habitat quality were observed up to 3 km offshore following significant wet-weather events (Kolpack and Drake 1985).

One problem that frequently occurs when trying to estimate runoff mass emissions, however, is accounting for naturally occurring constituents of concern. Trace metals, for example, are a commonly occurring runoff constituent

throughout the country's urban watersheds (U.S. EPA 1983, Smullen *et al.* 1999). Trace metals will be found in all watersheds, including undeveloped watersheds, because trace metals occur naturally in the environment (Horowitz and Elrick 1987, Trefry 1985, Turekian and Wedepohl 1961). Unlike other sources of pollutants, such as municipal or industrial wastewaters, where the sources of trace metals are predominantly human-induced, significant quantities of trace metals occur in surface runoff simply as a result of erosion. Most monitoring programs for urban runoff do not account for this naturally occupying fraction; hence, overestimating the actual load of trace metals that are contributed by human influences. Moreover, when reductions in loads are mandated, such as during a total maximum daily load (TMDL), inefficient or unrealistic reduction goals may be imposed.

The objective of this study was to comprehensively measure runoff from an urbanized southern California watershed to assess precise pollutant mass emissions and evaluate the proportion of trace metals loadings that are attributable to natural versus anthropogenic sources within the watershed.

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 100 miles southwesterly where it discharges into the Pacific Ocean at Huntington Beach. Approximately 50% of the 2,650 mi² watershed is comprised of urban and agricultural land uses (Figure 1). 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 250 feet wide and is entirely concrete-lined. Upstream uses, including Prado Dam (as flood control) and the Orange County Water District (to recharge groundwater) 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 the vast majority of the year and large runoff flows reaching the ocean only 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 gaging station before discharging 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 series and capable of collecting 48, 500 mL to 1,000 mL individual samples. Samplers

were activated when the flow rose above baseline conditions (0.7 m³/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 for tailing flows during extremely large storms when flow and runoff concentrations were changing slowly.

Analytical Chemistry

All stormwater samples were stored under refrigeration and analyzed for total suspended solids (TSS). Approximately 10% of the runoff samples 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 two and held at room temperature until digested.

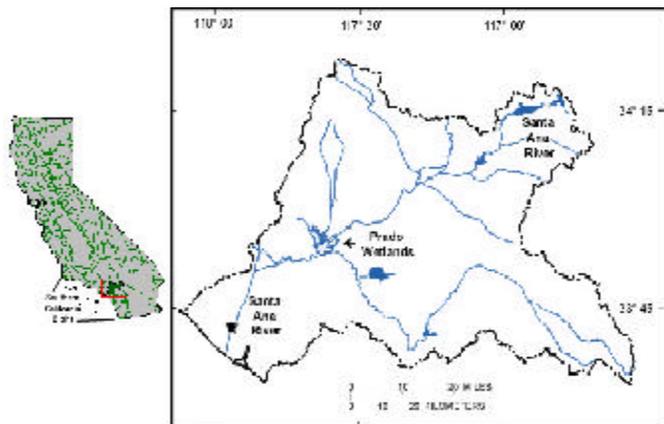
Suspended Solids

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. A detailed description of the method can be found in SCCWRP (1992). 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

Figure 1. Map of the Santa Ana River watershed.



thermal conductivity detector. Acetanilide was used as the external standard. Acetanilide and cyclohexanone were used for QC check standards. The Certified Reference Material was PACS-1 (3.69% C, National Research Council).

Trace Metal Analysis

Samples for trace metal analysis were first digested using strong acid techniques. A well-mixed 25 mL aliquot of acidified sample was dispensed to a Teflon digestion vessel 2 mL of ultra pure HNO₃ (Optima, Fisher Scientific) were added, and the vessel was 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 (arsenic, cadmium, chromium, copper, iron, lead, nickel, 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 run 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, Asheville, NC), was 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 our samplers was used to estimate the fraction of runoff volumes representatively sampled during the study.

