Contribution of natural catchments to levels of metals, nutrients, and solids in stormwater

Vada K. Yoon and Eric D. Stein

Abstract

One of the key challenges in managing water quality and meeting regulatory standards is accounting for the natural contribution of a range of water quality constituents. Such information provides context for anthropogenic constituent concentrations and helps inform managers about appropriate regulatory targets. This study quantified levels of suspended solids (TSS), metals, and nutrients in stormwater runoff from 18 sites across 11 watersheds representing a range of natural (undeveloped) conditions in southern California. Constituent concentration and flux were measured over the course of a variety of storms in order to investigate temporal and spatial patterns in constituent levels, and to identify the most important environmental attributes affecting background water quality. Concentrations of most constituents from the natural catchments were one to two orders of magnitude lower than those observed in previous water quality studies of developed catchments in southern California. In contrast, TSS levels were comparable to those found in urban stormwater. Geologic setting had the greatest effect on constituent levels. Unlike urban systems, natural catchments do no appear to exhibit a first flush phenomenon, with a substantial portion of the constituent load occurring later in the storm.

Introduction

Storm water runoff is a major source of pollution to many waterways (Davis *et al*. 2001) and has been shown to result in adverse ecological effects in local receiving waters (Noble *et al*. 2000). One of the challenges associated with stormwater management is accounting for the contribution of runoff from undeveloped areas to overall water quality. This is important to provide context for anthropogenic concentrations and to help guide regulatory and management decisions.

Unlike man-made compounds, constituents such as metals, nutrients, and suspended solids can originate from natural as well as anthropogenic sources (Horowitz and Elrick 1987, Seiler *et al*. 1999). Therefore, high levels of these constituents may not directly imply a water quality problem, and it can be difficult to distinguish anthropogenic effects from natural variability in the system. This challenge is exacerbated by the fact that even the most developed watersheds can contain substantial amounts of undeveloped area. To effectively manage pollutants of concern, it is necessary to understand relative contributions from natural as well as anthropogenic sources. Without such information, it is difficult for environmental managers to determine what proportions of stormwater pollutant loadings are contributed by human sources, and hence what portion might be controlled. Similarly, it is difficult for environmental regulators to set reasonable standards or management targets that incorporate realistic background concentrations or loads. Existing ambient monitoring programs typically include a few reference streams in relatively undeveloped areas that mainly focus on dry weather water quality and devote little, if any, resources to characterizing reference conditions for stormwater runoff.

This study begins to address the data gap for background/natural stormwater quality by investigating 11 watersheds in southern California to 1) assess the ranges of concentrations, loads, and fluxes of various water quality constituents associated with stormwater runoff from natural areas; 2) compare the ranges of constituent concentrations and fluxes associated with natural areas compare with those associated with southern California's developed areas; 3) identify environmental attributes most influence variability in water quality; and 4) investigate temporal patterns in background water quality.

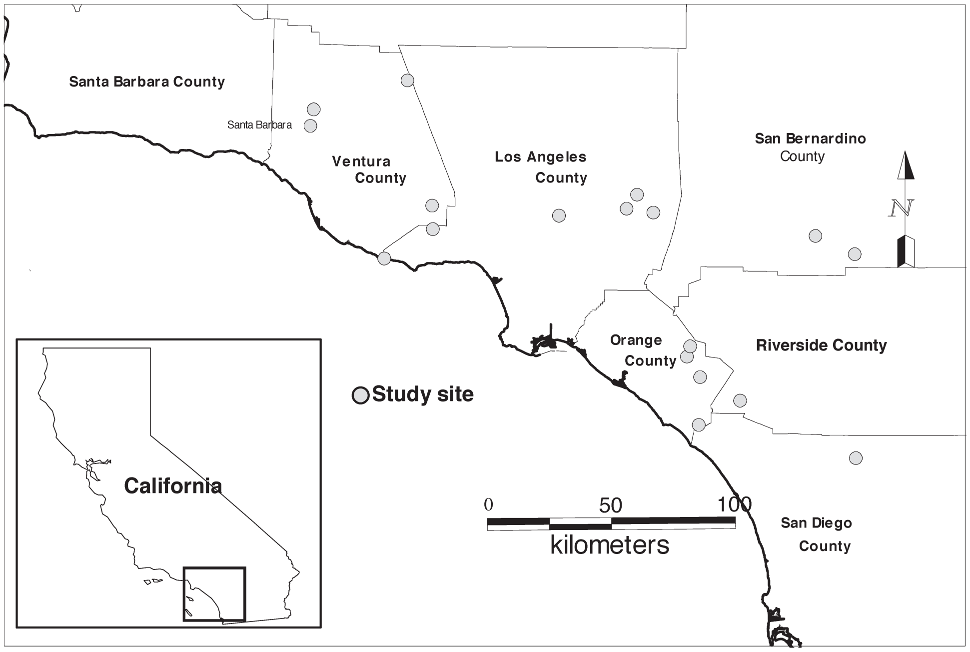

Figure 1. Map of wet-weather study sites.

METHODS

Study Areas

We sampled eighteen natural stream reaches across eleven coastal watersheds in southern California (Figure 1). Sites were selected to represent natural conditions without influence from land-based anthropogenic input using the following selection criteria: 1) All sampling sites were along streams with at least 95% undeveloped contributing drainage area; 2) No known grazing, agriculture or septic systems occurred in the drainage area; 3) Contributing drainage areas were homogenous in terms of underlying geology and land cover; and 4) No fires had occurred in the drainage area for at least three years prior to sampling. Sampling sites were selected to represent the dominant geology and land cover types present in southern California's coastal watersheds.

Prior to sampling, each catchment was characterized for its environmental settings in terms of: 1) land cover type (forest/shrub), 2) geology type (sediment/igneous), 3) catchment size, 4) average slope, 5) elevation, 6) latitude, and 7) percent canopy cover. Geology and land cover types were determined by plotting catchment boundaries over digitized geology maps (Jennings and Strand 1969; Rogers 1965, 1967; Strand 1962) and land cover maps (NOAA Coastal Change Analysis Program (CCAP), 2003). The rest of the catchment characteristics were assessed using ArcView GIS (ESRI, Redlands, CA). Percent canopy cover was measured using a spherical densitometer (Wildco, Buffalo, NY) in the field during each sampling event.

Stormwater Sampling and Laboratory Analyses

A total of 35 site-events were sampled during two wet seasons between December 2004 and April 2006, with each site being sampled during one to three storms (Table 1). Manual sampling was used at streams where safety and access permitted. Between 10 and 12 discrete grab samples were collected per storm at approximately 30- to 60-minute intervals for each site-event, based on optimal sampling frequencies in southern California described by Leecaster *et al*. (2002). Samples were collected using peristaltic pumps with Teflon® tubing and stainless steel intakes that were fixed at the bottom of the channel, pointed in the upstream direction in an area of undisturbed flow. Sampling occurred from prior to initial rise of the hydrograph to point in time when flow decreased to 50% of the peak flow. For prolonged events, water quality sampling was terminated after 24 hours. Even after the end of sampling, flow measurements often continued to monitor the prolonged descending tail of the hydrograph.

