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Dry Weather Flow Contribution of Metals, Nutrients, and Solids from Natural Catchments

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Abstract Dry weather flow can be a substantial source of pollutants, particularly in urbanized areas such as southern California. To effectively evaluate and manage watershed-based pollutants, it is essential to understand the contribution of constituents from both developed and natural areas. Such information can be used by managers to set appropriate regulatory targets and to better evaluate severity of anthropogenic effects. This study quantified levels of suspended solids (TSS), metals, and nutrients from nineteen representative natural (undeveloped) streams in ten watersheds in southern California. Dry-weather concentrations and fluxes were typically one to two orders of magnitude lower than those from developed catchments. Constituent concentrations varied based on the catchment characteristics, with geologic type being the dominant factor that influenced variability among constituent levels. Concentration and flux values were independent of latitude, elevation, and catchment size suggesting that results from this study can be extrapolated to provide regional estimates of background water quality.

Keywords Background water quality · Dry season flow · Natural catchments · RDA · Reference condition

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1 Introduction

Over the last decade efforts to manage water quality in California and other semi-arid climates have concentrated mainly on storm water, which is perceived to be the largest source of pollutant loading (Ackerman and Schiff 2003; Noble et al. 2000). This perception is based on a climate characterized by low natural baseflow during the extended dry season followed by intense winter storms. However, dry-weather flow may also constitute a significant threat to water quality in terms of both pollutant concentration and load (McPherson et al. 2005; Stein and Tiefenthaler 2005). Dry weather flow can be particularly important in areas such as southern California, where the Mediterranean climate results in less than 40 days of rain per year (Nezlin and Stein 2005). Although concentrations of pollutants in dry-weather flow may be relatively low (Duke et al. 1999; Mizell and French 1995; Stein and Ackerman 2007), dry-weather flow can be a chronic source of pollution that impacts aquatic life (Bay and Greenstein 1996; Stein and Tiefenthaler 2005). Furthermore, during years with low rainfall, dry weather flow can produce a substantial proportion of the annual load of constituents such as metals and nutrients (Stein and Ackerman 2007).

Water quality constituents in dry weather flow, such as metals, nutrients, and solids, can originate from natural sources as well as anthropogenic sources (Horowitz and Elrick 1987; Seiler et al. 1999). Most water quality assessments focus on anthropogenic constituent contribution, with little or no attention given to the contribution from natural sources. Addressing this data gap is important as the majority of costal watersheds in the USA contain considerable portions of open areas (NOAA Coastal Change Analysis Program [CCAP] 2003). To evaluate the relative extent of anthropogenic activities and to set realistic water quality targets, it is essential to assess the contribution of both developed and natural areas to downstream water quality.

Data from existing monitoring programs in southern California are not sufficient to characterize natural background concentrations across the region. First, relatively few samples have been collected from natural areas. Second, many of the sites considered as “background” were not entirely free of human influences from agricultural runoff or isolated rural residences (e.g., septic systems). Third, existing data do not capture the range of natural background conditions of southern California’s coastal watersheds. Southern California’s coastal watersheds occur in diverse geologic and topographic settings, have a variety of soil types, and contain several natural vegetation communities (USGS 2006). These environmental factors are known to influence levels of constituents in streams such as metals, nitrogen compounds, and phosphorus compounds (Holloway and Dahlgren 1999; Kelly et al. 1999; Richards et al. 1996).

The goal of this study is to assess dry-weather concentration and loads from natural watersheds and to investigate the effect of environmental settings on background water quality. Specific questions we address are: (1) What are the ranges of concentrations, loads, and fluxes of metals, nutrients, and solids associated with natural areas during dry weather? (2) How do the ranges of constituent concentrations and fluxes associated with natural areas compare to those associated with developed areas? (3) Which catchment characteristics most influence dry-weather concentrations?

2 Materials and Methods

2.1 Study Areas

Review of past studies and pre-existing data from ambient water quality monitoring programs in southern California suggests that surficial geology and dominant land cover likely influence water quality loading from minimally developed watersheds (Gergel et al. 1999; Horowitz and Elrick 1987; Johnes et al. 1996; Johnson et al. 1997; Larsen 1988; Richards et al. 1996; Trefry and Metz 1985). Consequently, our sampling design involved stratified sampling based on these two independent variables. The majority of undeveloped areas in the study region are underlain by either igneous or sedimentary rock and have either scrub–shrub or forested land cover (Jennings and Strand 1969; National Oceanographic and Atmospheric Administration 2003; Rogers 1965, 1967; Strand 1962). Therefore, we prioritized geology-land cover combinations to account for these areas.