Stormwater concentrations among storms were compared via an estimate of the central tendency called the event mean concentration (EMC, U.S. EPA 1983) (Equation 1). The EMC is a ratio estimator that weights concentrations by instantaneous flow at the time of sampling. A related estimator, but calculated to estimate the annual mean rather than by individual storm events, is the flow weighted mean concentration (FWM) (Equation 2).

Equation 1:

$$\text{EMC} = \frac{\sum_{i=1}^n (C_i * Q_j)}{\sum_{i=1}^n Q_j}$$

where:

- EMC = Event mean concentration for a storm
- C_i = Individual runoff sample concentration
- Q_j = Instantaneous flow rate at time of sampling
- i = First sample of storm event
- n = Last sample of storm event

Equation 2:

$$\text{FWM} = \frac{\sum_{p=1}^z (C_i * Q_j)}{\sum_{p=1}^z Q_j}$$

where:

- FWM = Flow weighted mean for the year
- C = Individual runoff sample concentration
- Q^p = Instantaneous flow rate at time of sampling
- p^p = First sample of year
- z = Last sample of year

Stormwater mass emissions were calculated by multiplying sample concentrations by the instantaneous flow at the time of sampling and the time between sampling (typically 15 min). Mass emissions were calculated on a storm-by-storm basis (equation 3). Annual loads were calculated by summing the loads from all storms.

Equation 3: Load = $\sum_{i=1}^n (C_i * Q_j * T_i)$

where

Load	=	Pollutant load
C_i	=	Individual runoff sample concentration
Q_j	=	Instantaneous flow rate at time of sampling
i	=	First sample of storm event
n	=	Last sample of storm event

Iron Normalization

Trace metals occur naturally in the environment. Therefore, an iron normalizing technique was used to assess the magnitude of anthropogenic trace metal enrichment in suspended sediments (Schiff and Weisberg 1999). Suspended sediments were used because 95% or more of the trace metals measured from this watershed were particulate-bound as opposed to dissolved (Cross et al 1992). The normalizing technique uses iron as a conservative tracer of naturally occurring concentrations for the six trace metals evaluated (cadmium, chromium, copper, lead, nickel, and zinc). In naturally derived sediments, iron and the selected trace metals co-occur in predictable ratios. Iron, however, is much more concentrated (in g/L) than the other trace metals (in $\mu\text{g/L}$). Therefore, small additions of iron and trace metals do not vary the iron concentration, but could lead to large variations in the other trace metals. Deviations in the ratios of iron to each of these six trace metals were used to identify anthropogenically enriched samples; the magnitude of enrichment was quantified by measuring the concentration beyond the naturally occurring prediction interval.

RESULTS

Hydrology

Rainfall in the lower portions of the Santa Ana River watershed was double the long-term average during this study (Table 1). Annual rainfall quantities between October 1, 1997, and September 30, 1998, was 77.8 cm compared to the long-term annual average of 30.02 cm (between 1966 and 1997). There were a total of 22 storms; 17 with precipitation greater than 0.6 cm. All 17 of these storms resulted in significantly elevated stream flows above baseline conditions of $< 0.7 \text{ m}^3/\text{sec}$. The range in rainfall, peak flows, and storm volume all varied two orders of magnitude or more among the 17 storm events.

Storm events accounted for more than 90% of the total annual discharge volume from the Santa Ana River. Total storm runoff for the year was $264.4 \times 10^{12} \text{ L}$ (Table 1). The main source (74%) of the annual discharge volume originated from overflows at Prado Dam, while only 9% of the volume was attributable to local runoff. The remaining 17% was a mixture of local runoff and Prado Dam release.

Ninety percent of the total storm volume of the 1998 water year was representatively sampled during this study (Table 1). The remaining 10% of unsampled volume was a result of stormwater flow lower than the pump intake (7%) and equipment malfunction or breakage (3%). Over 1,700 stormwater samples were collected during the 1998 water year. Every sample was analyzed for TSS. One hundred seventy-five samples were analyzed for TOC, TN, and trace metals.