When site accessibility and/or safety prohibited manual sampling, automatic samplers were used (Table 1). Samplers were installed before the storm

Table 1. Sample sites used in the study. Storm sampling occurred over two storm seasons between 2004 and 2006.

Site	Watershed	Catchment Size (km^2)	Sampling Method	# Events Sampled
Ventura County				
Piru Creek	Santa Clara	477	automatic	1
Bear Creek - Matilija	Ventura	10	manual	2
Sespe Creek at Sespe Gorge	Santa Clara	129	automatic	2
Runkle Canyon	Calleguas	4	automatic	2
San Bernardino County				
Mill Creek	Santa Ana	15	automatic	1
unnamed trib to Santa Ana	Santa Ana	10	automatic	1
Los Angeles County				
Chesebro Creek	Malibu	8	manual	2
Cattle Canyon Creek	San Gabriel	53	automatic	3
Coldbrook Creek	San Gabriel	3	automatic	2
West Fork San Gabriel River	San Gabriel	73	automatic	2
Arroyo Seco	Los Angeles	42	automatic	2
Arroyo Sequit	Arroyo Sequit	27	manual	3
Orange County				
Critianitos Creek	San Mateo	51	automatic	1
Silverado Creek	Santa Ana	21	automatic	2
Bell Canyon Creek	San Juan	18	manual	2
Santiago Creek at Madjesko Canyon	Santa Ana	17	automatic	3
San Diego County				
Fry Creek	San Luis Rey	1	manual	2
Tenaja Creek	San Mateo	42	automatic	2

event and streams were auto-sampled to collect four composite samples representing different portions of the storm hydrograph. The automatic sampler collected "microsamples" at set intervals during each portion of the storm. Samples were collected every five minutes for the first bottle. The interval between each microsample was increased for each subsequent bottle to allow a greater portion of the storm to be sampled. Samples for the second, third, and fourth bottles were taken at ten-, twenty-, and forty-minute intervals, respectively. Ultimately, each sample bottle consisted of a composite of 18 microsamples representing one portion of the storm. The interval was determined based on expected duration of storm. If a storm was expected to last for several days, the interval was set longer. If a storm was expected to last for a short period of time, the interval was set shorter. In most cases, the four sample bottles were analyzed individually.

After collection, the samples were stored on ice in pre-cleaned glass bottles with Teflon®-lined caps until they were shipped to the laboratory for analysis. The samples were analyzed for pH, hardness, conductivity, total-recoverable metals (arsenic, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc), nutrients (ammonia, total Kjeldahl nitrogen (TKN), nitrate, nitrite, total phosphorus (TP), orthophosphate (OP), total organic carbon (TOC), dissolved organic carbon (DOC)), total dissolved solids (TDS), and total suspended solids (TSS) followed protocols approved by the US Environmental Protection Agency (USEPA; 1983) and Standard Methods by the American Public Health Association (Greenberg *et al*. 2000). In addition, samples during winter 2006 were analyzed for both dissolved and particulate metals.

Data Analysis

Four analyses were used to characterize water quality from natural areas. First, the means, variances, and ranges of concentrations, loads, and fluxes were calculated to provide an estimate of expected baseline water quality. Event flow-weighted mean concentrations (FWMC), mass loadings, and flux rates were calculated for each site. Using samples from a single storm, the event FWMC was calculated according to Equation 1:

$$FWMC = \frac{\sum_{i=1}^{n} C_i \bullet F_i}{\sum_{i=1}^{n} F_i} \tag{1}$$

where: FWMC was flow-weighted mean concentration for a particular storm; Ci was individual runoff sample concentration of i^{th} sample; *Fi* was instantaneous flow at the time of i^{th} sample; *n* was number of samples per event. Event mass loadings were calculated as the product of the FWMC and the storm volume during the sampling period. Flux estimates facilitated loading comparisons among catchments of varying sizes. Flux was calculated as the ratio of the mass loading per storm and contributing catchment area. All data were log transformed to improve normality and results are presented as geometric means and upper and lower 95% confidence intervals.

Second, concentrations and loads in natural catchments were compared with previous data collected from developed catchments to determine if significant differences existed between natural and developed areas. Storm water data from six developed watersheds in the greater Los Angeles area were used as a basis of comparison (Stein *et al*. 2007). These data were collected using the same manual pollutograph sampling method described above. Differences between natural and developed catchments were investigated using a one-way ANOVA (Sokal and Rohlf 1995) with a significance level of $p < 0.05$. Flow-weighted mean concentration data and flux data were log-transformed and then compared. If data failed in either normality or an equal variance tests, Kruskal-Wallis ANOVA on ranks (Kruskall and Wallis 1952) was performed to examine difference between the groups. To determine how the variability observed in natural catchments related to that observed in developed catchments, coefficients of variation (CVs) of the two data sets were compared. Results were back-transformed for presentation in summary tables to allow easier comparison with other studies. In all cases non-detects were assigned values of one-half minimum detection limits. In addition to chemistry data, catchment hydrology was compared to that of developed watersheds. For each storm, the mean flow, peak flow, and total runoff volume was calculated relative to the total rainfall for that storm. Storm flow patterns relative to rainfall and catchment size were compared between developed and undeveloped watersheds to assess differences in hydrologic response using linear and log-linear regression analysis.

Third, the influence of environmental attributes on the variability of the data was examined in a two-step process. First, redundancy analysis (RDA) was used to identify the attributes that accounted for the majority of variance in the data set as a whole. RDA is a canonical extension of principal component analysis (PCA) and a form of direct gradient analysis that describes variation between two multivariate data sets (Rao 1964, ter Braak and Verdonschot 1995). RDAs were performed using the program CANOCO 4.54 (ter Braak and Šmilauer 1997). Response variables used in the study were FWMCs of constituents (constituent variables). Predictor variables were environmental attributes (environmental variables); geologic type (igneous or sedimentary), land cover (forest or shrub), latitude, catchment area (km^2), elevation of sampling location (m), slope of drainage area, total rainfall of storm event (cm), baseline flow (m^3/sec), mean flow (m^3/sec), peak flow of storm event (m^3/sec), total volume of stormwater runoff (m^3), and percent canopy cover (%). All variables were log transformed prior to analysis to improve normality. Each set of variables was centered and standardized so that the coefficients with different units of measurement would be comparable. Thus, constituent concentration data were transformed by scaling them all at the same range. The environmental variables were standardized to zero mean and unit variance. Interaction terms were not considered. The importance of the environmental variables was determined by stepwise selection. In each step, the extra fit was determined for each variable, i.e., the increase in regression sum of squares over all constituents when adding a variable to the regression model. The environmental variable with the largest extra fit was then included, and the process was repeated until no variables remained that could significantly improve the fit. The statistical significance of the effect of including a variable was determined by means of a Monte Carlo permutation test. The number of permutations to be carried out was limited to 199 because the power of the test increases with the number of permutations, but only slightly so beyond 199 permutations (Lepš and Šmilauer 2003). The results of the multivariate analysis were visualized by means of a biplot, which represents optimally the joint effect of the environmental variables on constituents in a single plane (ter Braak and Verdonschot 1995). Second, the entire constituent concentration data set was grouped based on the most influential environmental variables identified by the RDA model. The data were log-transformed and the significance of differences between the groups was analyzed using ANOVA.