To ensure that sampling would capture natural conditions without influence from any land-based anthropogenic input, we applied the following criteria to select study sites: (1) contributing drainage area should be at least 95% undeveloped. Catchment land use was determined by plotting watershed boundaries over (year 2003) land cover maps from the National Oceanographic Administration (NOAA) Coastal Change Analysis Program (CCAP) 2003 – http://www.csc.noaa.gov/crs/lca/ccap.html. (2) Sites should be in a relatively homogenous setting in terms of underlying geology and landcover, (3) sites should have either year-round or prolonged dry-weather flow to allow sampling during the dry season, and (4) sites should not be within watersheds that have burned during the previous three years. Based on these criteria, 19 sites in 10 watersheds were selected, encompassing a range of catchment sizes across southern California’s coastal watersheds (Fig. 1). The environmental setting of each catchment was characterized 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 (Table 1). Geology and land cover type for the

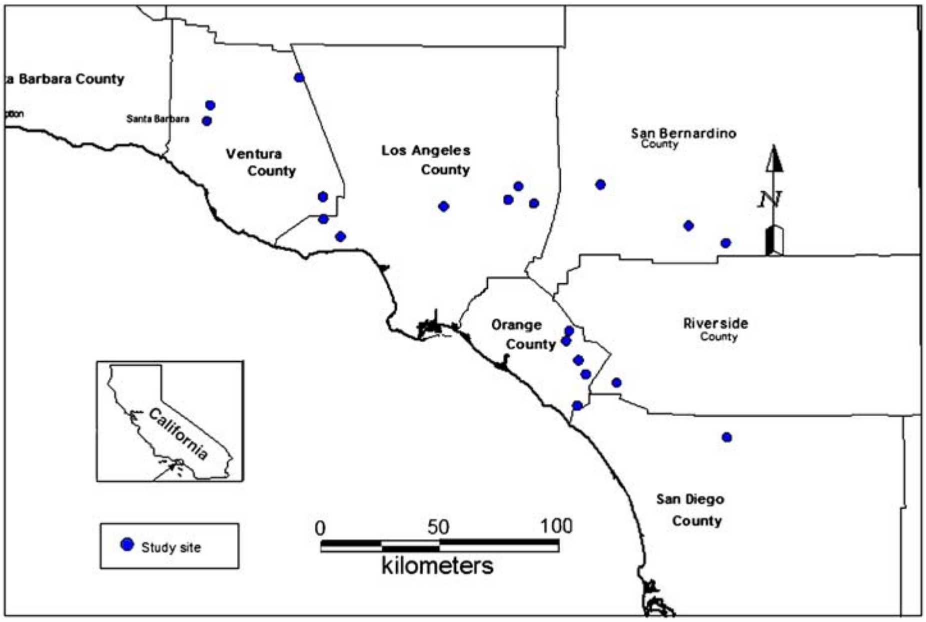

Fig. 1 Map of the dry-weather study sites

coastal watersheds in southern California were determined by plotting catchment boundaries over digitized geology maps (Jennings and Strand 1969; Rogers 1965, 1967; Strand 1962) and land cover maps (National Oceanographic and Atmospheric Administration 2003). The rest of the catchment characteristics were assessed using ArcView GIS7.0 (ESRI, Redlands, CA). Percent canopy cover was estimated as percent vegetation cover over a stream based on field measurements using a spherical forest densitometer (Wildco, Buffalo, NY).

2.2 Sampling

Three dry-season sampling events were conducted at all 19 sites during spring 2005, fall 2005, and spring 2006. Dry-season sampling was initiated following at least 30 consecutive days with no measurable rain to minimize effects of residual stormwater return flow. Water samples were collected as composite grab samples, with equivalent volumes collected from three different points across the stream (approximately 10, 50, and 90% distance across). A replicate water sample was collected in the same way 10 min after completion of the initial water sampling. All water samples were collected (and in some cases preserved) in accordance with protocols approved by the USEPA (1983) and standard methods approved by the American Public Health Association (Greenberg et al. 2000). Collected water samples were immediately placed on ice for subsequent analyses. At each sampling location and during each round of sample collection, temperature, pH, and DO were measured in the field using Orion 125 and Orion 810 field probes (Thermo Electron Corporation, Waltham, MA). Measurements were taken in triplicate at each transect. Stream discharge was measured as the product of the channel cross-sectional area and the flow velocity. Channel cross sectional area was measured in the field. At each sampling event, velocity was measured using a Marsh–McBirney Model 2000 flow meter (Frederick, MD). The velocity, width, and depth were measured at three points along each transect and flow for each subsection of a transect was computed and summed for a total flow for the transect. Values from three transects were averaged to estimate overall flow at each site (Rantz 1982).

To estimate the extent of daily variability in constituent concentrations, water samples were collected using automatic samplers over 48 h from July 6 through July 9, 2005 at two selected sites: Arroyo Seco and Santiago Creek. The automatic sampler measured flow every minute and collected a microsample at 20-min intervals. Every eighteen microsamples were composited into a single bottle for analysis, resulting in eight discrete composite samples over the 48-h period. In addition, pH, temperature,