The EMC for each of the constituents ranged one to two orders of magnitude among individual events (Table 2). As expected, the distribution of EMCs was not normally distributed about the median. Therefore, we calculated an annual flow-weighted mean based upon all samples, rather than averaging EMCs.

Assessment of Anthropogenically Enriched Concentrations

All trace metals investigated showed some level of enrichment (Table 2). Cadmium, copper, lead, and zinc showed the greatest enrichment (33-63% of the annual FWM), while chromium and nickel showed the least enrichment (0.5-0.7% of the annual FWM). Trace metal enrichment was found during every storm.

Interestingly, the source of trace metal enrichment varied among sources of runoff volume (Figure 2). Local runoff from the urbanized portions of the lower watershed produced the greatest proportion of anthropogenic enrichment (38-60%) for all metals except nickel. Prado Dam releases contributed the least to anthropogenic enrichment (18-38%). The trace metals that were most influenced by anthropogenic enrichment from local runoff included chromium, lead, and zinc.

Pollutant Mass Emission Estimates

The Santa Ana River delivered 90% of its TSS load during 10% of the water year (Figure 3). This is typical of many rivers, but particularly those in semi-arid environments such as southern California. Rainfall is infrequent and flows during the majority of the year are non-existent. In the case of the Santa Ana River, any dry-weather and some wet-weather flows are diverted to retention ponds for groundwater recharge. The disparity in loading over time is likely more pronounced in average to dry years when even less water makes it to the ocean.

There was a disproportionate amount of constituent loading relative to discharge volume from various portions of the watershed (Table 3). Approximately 74% of the total runoff volume during storm events originated from releases at Prado Dam. However, only 66% of the TSS and less than 40% of the trace metal or TOC/TN emissions was

TABLE 1. Hydrologic information for storm sampling on the Santa Ana River during the 1998 water year including precipitation (PPT), peak flow (Q_{peak}), volume representatively sampled (percent capture) and percent of volume from different areas in the watershed. Source areas included local urban areas, releases from Prado Dam, and a mixture of both sources. NS = Storm not sampleable.

Storm No.	Date	Total PPT (cm)	Q_{peak} (cf/s)	Volume ($\text{L} \times 10^6$)	Percent Capture	Volume (%)		
						Local	Mix	Prado
1997								
1	Sept. 25-27	< 0.1	133.7	63.2	NS	0.0	100.0	0.0
2	Nov. 13-14	0.9	228.6	229.2	NS	0.0	100.0	0.0
3	Nov. 26-27	1.5	1,523.1	580.6	55.5	24.8	16.8	58.4
4	Nov. 30 - Dec. 1	1.4	198.0	133.5	NS	0.0	100.0	0.0
5	Dec. 6-8	11.6	9,562.6	10,698.1	96.8	43.7	26.4	29.9
6	Dec. 18-19	1.6	1,692.6	824.9	82.2	0.0	100.0	0.0
1998								
7	Jan. 9-11	2.0	3,219.1	4,938.2	79.1	28.3	0.0	71.7
8	Jan. 19	0.1	51.0	17.9	NS	0.0	100.0	0.0
9	Jan. 29	0.9	663.8	248.2	30.3	47.0	0.0	52.9
10	Feb. 3-5	4.7	4,751.8	6,910.4	89.2	41.1	27.4	31.5
11	Feb. 6-11	6.6	11,613.2	58,730.0	90.8	2.1	38.2	59.7
12	Feb. 14-18	6.5	7,448.9	28,389.6	77.4	16.1	5.3	78.6
13	Feb. 19-21	1.7	1,649.0	3,207.0	81.9	0.0	27.0	73.0
14	Feb. 22 - Mar. 2	5.2	11,613.2	104,381.2	98.6	2.7	9.0	88.4
15	Mar. 6-11	0.7	1,523.1	19,158.6	12.03	0.0	3.7	96.3
16	Mar. 13-14	1.6	946.8	606.4	76.5	100.0	0.0	0.0
17	Mar. 25-26	3.6	7,744.0	3,089.8	90.9	68.2	0.0	31.8
18	Mar. 27-29	0.7	3,725.3	3,668.7	96.4	0.0	14.9	85.1
19	Mar. 31 - Apr 2	1.7	1,692.6	2,960.7	92.7	32.0	11.4	56.7
20	Apr. 11-12	0.5	245.3	359.9	NS	0.0	100.0	0.0
21	May 5-7	3.2	3,633.3	8,230.6	57.1	18.2	25.2	56.6
22	May 12-15	4.9	6,681.7	19,478.3	91.2	7.1	21.8	71.2
All Storms		77.8	11613.2	264,386.4	89.5	9.0	17.3	73.7