Lastly, temporal variability of levels of constituents within a storm event, within a season, and between years was examined. Within a storm event, flows and concentrations were evaluated by examining the time-concentration series relative to the hydrograph using a plot we term a pollutograph. A first flush in concentration from individual storm events, which was defined as when the peak in concentration preceded the peak in flow, is often observed in small urban watersheds (Stein *et al*. 2006). This was quantified using cumulative discharge plots whereby cumulative mass emission was plotted against cumulative discharge volume during a single storm event (Bertrand-Krajewski *et al*. 1998). When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined as when ≥75% of the mass was discharged in the first 25% of runoff volume. A moderate first flush was defined as when ≥30% and ≤75% of the mass was discharged in the first 25% of runoff volume. No first flush was assumed when ≤30% of the mass was discharged in the first 25% of runoff volume. Changes in proportions of metals between particulate phase and dissolved phase over the course of storm were also examined and compared with concentrations of total suspended solids, total dissolved solids, and flow. A Pearson correlation analysis was conducted to test correlation of the ratios with flow. Seasonal variability of concentrations, loads, and fluxes were analyzed relative to cumulative annual rainfall. Cumulative rainfall was calculated as the sum of rainfall from the first day of a wet season, October 1 of the year, to the sampling day. Rainfall data were from the closest rainfall gauging station for each site. If there were more than one station nearby, the average of the closest stations was used. For this analysis, all study sites were analyzed as a group to examine differences between early- and late-season storms across sites.

Results

Annual rainfall during the study period (2004-05) was compared to the average annual rainfall at a rain gauge station at Ducommun St., Los Angeles, CA, from 1872 to 2006 (http://ladpw.org/wrd/Precip/index.cfm). Rainfall for the 2004 storm season was significantly above the long-term average annual rainfall of 40 cm. In contrast, annual rainfall during winter 2005 was approximately two third of the average. Therefore the two study years represented an unusually wet year and a below average rainfall year. Event total rainfalls over the study period ranged from 0.81 to 17.20 cm. Peak flows ranged from 6.88 x 10^{-2} to 53.72 (m^3/sec) with a mean of 4.82 ±11.42 (m^3/sec). The mean total rainfall per storm event among the study catchments varied between the two years of sampling. During 2004-05, mean rainfall was 7.3 cm/storm event, while in 2005-06 it was 4.6 cm/storm event. The higher magnitude, frequency and duration of rainfall translated to average mean flows during 2004 being approximately four times larger than in 2005. Mean peak flow was 1.3 ±1.6 (m^3/sec) in 2004-05 vs. 8.1 ±15.3 (m^3/sec) in 2005-06.

Concentrations and fluxes for each constituent are summarized as geometric means and upper and lower ends of 95% confidence interval in Table 2. In all cases, concentrations observed from the natural catchments exhibited relatively large variability, as indicated by large 95% confidence intervals; concentrations and fluxes generally varied over one order of magnitude.

Hydrologic responses of natural catchments were different from those of developed catchments. The ratios of peak flow to catchment size, increased less sharply in response to the increase of rainfall in natural catchments than in developed catchments (Figure 2a). Ratios of both mean flow and total runoff volume to catchment size also increased less sharply in response to the increase of rainfall in natural catchments than in developed catchments. In addition, storms at the natural sites were bigger than storms at the developed sites in terms of total rainfall of a storm event. Most of storms at the natural sties were distributed above the seven-year average of total rainfall per storm event at the rain gauge station at Ducommun Street, Los Angeles, CA, from 1997 to 2003 (Figure 2b).

FWMCs from the natural catchments were significantly different ($p < 0.05$) from those of developed catchments for all constituents examined except TSS. In addition, fluxes for arsenic, copper, iron, lead, nickel, zinc, and ammonium were significantly different ($p < 0.05$) between the natural catchments and the developed catchments. Comparisons were conducted for a total of nine metals (arsenic, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc), four nutrients (ammonia, TKN, TP, and nitrate+nitrite), and TSS. Metal concentrations at the natural catchments were approximately one to two orders of magnitude lower than concentrations observed in the developed catchments (Figure 3a).

Table 2. Geometric means and upper and lower limits of 95% confidence interval (CI) for flow-weighted mean concentrations (FWMC) and fluxes (mass load per unit area). Total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC); total Kjeldahl nitrogen (TKN); total phosphorus (TP); orthophosphate (OP).

	FWMC (µg/L)			Flux (g/km^2)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Arsenic	0.39	0.71	0.21	0.87	1.91	0.40
Cadmium	0.14	0.24	0.08	0.31	0.73	0.14
Chromium	1.40	3.09	0.63	3.13	7.98	1.23
Copper	1.51	3.17	0.75	3.45	8.68	1.37
Iron	962	2313	400	2158	6160	765
Lead	0.51	1.06	0.24	1.14	2.94	0.44
Nickel	1.03	2.46	0.43	2.32	6.36	0.84
Selenium	0.33	0.61	0.18	0.75	1.85	0.30
Zinc	5.32	11.16	2.54	11.94	31.52	4.52

	FWMC (mg/L)			Flux (kg/km^2)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Ammonia	0.04	0.08	0.02	0.10	0.21	0.04
DOC	6.26	9.54	4.11	11.83	30.35	4.61
Nitrate+Nitrite	0.34	0.58	0.19	0.75	1.54	0.37
OP	0.04	0.06	0.02	0.10	0.20	0.05
TKN	1.21	1.55	0.95	2.63	7.18	0.96
TOC	6.28	9.91	3.98	11.86	31.31	4.49
TP	0.12	0.21	0.07	0.09	0.55	0.02
TDS	0.04	0.08	0.02	0.10	0.21	0.04
TSS	6.26	9.54	4.11	11.83	30.35	4.61

Concentrations of ammonia and TKN in the natural catchments were about one order of magnitude lower than those in the developed catchments, concentrations of nitrate+nitrite were less than one order of magnitude lower, and TSS concentrations were not significantly different (Figure 3a). Comparison of fluxes between the natural and the developed catchments showed that fluxes for arsenic, copper, iron, lead, nickel, zinc, ammonia, and TP were also lower in natural catchments (Figure 3b). In all cases, the