Table 1 Sampling sites and corresponding catchment characteristics

Site	Watershed	Catchment size (km^2)	Flow duration	Land cover	Geology
Ventura County					
Piru Creek	Santa Clara	477	Perennial	Shrub	Sedimentary
Bear Creek – Matilija	Ventura	10	Perennial	Forest	Sedimentary
Sespe Creek at Sespe Gorge	Santa Clara	129	Perennial	Shrub	Sedimentary
San Bernardino County					
Mill Creek	Santa Ana	15	4 months	Shrub	Igneous
Cajon Creek	Santa Ana	83	4 months	Shrub	Igneous
unnamed trib to Santa Ana	Santa Ana	10	Perennial	Shrub	Igneous
Los Angeles County					
Chesebro Creek	Malibu	8	2 months	Forest	Sedimentary
Cattle Canyon Creek	San Gabriel	53	Perennial	Shrub	Igneous
Coldbrook Creek	San Gabriel	3	Perennial	Forest	Igneous
West Fork San Gabriel River	San Gabriel	73	Perennial	Forest	Igneous
Arroyo Seco	Los Angeles	42	Perennial	Forest	Igneous
Cold Creek	Malibu	2	Perennial	Shrub	Sedimentary
Orange County					
Critianitos Creek	San Mateo	51	3 months	Shrub	Sedimentary
Silverado Creek	Santa Ana	21	Perennial	Shrub	Sedimentary
Bell Canyon Creek	San Juan	18	4 months	Shrub	Sedimentary
San Juan Creek	San Juan	100	4 months	Shrub	Sedimentary
Santiago Creek at Madjesko Canyon	Santa Ana	17	4 months	Shrub	Sedimentary
San Diego County					
Fry Creek	San Luis Rey	1	1 month	Forest	Igneous
Tenaja Creek	San Mateo	42	3 months	Shrub	Igneous

and special conductivity were sampled every minute via an automatic water parameter logger (YSI 600XLM, SonTek/YSI, San Diego, CA). These composite samples were analyzed in the same way as the grab samples to allow assessment of potential diel patterns in water chemistry.

2.3 Laboratory Analysis

Samples from both the dry-season sampling and the 48-h sampling were analyzed for pH, hardness, conductivity, total-recoverable metals (arsenic, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc), nutrients (ammonia [NH_3], total Kjeldahl nitrogen [TKN], nitrate, nitrite, total phosphorus [TP], ortho-phosphate [OP], total organic carbon [TOC], and dissolved organic carbon [DOC]), total dissolved solids (TDS), and total suspended solids (TSS) followed protocols approved by the US Environmental Protection Agency (1983) and Standard Methods by the American Public Health Association (Greenberg et al. 2000).

2.4 Data Analysis

Four analyses were used to characterize water quality from natural catchments. First, the means, variances, and ranges of concentrations, loads, and fluxes were calculated to provide an estimate of expected natural background water quality. Loads were calculated by multiplying flow by concentration for each site:

$$\text{Load} = \sum F_i C_i$$

where F_i was a mean flow at sampling site i and C_i was a concentration at site i.

Mass loading was expressed as load/day. Flux was calculated both as the ratio of the mass loading per contributing catchment area and as the ratio of mass loading per catchment discharge. All data were log transformed to improve normality and results are presented as geometric means, minima, maxima, and upper and lower 95% confidence intervals. In all cases non-detects were assigned values of half the minimum detection limits (MDLs).

Second, concentrations and fluxes in natural catchments were compared with previous data collected from developed catchments to determine if significant differences existed between the two groups. Data from dry weather studies of metals, nutrients, and TSS in Ballona Creek, Coyote Creek, Los Angeles River, San Gabriel River, San Jose Creek, and Walnut Creek in the greater Los Angeles area, California (Ackerman and Schiff 2003; Stein and Ackerman 2007; Stein and Tiefenthaler 2005) were used for comparison because they were collected in the same manner as data collected for this study and because the raw data were available for use in statistical comparisons. Differences between natural and developed catchments were investigated using Analysis of Variance, ANOVA, (Sokal and Rohlf 1995) with a significance of $p<0.05$. Mean concentration and flux data were log-transformed and compared between the natural catchments and the developed catchments using ANOVA. To determine how variability observed in natural catchments was related to variability observed in developed catchments, coefficients of variance (CVs) of the two data sets were compared. The CV accounts for differences in sample size and in the magnitude of means and provides a relative measure of variability. Results were back-transformed for presentation in summary tables to allow easier comparison with other studies.

Third, the influence of environmental variables on water chemistry was examined using redundancy analysis (RDA). 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 Smilauer 1997). Response variables used in the study were constituent concentrations (constituent variables). Predictor variables were environmental attributes (environmental variables); geologic types (igneous

Table 2 Geometric means and minima and maxima for concentrations, mass loads, and fluxes (shown as both mass load per unit area and per unit flow)