TABLE 2. Range of event mean concentrations and the annual flow weighted mean (FWM) concentration on the Santa Ana River during the 1998 water year. Also included is the anthropogenically enriched concentration for six trace metals of interest.

Parameter	Event Mean Concentration			Annual FWM	Enriched FWM	Percent Enriched
	Min	Median	Max			
Suspended Solids (mg/L)	174.6	534.7	2,936.7	809.0	-	-
Organic Carbon ($\mu\text{g/L}$)	14.9	42.2	1,838.0	29.2	-	-
Organic Nitrogen ($\mu\text{g/L}$)	2.0	4.8	282.0	3.5	-	-
Cadmium ($\mu\text{g/L}$)	0.2	1.0	8.6	1.6	1.0	62.9
Chromium ($\mu\text{g/L}$)	12.2	41.7	169.2	71.8	0.4	0.5
Copper ($\mu\text{g/L}$)	12.0	39.9	223.6	65.6	27.3	41.5
Iron (mg/L)	7.9	32.9	124.6	60.4	-	-
Lead ($\mu\text{g/L}$)	6.6	24.3	163.1	34.9	13.4	38.3
Nickel ($\mu\text{g/L}$)	8.2	26.1	153.3	43.6	0.3	0.7
Zinc ($\mu\text{g/L}$)	43.3	140.6	1,048.9	228.5	76.0	33.3

attributable to Prado Dam releases. In contrast, local runoff contributed disproportionately more mass emissions than the volume it delivered. Although local runoff contributed only 9% of the total discharge volume, it discharged 14% of the TSS and 34% to 41% of the trace metal loadings, depending upon the metal examined.

DISCUSSION

Estimating total loads from coastal watersheds can be deceiving. Although large quantities of trace metals were discharged from the Santa Ana River, nearly all of the chromium and nickel emissions were of natural origin while nearly two-thirds of the copper, lead, and zinc were naturally derived. Therefore, caution must be exercised when comparing total loads of pollutants. The methods used to

FIGURE 2. Relative proportion of anthropogenic trace metal enrichment from three distinct runoff areas including the local urban watershed, Prado Dam releases, and a mixture of both sources.