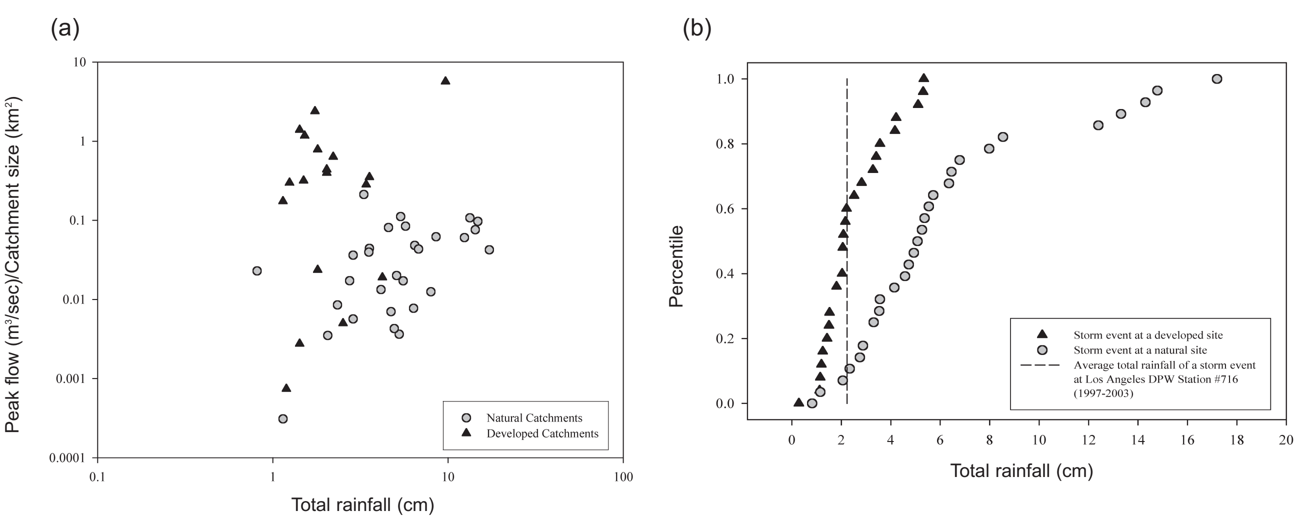

Figure 2. Comparison of ratio of peak flow over catchment size vs. rainfall between natural catchments (circles) and developed catchments (triangles); X- and Y-axes are in log scale (a). Distribution of storm events in terms of total rainfall per storm event (b).

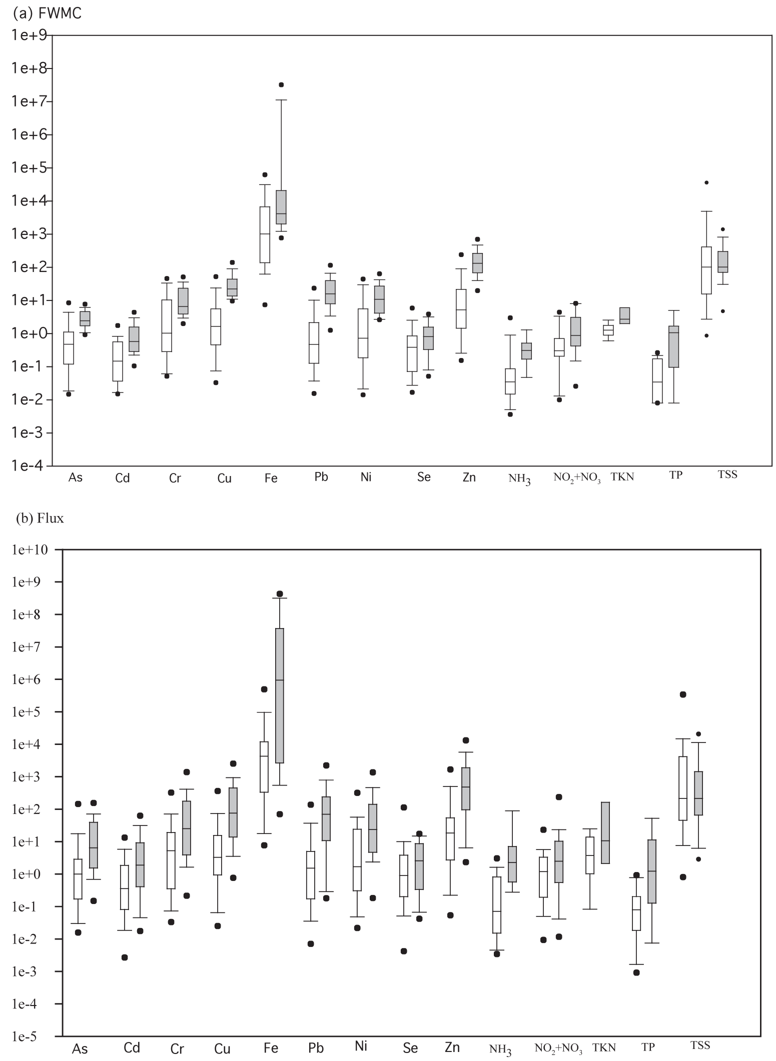

Figure 3. Comparison of flow-weighted mean concentrations (FWMCs) of metals, nutrients, and solids (a) and fluxes between natural and developed catchments (b); white boxes represent natural catchments, while gray boxes represent developed catchments. Solid line is a median of all values in the category. Boxes indicate 25th and 75th percentile and whiskers indicate 10th and 90th percentiles. Solid dots are for 5th and 95th percentiles. Concentrations of metals are expressed in µg/L and those of nutrients and solids are expressed in mg/L.

variability observed in the natural catchments was substantially larger by one to two orders of magnitude than that observed in the developed catchments both in terms of FWMCs and fluxes based on CVs. For example, the CV for copper in the developed catchments was 8, while in the natural catchments it was 474.

Geologic setting was the main determinant of variability in constituent concentration data. According to the RDA stepwise selection, geology and elevation showed higher extra fit than the other eleven environmental variables tested, and substantially increased the fitness of the model (Table 3). Subsequent RDA analysis was conducted with only these three environmental variables, thereby maximizing the ability of the model to resolve differences among environmental variables. The resultant RDA model explains 66.6 % of variance in constituent concentration data (Table 4). In contrast, the model that included all fourteen environmental variables explained only 44.3% of variance. Most metals, TSS, and a few nutrients were correlated with geology variables. Correlation between the constituent variables and the environmental variables are explained in the biplot (Figure 4). TSS and most metals except arsenic are positively correlated with sedimentary rock and negatively correlated with igneous rock. DOC and TOC were negatively corre-

Table 3. Result of stepwise selection of environmental variables using redundancy analysis (RDA). Variables are given in the order of inclusion. The extra and cumulative fits are given as percentages relative to the total sum of squares over all constituents (comparable to the percentages explained variance in univariate regression). Significance was determined by Monte Carlo permutation using 199 random permutations. Differences in the cumulative fit in the preceding row are due to rounding errors; * = p> 0.39.

Environmental Variable	Extra Fit	Cumulative Fit	Significance (p value)
Sedimentary Rock	0.12	0.12	0.02
Igneous Rock	0.12	0.24	0.02
Elevation	0.09	0.33	0.10
Peak Flow	0.05	0.39	*
Mean Flow	0.05	0.44	*
Catchment Size	0.04	0.48	*
Canopy Cover	0.04	0.52	*
Total Runoff Volume	0.04	0.56	*
Latitude	0.04	0.60	*
Baseline Flow	0.03	0.63	*
Total Rainfall	0.03	0.66	*
Shrub	0.02	0.68	*
Forest	0.02	0.71	*
Slope	0.02	0.72	*

Table 4. Statistical summary of RDA for wet-weather concentrations of metals, nutrients, and solids.