	Concentration			Flow-normalized flux (g/day-(m^3/s)$^{-1}$)			Area-normalized flux (g/day km^2)		
	Geometric mean	Minimum	Maximum	Geometric mean	Minimum	Maximum	Geometric mean	Minimum	Maximum
	μg/L								
Arsenic	0.66	0.04	6.49	57.42	3.24	560.30	0.33	0.21	0.51
Cadmium	0.11	0.05	1.15	9.70	4.32	99.14	0.06	0.03	0.1
Chromium	0.17	0.05	1.43	14.75	4.32	123.34	0.08	0.05	0.14
Copper	0.56	0.05	5.06	48.24	4.32	436.97	0.28	0.18	0.43
Iron	83.9	7.85	517.75	7249.69	678.24	44733.60	41.37	24.73	69.19
Lead	0.05	0.03	3.12	3.97	2.16	269.78	0.02	0.01	0.04
Nickel	0.3	0.03	5.11	25.85	2.16	441.50	0.15	0.09	0.24
Selenium	0.58	0.05	67.93	50.48	4.32	5868.72	0.29	0.17	0.49
Zinc	0.56	0.05	10.21	48.66	4.32	882.14	0.28	0.16	0.5
	mg/L								
Ammonia	0.01	0.005	0.02	0.52	0.43	1.73	0.003	0.002	0.005
Nitrate + nitrite	0.05	0.01	2.88	4.36	0.86	248.82	0.02	0.01	0.05
TKN	0.28	0.23	1.11	23.91	19.87	95.69	0.14	0.09	0.22
DOC	2.68	0.02	9.80	231.59	1.38	846.72	1.32	0.8	2.17
TOC	2.85	1.05	25.00	246.16	90.72	2160.00	1.4	0.91	2.18
OP	0.02	0.00	1.24	1.41	0.32	107.18	0.01	0	0.01
TP	0.05	0.01	0.23	4.13	0.69	19.96	0.02	0.01	0.04
TDS	274.43	0.05	2270.00	23710.77	4.32	196128.00	137.86	75.87	250.53
TSS	0.85	0.25	41.00	73.54	21.60	3542.40	0.42	0.23	0.78

Metals data are total recoverable metals

TKN Total Kjeldahl nitrogen, *DOC* dissolved organic carbon, *TOC* total organic carbon, *OP* orthophosphate, *TP* total phosphate, *TDS* total dissolved solids, *TSS* total suspended solids

Table 3 Extent of daily variability of flow-normalized flux estimates at Arroyo Seco and Santiago Creek

Parameter	Unit	Santiago Creek			Arroyo Seco		
	load/average flow	Minimum flux	Maximum flux	Percent difference	Minimum flux	Maximum flux	Percent difference
Arsenic	(g/day)/(m^3/s)	74.5	84.3	13	121	211	75
Cadmium	(g/day)/(m^3/s)	4.1	4.7	14	4.0	4.6	14
Chromium	(g/day)/(m^3/s)	4.1	4.7	14	4.0	4.6	14
Copper	(g/day)/(m^3/s)	58.5	96.3	65	75	116	54
Iron	(g/day)/(m^3/s)	5422	7367	36	2186	3218	47
Lead	(g/day)/(m^3/s)	2.1	21.5	923	2.0	4.6	127
Nickel	(g/day)/(m^3/s)	25.5	32.3	27	4.0	4.6	14
Selenium	(g/day)/(m^3/s)	135	170	26	4.2	155	3604
Zinc	(g/day)/(m^3/s)	4.2	202.1	4702	45	312	592
Ammonia	(kg/day)/(m^3/s)	0.4	0.9	113	0.4	6.4	1490
Nitrate	(kg/day)/(m^3/s)	0.8	7.1	761	11.3	33.0	192
Nitrite	(kg/day)/(m^3/s)	0.8	2.2	161	0.8	2.6	225
TP	(kg/day)/(m^3/s)	0.7	17.8	2596	0.6	9.9	1432
TDS	(kg/day)/(m^3/s)	3441	17574	411	4.0	8089	200453
TSS	(kg/day)/(m^3/s)	20.6	71.8	249	20.2	22.9	14

Percent difference is between the maximum value and minimum values

rock or sedimentary rock), land cover types (forest or shrub), latitude, catchment area (km^2), elevation of sampling location (m), slope of drainage area, mean flow (m^3/s), and percent canopy cover (%). Prior to conducting the RDA, variables were log transformed to improve normality. Each set of variables was centered and standardized to normalize the units of measurement so that the coefficients would be comparable to one another. 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 variables 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 none of the excluded variables 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 using biplots that represent optimally the joint effect of the environmental variables on water quality variables in a single plane (ter Braak and Verdonschot 1995). The constituent concentration data were 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 in the data was assessed by examining flow, field parameters, concentrations and fluxes of constituents from the 48-h sampling at the two selected sites, Santiago Creek and Arroyo Seco. The minimum estimates of fluxes were calculated using the minimum flow and the minimum concentration measured during the 48-h study and the maximum estimates of fluxes were using the maximum flow and the maximum concentration. The percent difference between the minimum and maximum estimates were computed to investigate the effect of daily variability on estimates of load and flux. Finally, seasonal variability was evaluated by comparing 2005 and 2006 data using ANOVA (Sokal and Rohlf 1995).