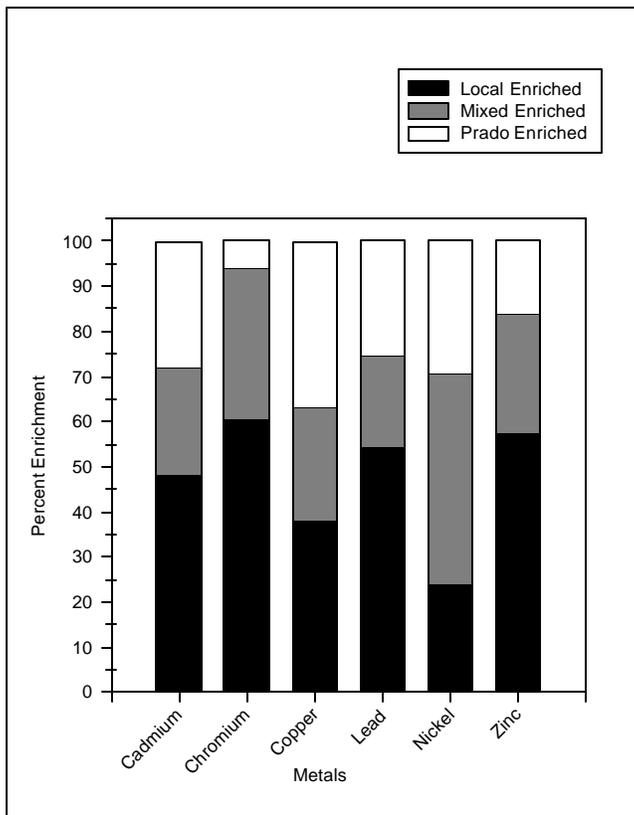


FIGURE 3. Mass duration curve for total suspended solids loadings from the Santa Ana River to the coastal oceans during the 1998 water year.

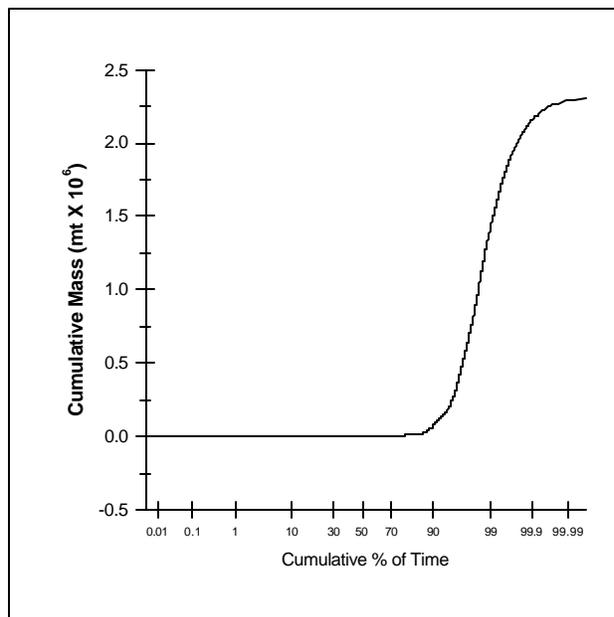


TABLE 3. Total mass emissions from the Santa Ana River during the 1998 water year and the proportion of the load from various runoff source areas including local urban, Prado Dam releases, and a mixture of both sources.

Parameter	Mass Emissions metric tons	Percent of Annual Load		
		Local	Mix	Prado
Suspended Solids	191,447	13.9	20.0	66.1
Cadmium	0.3	41.4	22.0	36.7
Chromium	15.6	35.1	25.4	39.6
Copper	12.2	34.6	26.4	39.0
Iron	14.3	34.1	27.0	38.9
Lead	7.0	38.4	25.8	35.8
Nickel	7.6	34.2	26.7	39.1
Zinc	45.5	38.9	25.9	35.2

calculate loadings from traditional sources, such as POTWs where the majority of inputs are potentially anthropogenic, may not be adequate for non-point sources where large fractions could be of natural origin.

To test our concern, we compared our estimates of natural and anthropogenic mass emissions from the Santa Ana River to the mass emissions from the Orange County Sanitation District, a nearby publicly owned treatment work (POTW) (Table 4). The POTW services approximately 4 million people, provides a blend of secondary and advanced primary treatment (ca. 50:50), and also discharges directly to the ocean offshore the mouth of the Santa Ana River (Raco-Rands 1999). In this case, we did not have iron concentrations to adjust the POTW effluent, so we used mean drinking water concentrations as the “natural” fraction of the wastewater discharge (Orange County Water District, personal communication).

The total load of suspended solids from the Santa Ana River was 191.4×10^3 metric tons (mt), more than 14 times greater than POTW emissions. Mass emissions of selected trace metals from the Santa Ana River were also much greater than POTW emissions. Loads of chromium, lead, and zinc were between 4 and 10 times greater than POTW emissions. The emissions of cadmium, copper, and nickel

were similar between runoff and POTW discharges.