	Axes			
	1	2	3	4
Eigenvalues	0.15	0.03	0.37	0.12
Constituent-environment Correlations	0.60	0.56	0.00	0.00
Cumulative Percentage Variance				
Constituent Concentration Data	15.10	17.90	55.00	66.60
Constituent-environment Relation	84.50	100.00	0.00	0.00

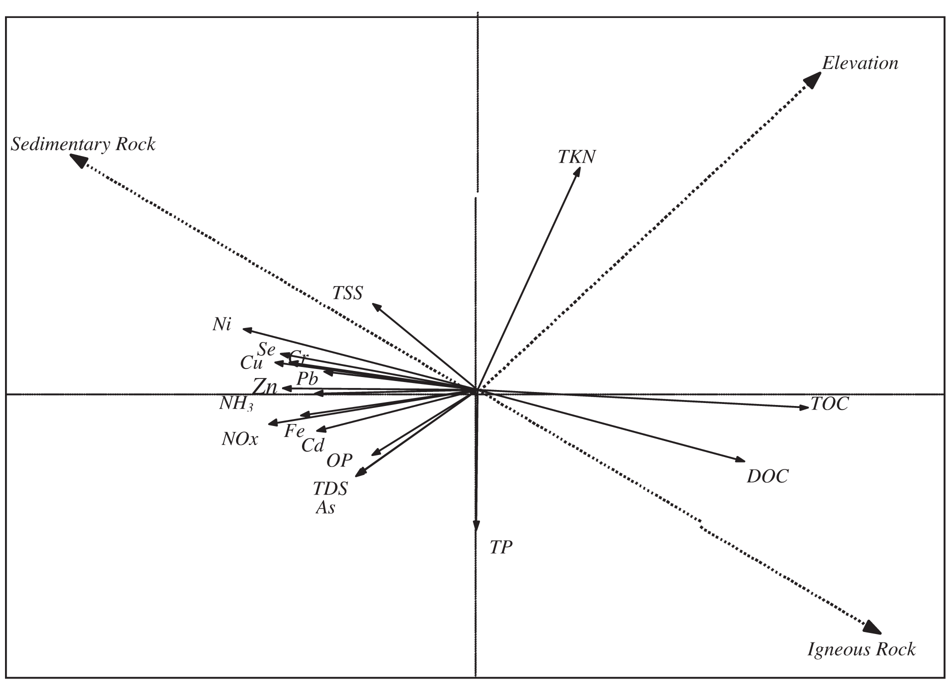

Figure 4. Correlation biplots showing the relations between concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows), total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC); total Kjeldahl nitrogen (TKN); total phosphorus (TP); orthophosphate (OP); Nitrate+Nitrite (Nox); ammonia (NH_3).

Table 5. Summary of ANOVA of concentrations between sedimentary group and igneous group. Each metal and nutrient was analyzed separately; DF, degree of freedom; MS, mean squares; F, F-ratio test; P, p value.

	Copper					Nickel				
Source of Variation	DF	SS	MS	F	P	DF	SS	MS	F	P
Between Groups	1	3.22	3.22	4.94	0.04	1	7.51	7.51	8.97	0.01
Residual	27	17.60	0.65			27	22.60	0.84		
Total	28	20.82				28	30.11			

	Selenium					Ammonia				
Source of Variation	DF	SS	MS	F	P	DF	SS	MS	F	P
Between Groups	1	2.44	2.44	5.65	0.025	1	2.87	2.87	5.78	0.02
Residual	27	11.653	0.43			27	13.40	0.50		
Total	28	14.093				28	16.276			

lated with sedimentary rock and positively correlated with igneous rock. Nitrate+nitrite, ammonia, and OP were negatively correlated with elevation, while TKN was positively correlated with elevation. Other constituents exhibited no strong correlation with any of environmental variables. The regression analysis confirmed the correlations between the constituent variables and the environmental variables suggested by the RDA results.

Concentrations of several constituents varied significantly between sites underlain by sedimentary vs. igneous rock. ANOVA results indicated that copper, nickel, selenium, and ammonia concentrations were significantly higher in storm runoff from natural catchments underlain by sedimentary rock than those underlain by igneous rock ($p < 0.05$; Table 5). Other constituents did not exhibit significant difference between the geologic groups.

No mass first flush was observed in stormwater runoff for any constituent from any of the natural catchments sampled, as indicated by the cumulative mass loading. In all cases, less than 30% of total mass was discharged during the first 25% of the storm runoff volume. For example, the mass loading for Piru Creek was roughly proportional to the percent volume discharged in Piru Creek (Figure 5a). From a concentration perspective, concentrations varied over the course of the storm; however, peak concentrations for metals, nutrients, and solids occurred after the peak flow, unlike the pattern typi-

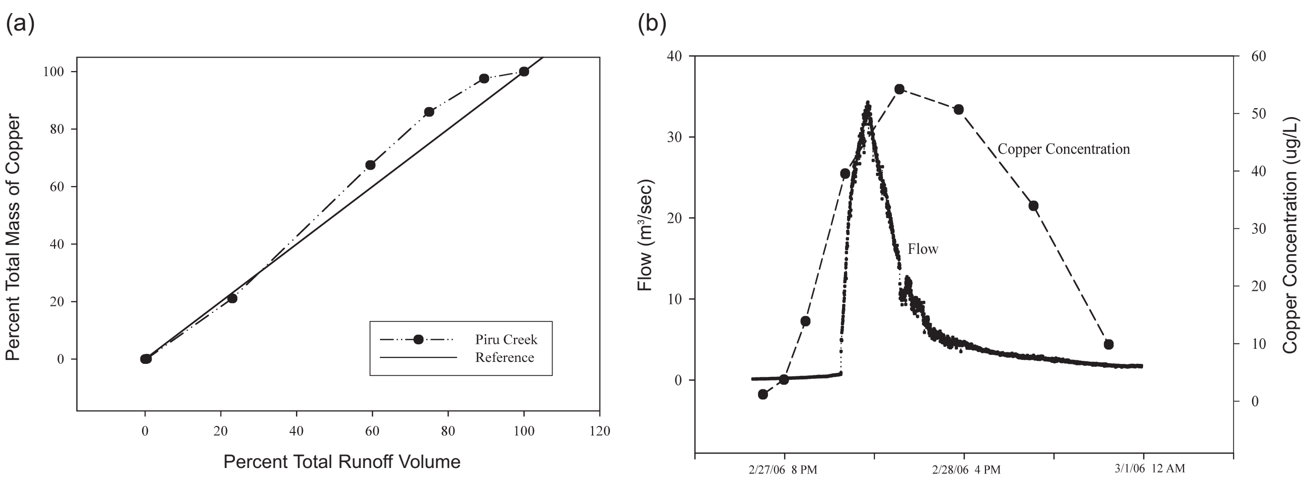

Figure 5. Variation of copper levels in storm runoff for storm event at Piru Creek from February 27 through March 1, 2006; Cumulative copper mass loads for a storm (a). The plot shows % of mass washed off for a given percent of the total runoff. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume. Portion below the line indicate the reverse pattern. Total copper concentrations and flow with time (b).