3 Results

Nine of the nineteen streams sampled were intermittent, while the rest were perennial (Table 1). Mean dry season flow ranged from 0 to 0.72 m^3/s, with an

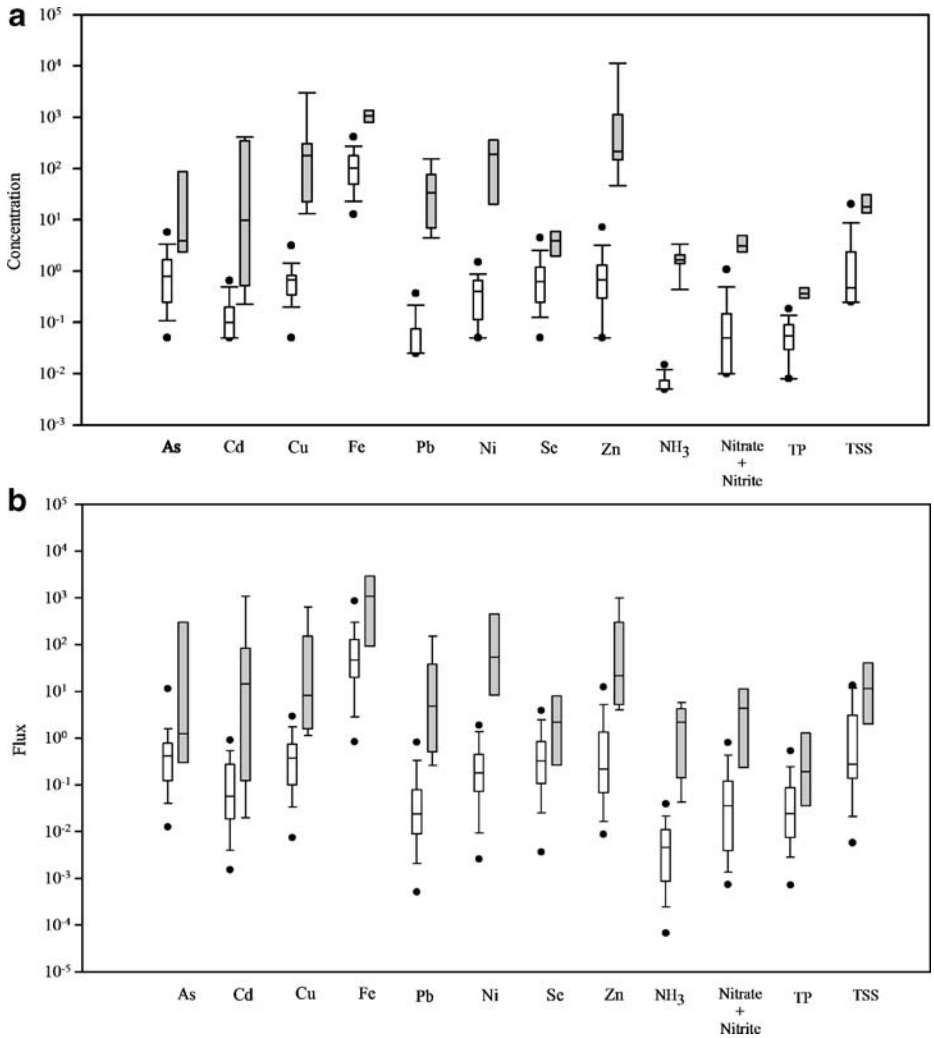

Fig. 2 Comparison of dry-weather **a** concentrations and **b** fluxes of metals, nutrients, and solids between natural and developed catchments. *White boxes* represent natural sites, while *gray boxes* represent developed sites. *Solid line* is a median of all values in the category. A *box* indicates 25th and 75th percentiles and *error bars* 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. Fluxes of metals are expressed in g/day km^2 and those of nutrients and solids are expressed in kg/day km^2

overall mean of 0.33 m^3/s. Dissolved oxygen was 6.14±3.4 mg/L (mean±standard deviation), total hardness was 225.9±182.29 mg/L, pH was 8.0±0.4, water temperature was 16.77±3.04°C, and percent canopy cover along the sampled reaches was 87± 11%. Flow at natural sites varied at multiple time scales. Flow in intermittent streams decreased consistently after the last storm of the season to zero after a period of months. Base flow in gauged perennial streams varied over one order magnitude, with the highest flows occurring in May and the lowest in September.

Concentrations, loads, and fluxes observed from the natural sites exhibited a great deal of variability, as indicated by large range of values (Table 2). For example, the geometric mean of TDS was 274.4 mg/L, but observed values ranged from 0.05 to 2,270 mg/L. Because concentration and flux are influenced by flow (particularly in highly variable systems), the ranges of constituent flux were narrower once values were normalized for stream discharge (Table 2).

Flow, pH, temperature, and conductivity varied over the course of the day; however, constituent concentrations did not show any clear diurnal pat-

Table 4 Comparison of coefficients of variance (CVs) between natural catchments and developed catchments for metals, nutrients, and solids in the dry-weather condition

	Natural			Developed		
	Number of samples	Concentration CV	Flux CV	Number of samples	Concentration CV	Flux CV
Arsenic	51	534	6.2	4	81	339.9
Cadmium	51	2262	26.2	4	977	4494.2
Chromium	51	1404	16.2	8	41.3	102.3
Copper	51	462	5.3	11	4	11.1
Iron	51	3	0.0	8	0.1	0.5
Lead	51	6116	70.8	10	15	44.0
Nickel	50	1011	11.7	8	5	13.9
Selenium	51	647	7.5	8	52	145.5
Zinc	51	706	8.2	11	2	4.0
Ammonia	51	23680	274.1	10	321	481.5
Nitrate + nitrite	51	8516	98.6	8	97	208.0
TKN	50	543	6.3	0	–	–
DOC	51	88	1.0	0	–	–
TOC	51	65	0.8	0	–	–
OP	51	25231	292.0	0	–	–
TP	49	5088	58.9	8	348	1434.7
TDS	51	2	0.0	0	–	–
TSS	50	502	5.8	8	11	22.7