When viewed relative to the anthropogenically derived trace metals, the contributions from runoff compared to POTWs are much different (Table 4). The Santa Ana River contributed less mass than the POTW for three of the six trace metals including chromium, copper, and nickel. Contributions of cadmium and zinc between the two sources were relatively similar. The only trace metal that was significantly pronounced in runoff was lead. The Santa Ana River contributed approximately five times the load of lead compared to the POTW.

Undoubtedly, there are anthropogenic contributions of trace metals within urbanized watersheds. Trace metals are found routinely in runoff water quality monitoring programs in southern California (Schiff 1999) and through-

TABLE 4. Total mass emissions (in metric tons) from the Santa Ana River and from the Orange County Sanitation Districts' municipal wastewater treatment plant (OCSD). The anthropogenic fraction of mass emissions for the Santa Ana River was determined using iron as a conservative tracer. the anthropogenic fraction of OCSD was determined by subtracting the contribution from drinking water.

Parameter	Santa Ana River		OCSD	
	Total Mass Emissions	Anthropogenic Fraction	Total Mass Emissions	Anthropogenic Fraction
Suspended Solids	191,447	-	15,867	-
Cadmium	0.3	0.2	0.10	0.07
Chromium	15.6	0.1	1.4	1.2
Copper	12.2	5.1	11.0	10.2
Lead	7.0	2.7	0.52	0.40
Nickel	7.6	0.1	6.6	6.3
Zinc	45.5	15.1	14.0	12.4

out the nation (U.S. EPA 1983). Trace metals are responsible for more than 170 total maximum daily loads (TMDLS) in southern California alone. Other investigators have been able to attribute trace metals to mobile sources such as vehicles (City of Palo Alto 1989). We found that the anthropogenically enriched fraction of trace metals was more pronounced in the heavily urbanized lower reaches of the Santa Ana River and helped to generate a disproportionate load relative to volume discharged compared to other sources of runoff volume such as dam releases. Prado Dam likely acted as a large detention basin minimizing anthropogenic pollutant loadings.

Although assessing anthropogenic contributions of trace metals in west coast urban watersheds has not been attempted previously, it is not a new technique. The reference element technique has been used in the near-coastal water column and sediment of southern California (Sanudo-Wilhelmy and Flegal 1991, Schiff and Weisberg 1999), and for river discharges in other parts of the nation (Trefry 1985). We observed that all of the trace metals were enriched to some degree; one-third to two-thirds of the cadmium, chromium, copper, and zinc were from anthropogenic contributions. The exact source of these trace metals within urban watersheds such as the Santa Ana River is still not precisely known. However, the trace metal enrichment can be observed in sediments offshore of river and creek mouths throughout southern California. Schiff (2000) found that one-half of the area surrounding the 11 largest rivers and creeks were enriched with chromium, copper, lead, and/or zinc. Moreover, trace metals have been identified as the likely constituents responsible for toxicity to marine organisms after exposure to stormwater samples (Bay and Schiff 1997, See *Characterization of Stormwater Toxicants from an Urban Watershed to Freshwater and Marine Organisms*, this volume).

While the iron normalization technique has promise for assessing anthropogenic versus natural fractions of runoff discharges, it was originally developed for coastal shelf sediments. We feel that the extrapolation from near-coastal sediments is an adequate assumption since the near-coastal sedimentary materials are derived from coastal watersheds and the influence of river discharges on near-coastal sediment composition has been documented (Kolpack and Drake 1985). However, there is still more research that needs to be conducted to further calibrate and validate naturally-occurring iron:trace metal ratios in surface runoff from

undeveloped watersheds. For example, some bias was observed in iron:nickel relationships in coastal sediments, presumably from variations in crustal ratios of nickel in different geologic formations. However, if these relationships can be quantitatively developed on a regional scale, then this will provide a powerful tool for runoff monitoring programs and resource managers charged with protecting receiving waters.

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