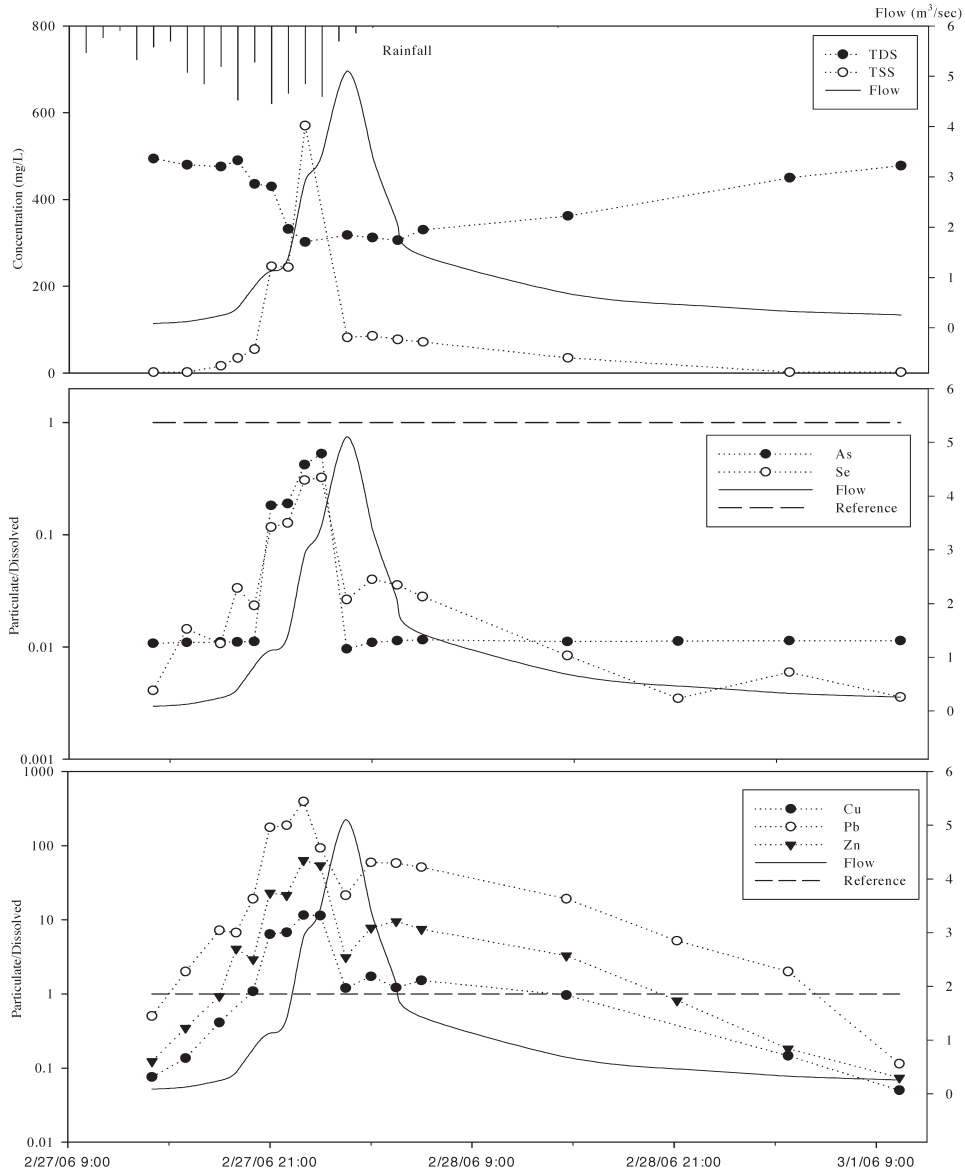

Figure 6. Change in the ratio of particulate metals over dissolved metals and concentrations of TSS and TDS over the course of a storm event at Bear Creek, a tributary to North Fork Matilija, CA. The reference line indicates 1:1 ratio between particulate and dissolved concentrations. The y axes are in log scale. Total storm rainfall was 14.6 cm.

cally observed in developed catchments where peak concentrations occur during the rising limb of the hydrograph (Figure 5b). Furthermore, the pollutograph was more spread out in natural areas than is typically observed in developed watersheds.

Ratios of particulate to dissolved metals concentrations changed over the course of storms. Particulate metals increased with increasing flow, and were significantly associated with an increase in TSS concentration ($p < 0.05$). Figure 6 shows an example of this pattern from a storm event at Bear Creek. The concentration of TSS sharply increased with the increase of rainfall and flow, while the concentration of TDS dropped. Once the flow dropped, the concentration of TSS also dropped but the concentration of TDS did not return to the pre-storm levels for approximately two days (Figure 6). The pattern of TSS concentrations was synchronized with the increase in particulate metals and was inversely related to TDS concentrations. Although this pattern was consistent among all metals, the ratio of particulate to dissolved concentration varied by metal. Arsenic and selenium existed primarily in a dissolved phase throughout storms, indicated by the fact that all samples were below the 1:1 reference line of equal distribution between the two phases, even during peak flows (Figure 6). Copper, lead, and zinc are mainly in the dissolved phase during baseflow conditions. However, during peak flow particulate metals increase by three orders of magnitude and the majority of metals in storm runoff occur in the particulate phase. Increased particulate metals concentration persisted long after flow subsided; the ratio of particulate to dissolved metals did not return back to the pre-storm levels for several days following peak flow.

No significant difference in constituent concentrations, loads, and fluxes was observed between early-season storms and late-season storms. In addition, there was no significant correlation between cumulative rainfall and concentrations, loads, and fluxes for any of the constituents sampled. No significant correlations were observed between FWMCs or fluxes and event rainfall.

Discussion

Constituent concentrations from natural catchments were about one order of magnitude lower than those from the developed catchments, with the exception of TSS. Both flow-weighted concentration and flux of TSS in the natural catchments were similar to those in the developed catchments, implying that natural areas may be a substantial source of TSS. Previous studies on developed catchments have reported a strong correlation between particle-bound pollutant load and TSS, particularly for metals (Stenstrom *et al*. 1997). However, as shown in this study, high TSS from natural catchments does not automatically imply high pollutant load. There are several potential reasons for this discrepancy. First, natural areas may intrinsically produce less pollutant washoff (i.e., less source material). Second, the particle size distribution, and hence the affinity between pollutants and particles, may be different between natural and developed areas. Third, pollutant partitioning to various particle size fractions may be different between natural and developed sites. The results of this study strongly suggest the first reason (i.e., less source material) contributes to lower loads. However, differences in the nature of the particle sizes and the associated pollutant partitioning remain to be investigated. This information would provide additional insight into the contribution of natural areas to downstream pollutant transport and deposition patterns.

Several factors could have influenced the estimates of natural concentrations and fluxes provided by this study. First, is the treatment of non-detects (NDs), which occur fairly frequently given the inherently low concentrations of constituents in natural catchments; the percent NDs were as high as 53% for TP. However, we do not expect that our assignment of a value of one-half the detection limit to NDs would change the conclusion that concentrations from natural areas are significantly lower than those from developed areas. This can be illustrated by examining the nutrient data, which had a higher incidence of NDs than metals due to higher detection limits. If we assigned a value equal to the detection limit to TP samples (instead of half the detection limit), the overall geometric mean concentration would only increase by 0.05%. This is mainly due to the large fluctuation of concentrations over the course of each storm event. Since several high concentrations during a storm event determine the FWMC, the value assigned to a few samples at lower concentrations does not substantially affect the storm event mean.