'–'=Data were not available

terns. Flow and conductivity increased during the night, reaching maximum values shortly after sunrise (8:30 P.M.–5:30 A.M.) and then decreased to minimum values around midday. Temperature and pH cycles lagged several hours behind those of flow and conductivity. Concentrations varied over 48 h; however, no consistent or systematic daily pattern was observed in concentrations of metals, nutrients, and solids at either study site used for the 48-h sampling. No significant correlation between the time of highest (or lowest) flow and the time of highest (or lowest) concentration for each constituent was found. Table 3 shows the maximum and the minimum estimates of daily flux for each constituent for the two sites where

Table 5 Result of stepwise selection of environmental variables using redundancy analysis (RDA) in dry weather

Environmental variables	Extra fit	Cumulative fit	Significance (p value)
Igneous rock	0.07	0.07	0.005
Sedimentary rock	0.07	0.15	0.005
Slope	0.04	0.19	0.04
Mean Flow	0.04	0.23	*
Elevation	0.03	0.26	*
Catchment Size	0.03	0.29	*
Canopy Cover	0.03	0.32	*
Latitude	0.02	0.35	*
Forest	0.02	0.37	*
Shrub	0.02	0.40	*

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 water quality variables (comparable to the percentage explained variance in univariate regression). Number of observations: 1,006. Total number of water quality variables: 18. 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>0.05

Table 6 Statistical summary of RDA for dry-weather water quality data

	Axes			
	1	2	3	4
Eigen values	0.075	0.038	0.22	0.12
Constituent–environment correlations	0.65	0.66	0.00	0.00
Cumulative percentage variance of				
Constituent concentration data	7.50	11.30	33.80	45.40
Constituent–environment relation	66.40	100.00	0.00	0.00

diurnal patterns were measured. Estimates of daily flux varied from less than 15% to more than several hundred percent depending on the constituent. Where large ranges in daily values were observed, they typically resulted from one or two extremely high or low values. In general, diurnal fluctuations in constituent concentrations were modest.

Most dry-weather constituent concentrations at the natural sites did not vary significantly between the three sampling events (Fall 2005, Spring 2005, Fall 2006). Metals concentrations varied between 5 and 50% between the three sampling season. The exception was cadmium which had significantly higher concentrations during Spring 2006. Nutrient concentrations varied more based on season than metals. Differences in dry weather nutrient concentrations ranged from 23 to 90%, but these differences were only significant for ortho-phosphate. Concentrations of TSS, TDS and DOC showed the greatest differences, with values for Spring 2005 being between 71 and 110% higher than during the other two sampling periods. Mean flow was significantly lower in Fall 2005 reflecting higher rainfall during the 2005–2006 season. Despite the differences listed above, there were no consistent or systematic differences between sampling seasons and flow differences were not a good predictor of differences in dry weather constituent concentrations.

Table 7 Canonical coefficients of environmental variables with the first two axes of RDA for dry-weather concentrations of metals, nutrients, and solids

Environmental variables	Water quality constituent axes	
	1	2
Sedimentary rock	−0.6319	−0.1535
Igneous rock	0.6319	0.1535
Slope	0.1608	0.6376

Concentrations differed significantly between natural and developed catchments for all constituents ($p<0.005$). Metal concentrations at the natural catchments were one to two orders of magnitude lower than concentrations observed in the developed catchments (Fig. 2a). Concentrations of ammonia, TP, nitrate + nitrite, and TSS in the natural catchments were two to three orders magnitude lower than concentrations in the developed catchments (Fig. 2a). Fluxes also differed significantly between the natural and developed catchments for all constituents ($p<0.005$). Differences between the natural and developed catchments were smaller based on flux than based on concentration (Fig. 2a and b). In all cases, the variability observed in dry-weather concentrations from the natural catchments was higher than that observed in developed catchments (Table 4). The CVs of copper, lead, and zinc in the natural catchments were more than two orders of magnitude greater than those in the developed catchments. In contrast, CVs for flux in natural catchments were generally lower than those in developed areas, suggesting that differences in flow are likely an important source of variability in natural areas.

Geology and slope were the main sources of variance in dry-weather water quality data from natural catchments. The stepwise selection in the RDA resulted in these variables significantly increasing overall model fitness (Table 5). The remaining six variables tested did not appreciably increase the fitness of the model and were excluded in subsequent RDAs. Excluding less significant environmental variables increased the percent of variance explained by the model to 45.4% (Table 6), compared to 20.3% for the model that included all nine variables. The predominant source of variability among the data was geology. The first axis of the RDA model explained 66.4% of variance in the data set and was primarily determined by the two geology variables (Tables 7). Among the variables

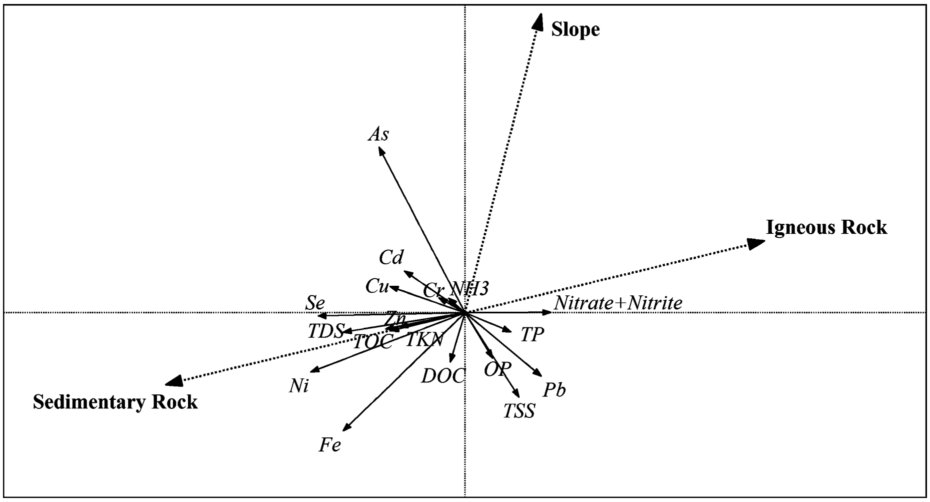

Fig. 3 Correlation biplots showing the relations between dry-weather concentrations of metals, nutrients, and solids (*solid arrows*) and environmental variables (*dotted arrows*). Eigen values: 0.151 and 0.0280 for the first (*horizontal*) and second (*vertical*). Longer arrow indicates which factor is more important in generating variability (Ter Braak and Verdonschot 1995). *TDS* Total dissolved solids, NH_3 ammonia, *TSS* total suspended solids, *TOC* total organic carbon, *DOC* dissolved organic carbon, *TKN* total Kjeldahl nitrogen, *TP* total phosphorus, *OP* orthophosphate

retained in the RDA model, slope contributed least to variation along the first axis and most along the second axis (Table 7). Correlation between water quality and environmental variables are explained in the biplot (Fig. 3). Copper, selenium, zinc, nickel, iron, TDS, TOC, and TKN were positively correlated with sedimentary rock. Nitrate + nitrite was negatively correlated with sedimentary rock and positively so with igneous rock. Other constituents exhibited no strong correlation with any of environmental variables.

Concentrations of several constituents exhibited significant difference between the different geology groups (Table 8). Results of the ANOVA indicate that copper, iron, nickel, selenium, orthophosphate, and total dissolved solids concentrations were significantly higher in natural catchments underlain by sedimentary rock than those underlain by igneous rock (Table 8). Differences ranged from 72% for copper to more than 1,000% for nickel, with the average difference being more than 500%. Other constituents did not exhibit any significant difference between the geologic groups.

4 Discussion

Dry weather runoff from natural catchments contained measurable (background) levels of all constituents typically associated with urban runoff. The background levels varied considerably, with geology being the primary factor affecting dry-weather water quality in natural catchments. This finding is consistent with previous studies, which have also shown that environ-

Table 8 Influence of geology on dry weather water quality

Constituent	Units	Igneous			Sedimentary			*p*
		25%	50%	75%	25%	50%	75%	
TDS	mg/L	123.58	185.00	280.75	406.50	525.00	793.50	0.001
Copper	µg/L	0.30	0.44	0.77	0.63	0.76	0.90	0.007
Iron	µg/L	24.56	50.75	128.38	86.18	113.50	196.75	0.002
Nickel	µg/L	0.12	0.05	0.31	0.40	0.58	0.80	0.001
Selenium	µg/L	0.16	0.26	0.47	0.70	1.06	1.85	0.001
Orthophosphate	µg/L	3.75	3.75	23.50	8.34	22.50	54.50	0.016

Values are the 25%, median (50%), and 75% values of the range of results for each constituent that varied based on geologic setting. Constituents not shown did not differ based on geology mental settings such as geology and land cover affect surface water quality in natural catchments (Johnes et al. 1996; Johnson et al. 1997; Richards et al. 1996). Levels of TDS and other constituents were generally higher in streams draining sedimentary than igneous catchments. This difference can be explained by the higher erodibility of sedimentary rock (as indicated by resistance to weathering), which results in the release of more sediment and associated constituents into the water (Koloski et al. 1989; Williamson 1984). Differences in constituent concentrations based on geologic setting were most pronounced for compounds that are typically associated with particles, such as copper, lead, nickel, and zinc. Less difference was observed for compounds typically found primarily in the dissolved phase, such as arsenic and selenium. Constituent concentrations also varied as a function of catchment slope. This effect can be attributed to an increase in erosion and washoff associated with steeper watersheds (Naslas et al. 1994). Other environmental characteristics, such as latitude, elevation, or catchment size did not affect constituent concentrations or fluxes. Consequently, the results of this study can be extrapolated to provide regional estimates of dry weather background water quality, regardless of watershed position, elevation, or latitude.