A second factor that could have influenced our estimates is the role of aerial deposition, which was not corrected for in our estimates. If aerial deposition were considered, the natural background levels estimated by this study would be even lower. Atmospheric deposition can be a significant factor that affects loadings in natural areas, particularly in xeric climates where deposition rates are particularly high (Clark *et al*. 2000). Smith *et al*. (2003) reported that stormwater loadings of TN and TP could be 16 - 30% lower when they were corrected for atmospheric deposition. Sabin *et al*. (2005) showed that atmospheric deposition potentially accounted for as much as 57 - 100 % of the total metal loads in stormwater in a small impervious urban catchment in Los Angeles, CA. Mountainous areas within the South Coast air basin, which include portions of four counties in the Los Angeles area, received the highest nitrogen deposition in the country (Fenn *et al*. 2003). This suggests potential strong contribution of atmospheric deposition to metals and nutrients in the natural catchments of southern California. Consequently, the contribution of atmospheric deposition should be investigated to assess more accurate natural contribution to loadings.

Geology and elevation were the two factors that influenced differences in water quality among natural catchments. Higher constituent levels in streams draining sedimentary catchments can be explained by the higher erodibility of sedimentary rock, which results in the release of more sediment and associated constituents into the water. Previous studies have suggested that underlying geologic formations in undeveloped areas can be a source of many chemical constituents in the water (Bisson *et al*. 1987, Richards 1982). In particular, geology has been shown to affect levels of metals and nutrients, which are pollutants of concern in many watersheds (Horowitz and Elrick 1987, Trefry and Metz 1985). In southern California, the Monterey formation has been reported to be a source of phosphate loadings (Dickert 1966), which may contribute to algal growth in streams or estuaries.

The effect of elevation on levels of constituents, especially on nitrate+nitrite, is likely due to other environmental characteristics that are associated with elevation such as declining atmospheric deposition, increasing slope, and higher organic carbon available in the contributing drainage area with increasing elevation (Scottlemyer *et al*. 1997).

Our finding of no significant relationship between natural land cover type and water quality appears to contradict previous studies (Johnson *et al*. 1997, Richards *et al*. 1996). However, previous studies have focused on the influence of natural vs. developed land cover on surface water quality or on the effect of different types of developed land use/land cover. The influence of different natural land cover on stormwater quality loading has not been extensively examined prior to this study. The lack of a relationship between land cover type and water quality suggests that any differences that might occur due to natural land cover type are subtle, and not a key deterministic factor in water quality, unlike the relatively dramatic differences between natural vs. developed land cover previously investigated. The one exception is Miller *et al*. study (2005), who assessed the role of natural land cover on water quality. They presented that the forested system in mature forested Sierra catchments could be a significant source for nutrients. The concentrations of ammonia, nitrate, and phosphate were high in surface runoff from forested systems; as high as 87.2 mg/L, 95.4 mg/L, 24.4 mg/L for ammonia, nitrate, and phosphate, respectively. These values are even greater (by an order of magnitude) than the maximum values for developed land uses that were observed in southern California coastal catchments (Ackerman and Schiff 2003). Miller's values were one to two orders of magnitude higher than the upper ends of 95% confidence interval values for nutrients presented in our study. Miller explained the high nutrient levels by suggesting that nutrients that were driven from mature organic horizons might have had little contact with mineral soil or root zone where strong retention and/or uptake of these ions would be expected, resulting in high downstream loading. Difference between our study and Miller' can be explained by differences in substrate type. The Sierran catchments studied by Miller *et al*. had a thick O-horizon that produced high nutrient levels in runoff. In contrasts, the coastal catchments in southern California are characterized by young soils with poorly-developed O-horizons and substantially lower standing biomass than the Sierran catchments (Griffin and Critchfield 1972 (reprinted with supplement, 1976)).

Other environmental factors such as catchment size, flow-related factors, rainfall, slope, and canopy cover as well as land cover did not significantly affect water quality. In general, concentrations would be expected to vary with increasing catchment size due to loss processes that reduce constituent mass as it travels downstream through stream channels (Alexander *et al*. 2000, Peterson *et al*. 2001). However, no significant difference of natural background concentrations among catchments with different size was observed in this study. The lack of a strong effect of catchment size suggests that the findings of this study could be extrapolated to estimate natural background water quality for other watersheds in southern California.

Temporal patterns (within and between storm variability) were different in natural catchments than what is typically observed in developed catchments. No first flush was observed in natural catchments, even for small catchments where first flush is most commonly observed in developed areas (Tiefenthaler *et al*. In press). First flush occurs because pollutants deposited onto exposed areas can be dislodged and entrained by the rainfall-runoff process. In developed areas, the stormwater that initially runs off an area will be more polluted than the stormwater that runs off later, after the rainfall has 'cleansed' the catchment. The lack of first flush in natural catchments may be explained by the fact that first flush is generally seen only where sediment (and hence constituent) supply is limited. In natural catchments, sediment (and associated bound pollutants) does not exhibit a first flush because the supply of soil particles is practically unlimited. As long as rainfall continues and generates storm runoff, there is a continuous input of the sediments (TSS and TDS). Thus, there is also almost no limitation in supply of particle-bound constituents during storms, as indicated by the wide shape of the pollutographs from natural areas. This may partially explain why TSS FWMCs were comparable between natural and developed areas. Differences in timing of delivery of pollutants from natural areas compared to developed areas may provide some ability to segregate downstream loads between those that are anthropogenic in origin and are most prevalent in the early part of storms, from those that are natural in origin and are prevalent later in the storm. This should be investigated further through additional empirical and modeling analysis.

Literature Cited

Ackerman, D. and K. Schiff. 2003. Modeling stormwater mass emissions to the southern California bight. Technical Report 390. Southern California Coastal Water Research Project. Westminster, CA.

Alexander, R.B., R.A. Smith and G.E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. *Nature* 403:758-761.

Bertrand-Krajewski, J., G. Chebbo and A. Saget. 1998. Distribution of pollutant mass vs volume in stormwater discharges and the first flush phenomenon. *Water Research* 32:2341-2356.

Bisson, P.A., R.E. Bilby, M.D. Bryant, C.A. Dolloff, G.B. Grette, R.A. House, M.L. Murphy, K.V. Koski and J.R. Sedell. 1987. Large woody debris in forested streams in the Pacific Northwest: past, present, and future. pp. 143-190 *in*: E.O. Salo and T.W. Cundy (eds.), Streamside Management: Forest and Fishery Interactions. Institute of Forest Resources, University of Washington, Seattle. Seattle, WA.

Clark, G.M., D.K. Mueller and M.A. Mast. 2000. Nutrient concentrations and yields in undeveloped stream basins of the United States. *Journal of the American Water Resources Association* 36:849-860.