Several factors could have influenced estimates of dry-weather natural concentrations and fluxes provided by this study. First, is the treatment of non-detects (NDs). The percent of NDs for a given constituent ranged from 1.8% for total suspended solids to 59.6% for total phosphorus (Table 9). Samples that are ND can be assigned a value ranging from zero to the MDL. In this study, zero was not considered because zero values do not allow calculation of geometric statistics. To be conservative, in this study, we assigned a value of half the MDL to ND samples. Use of the MDL instead of 0.5 MDL for ND samples would have resulted in less than a 2% increase in median concentration for most constituents. The exceptions were ammonia, nitrate + nitrite, orthophosphate, and total suspended solids, which would have increased by 12, 18, 30, and 8%, respectively.

A second factor that could have influenced our estimates is the role of aerial deposition, which we did not correct for. Dry deposition has been shown to be significant source of metals, organics, and nutrients to surface water runoff via both direct deposition to the stream surface and deposition to the watershed, followed by subsequent erosion or washoff (Brun et al. 2004; Davis et al. 2001; Fulkerson et al. 2007; Sabin et al. 2005; Sigua and Tweedale 2003). Concentration and flux data presented here include contributions from both natural loading and atmospheric deposition to the catchment. The contribution of atmospheric deposition is expected to generally be less for dry weather flow than for storm flow. However, this may not be the case for nitrogen deposition over large areas of California, where dry deposition typically exceeds wet deposition due to the arid climate, confined air basin, and prevalence of nitrogen emissions from cars (Bytnerowicz and Fenn 1996). In addition, the contribution of atmospheric deposition could be even higher in late summer, when nitrogen may be scavenged by fog resulting in unusually high aerial NO_3^- and NH_4^+ concentrations (Fenn et al. 2002). Quantification of aerial deposition flux would allow for more precise estimation of natural background water quality concentrations.

Table 9 Percent non-detects (%ND); constituents that are not shown here do not have NDs

	Number of ND	Number of samples	%ND
Arsenic	21	163	12.9
Cadmium	74	165	44.8
Chromium	45	164	27.4
Copper	18	164	11.0
Lead	5	163	3.1
Nickel	92	164	56.1
Selenium	31	165	18.8
Zinc	36	169	21.3
Ammonia	35	165	21.2
DOC	67	115	58.3
Nitrate	4	104	3.8
Nitrite	24	120	20.0
OP	64	119	53.8
TKN	32	108	29.6
TP	62	104	59.6
TDS	21	108	19.4
TSS	2	109	1.8

Dry-weather concentrations of metals, nutrients, and solids from natural catchments in the southern California Coastal region were lower than those from developed catchments. From a mass flux perspective, natural areas also contribute substantially less constituents relative to the proportion of watershed area than developed areas. For example, based on the annual flux estimates from this study and watershed loading data from Stein and Ackerman (2007), the undeveloped portion of the Ballona Creek watershed in southern California would contribute 4% of the total annual dry season copper yield, despite comprising more than 18% of total watershed area. This discrepancy likely results from differences in water source between natural and developed areas. Dry weather flows from undeveloped areas are from residual interflow, rising groundwater, springs, and seeps. This water probably originated as local precipitation, then assimilates additional constituents along its flow path through the ground. In contrast, dry weather flows from developed areas comes from many different sources (Stein and Ackerman 2007). In many southern California streams, treated wastewater (reclaimed water) makes up the bulk of the flow, and is augmented by irrigation overflow, urban runoff, and permitted NPDES discharges. This water likely originated in another basin altogether (e.g., from the northern California Delta or from the Colorado River), and will have a different geochemical composition from ground water derived exclusively from local precipitation. It is also more likely to be influenced by dry deposition, as much of it will contact ground surfaces and flow overland (or in gutters and etc.), and will not be filtered by soil, prior to reaching receiving waters. With some exceptions (e.g., San Diego Creek in Orange County), ground water, either seepage or the small component of local groundwater that augments many southern California water supplies, is unlikely to be a large component of these flows. Thus, their composition can be expected to be quite different from dry weather flows from natural areas.

Dry-weather concentrations in streams draining natural catchments were consistently lower than established water quality management targets. Mean concentrations of metals were below the chronic standards of the California Toxic Rules for inland surface waters (freshwater aquatic life protection standards).

The geometric means of all nutrients were similar, or slightly lower than the proposed USEPA regional nutrient criteria of 0.36, 0.16, 0.52, and 0.03 mg/L for TKN, nitrate + nitrite, TN, and TP, respectively, for Ecoregion III, 6, which includes southern California (USEPA 2000). Although these proposed standards have not been approved, they provide a reasonable basis of comparison to levels of potential environmental concern. One reason for the apparent similarity between the proposed criteria and levels we observed in natural catchments is that the USEPA criteria were developed for the entire year and do not separate dry weather condition from wet weather condition. When comparing geometric means from this study with the proposed USEPA nutrient criteria, it is important to realize that the USEPA criteria are based on the 25th percentile of concentrations from four seasons that include wet and dry weather. Since background levels of nutrients, and other constituents, can vary considerably between dry and wet weather (Stein and Yoon 2007), it will be important to consider natural contributions during storm and non-storm conditions separately in future criteria development and management decisions.

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