Davis, A.P., M. Shokouhian and S. Ni. 2001. Loading estimates of lead, copper, cadmium, and zinc in urban runoff from specific sources. *Chemosphere* 44:997-1009.

Dickert, P.F. 1966. Tertiary phosphatic facies of the coast ranges. *California Division of Mines and Geology Bulletin* 190:289-304.

Fenn, M.E., R. Haeuber, G.S. Tonnesen, J.S. Baron, S. Grossman-Clarke, D. Hope, D.A. Jaffe, S. Copeland, L. Geiser, H.M. Rueth and J.O. Sickman. 2003. Nitrogen emissions, deposition, and monitoring in the Western United States. *BioScience* 53:391-403.

Greenberg, A.E., L.S. Clesceri and A.D. Eaton. 2000. Standard methods for the examination of water and wastewater. 20th Ed. American Public Health Association, United Book Press. Washington, DC.

Griffin, J.R. and W.B. Critchfield. 1972. The Distribution of Forest Trees in California. USDA Forest Service, Pacific Southwest Forest and Range Experiment Station. Berkeley, CA.

Horowitz, A.A. and K.A. Elrick. 1987. The relationship of stream sediment surface area, grain size, and trace element chemistry. *Applied Geochemistry* 2:437-445.

Jennings, C.W. and R.G. Strand. 1969. Geologic map of California, Los Angeles sheet. California Department of Conservation, Division of Mines and Geology. Sacramento, CA.

Johnson, L.B., C. Richards, G.E. Host and J.W. Arthur. 1997. Landscape influence on water chemistry in Midwestern stream ecosystems. *Freshwater Biology* 37:193-218.

Kruskall, W.H. and W.A. Wallis. 1952. Use of Ranks in One-criterion Analysis of Variance. *Journal of the American Statistical Association* 47:583-621.

Leecaster, M.K., K. Schiff and L. Tiefenthaler. 2002. Assessment of efficient sampling designs for urban stormwater monitoring. *Water Research* 36:1556-1564.

Lepš, J. and P. Šmilauer. 2003. Multivariate Analysis of Ecological Data Using CANOCO. Cambridge University Press. New York, NY.

Miller, W.W., D.W. Johnson, C. Denton, P.S.J. Verburg, G.L. Dana and R.F. Walker. 2005. Inconspicuous nutrient laden surface runoff from mature forest Sierran watersheds. *Water, Air, & Soil Pollution* 163:3-17.

Noble, R., J. Dorsey, M. Leecaster, V. Orozco-Borbon, D. Reid, K. Schiff and S. Weisberg. 2000. A regional survey of the microbiological water quality along the shoreline of the southern California Bight. *Environmental Monitoring Assessment* 64:435-447.

Peterson, B.J., W.M. Wollheim, P.J. Mulholland, J.R. Webster, M.J. L, J.L. Tank, E. Marti, W.B. Bowden, H.M. Valett, A.E. Hershey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S. Gregory and D.D. Morrall. 2001. Control of Nitrogen Export from Watersheds by Headwater Streams. *Science* 292:86-90.

Rao, C.R. 1964. The use and interpretation of principal component analysis in applied research. *Sankhya A* 26:329-358.

Richards, C., L.B. Johnson and G.E. Host. 1996. Landscape-scale influences on stream habitats and biota. *Canadian Journal of Fisheries and Aquatic Sciences* 53:295-311.

Richards, K. 1982. Rivers: Form and Process in Alluvial Channels. Methunen & Co. New York, NY.

Rogers, T.H. 1965. Geologic Map of California, Santa Ana Sheet. California Department of Conservation, Division of Mines and Geology. Sacramento, CA.

Rogers, T.H. 1967. Geologic Map of California: San Bernardino Sheet. California Department of Conservation, Division of Mines and Geology. Sacramento, CA.

Sabin, L.D., J.H. Lim, K.D. Stolzenbach and K.C. Schiff. 2005. Contribution of trace metals from atmospheric deposition to stormwater runoff in a small impervious urban catchment. *Water Research* 39:3929-3937.

Scottlemyer, R., C. Troendle and D. Markowitz. 1997. Change in snowpack, soil water, and stream water chemistry with elevation during 1990, Fraser experimental forest, Colorado. *Journal of Hydrology* 195:114-136.

Seiler, R.L., J.P. Skorupa and L.A. Peltz. 1999. Areas susceptible to irrigation-induced selenium contamination of water and biota in the western United States: U.S. Geological Survey Circular 1180. USGS. Menlo Park, CA.

Smith, R.A., R.B. Alexander and G.E. Schwarz. 2003. Natural background concentrations of nutrients in streams and rivers of the conterminous united states. *Environmental Science and Technology* 37:3039-3047.

Sokal, R. and F.J. Rohlf. 1995. Biometry: The Principles and Practice of Statistics in Biological Research. 3rd ed. W.H. Freeman and Co. New York, NY.

Stein, E.D., L.L. Tiefenthaler and K.C. Schiff. 2007. Understanding sources, patterns, and mechanisms of pollutant loading from urban, arid watersheds and land-uses of the greater Los Angeles, California, USA. Technical Report 510. Southern California Coastal Water Research Project. Costa Mesa, CA.

Stein, E.D., L.L. Tiefenthaler and K.C. Schiff. 2006. Watershed-based sources of polycyclic aromatic hydrocarbons in urban storm water. *Environmental Toxicology and Chemistry* 25:373-385.

Stenstrom, M.K., S.-L. Lau, H.-H. Lee, J.-S. Ma, H. Ha, L.-H. Kim, S. Khan and M. Kayhanian. 1997. Particles, Metals, and Water Quality in Runoff from Large Urban Watershed. *Journal of Environmental Engineering* 123:753-759.

Strand, R.G. 1962. Geologic Map of California, San Diego-El Centro Sheet. California Department of Conservation, Division of Mines and Geology. Sacramento, CA.

ter Braak, C.J.F. and P. Šmilauer. 1997. Canoco for Windows. Biometris-Plant Research International. Wageningen, Netherlands.

ter Braak, C.J.F. and P.F.M. Verdonschot. 1995. Canonical correspondence analysis and related multivariate methods in aquatic ecology. *Aquatic Sciences - Research Across Boundaries* 57:255.

Tiefenthaler, L.L., E.D. Stein and K.C. Schiff. In press. Watershed and land use-based sources of trace metals in urban storm water. *Environmental Toxicology and Chemistry*.

Trefry, J. and S. Metz. 1985. A decline in lead transport by the Mississippi River. *Science* 230:439-441.

United States Environmental Protection Agency (USEPA). 1983. Methods for chemical analysis of water and waste, Report EPA-600/4-79-020. US Environmental Protection Agency. Cincinnati, OH.

Acknowledgments

Funding for this study was provided by the U.S. Environmental Protection Agency Region IX (Contract No. CP97983901) and the Los Angeles Regional Water Quality Control Board (Agreement No. 04-075-554-0). We thank Jay Shrake, Sean Porter, Richard Rusnik, and the rest of the MacTec Engineering field crews for their assistance and dedication in collecting stormwater samples.