ASSESSMENT OF WATER QUALITY CONCENTRATIONS AND LOADS FROM NATURAL LANDSCAPES

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EXECUTIVE SUMMARY

More than 100 waterbodies in southern California have been designated as impaired for their beneficial uses under Section 303(d) of the Clean Water Act for a range of constituents. Despite the number of impaired waterbodies, currently there is no basis for differentiating water quality problems from natural variability. Without knowing the range of natural background levels, it is difficult to discern whether high levels of naturally occurring constituents indicate a pollution problem. Furthermore, lack of information on background concentrations, load, and flux complicates determination of appropriate management targets when remediating impaired waterbodies. To fully evaluate the effect of anthropogenic activities, it is important to describe water quality in streams draining natural environments and to understand the factors that control these "natural loadings". The overall goal of this study is to evaluate the water quality contributions and properties of stream reaches in natural catchments throughout southern California. Specific questions addressed by this study are:

- What are the ranges of concentrations, loads, and fluxes of various metals, nutrients, solids, algae, and bacteria associated with storm and non-stormwater runoff from natural areas?
- How do the ranges of constituent concentrations and loads associated with natural areas compare with those associated with urban (developed) areas and existing water quality standards?
- How do the environmental characteristics of catchments influence constituent concentrations and loads from natural landscapes?

These questions were addressed by measuring surface water quality at 22 natural open-space sites spread across southern California's coastal watersheds (Figure ES-1). Sites were selected to represent a range of conditions and were located across six counties and twelve different watersheds: Arroyo Sequit, Los Angeles River, San Gabriel River, Malibu Creek, San Mateo Creek, San Juan Creek, Santa Ana River, San Luis Rey River, Santa Clara River, Ventura River, and Calleguas Creek watersheds. Data were collected from each of the selected sampling sites during both dry weather and wet weather conditions. Three dry season sampling events were conducted; spring 2005, fall 2005, and spring 2006. A total of 30 storm sampling-events were conducted during two wet seasons between December 2004 and April 2006, with each site being sampled during two to three storms. At each survey location the flow and physical and biological parameters of the site, such as percent canopy cover, were documented. Water samples were collected and analyzed for pH, total dissolved solids (TDS), total suspended solids (TSS), hardness, total and dissolved organic carbon (TOC, DOC), nitrate, nitrite, ammonia, total Kjeldahl nitrogen (TKN), total phosphorus (TP) orthophosphate (OP), total metals (arsenic, cadmium, chromium, copper, iron, lead, mercury, nickel, selenium, and zinc), and bacteria (total coliform, *E. coli*, and *enterococcus*). During dry weather, algal samples were also collected for chlorophyll a and algal percent cover analysis.

Four basic 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. Second, water quality statistics from natural sites were compared with previous data collected by SCCWRP from watercourses draining developed areas of the greater Los Angeles basin to determine if significant differences existed between natural and developed areas (Stein and Tiefenthaler 2005, Stein *et al.* 2007, Ackerman *et al.* 2003). Third, wet and dry weather mean concentrations were compared with relevant water quality standards to evaluate how measured data compares to established management targets. Fourth, concentrations and loads from natural sites were analyzed to determine the factors that most influenced variability among sites.

The results of this study yielded the following conclusions:

- Concentrations and loads in natural areas are typically between one to two orders of magnitude lower than in developed watersheds.
- Wet-weather TSS concentration from natural catchments was similar to that from developed catchments.
- Differences between natural and developed areas are greater in dry weather than in wet weather (Figures ES-2 and ES-3).
- Dry weather loading can be a substantial portion of total annual load in natural areas.
- Peak concentration and load occur later in the storm in natural areas than in developed areas.
- Natural catchments do not appear to exhibit a stormwater first flush phenomenon.
- Concentrations of metals from natural areas were below the California Toxic Rules standards.
- The ratio of particulate to dissolved metals varies over the course of the storm.
- Wet-weather bacteria concentrations for *E. coli*, *enterococcus*, and total coliform exceeded freshwater standards in 40 to 50% of the samples.
- Concentrations of several nutrients were higher than the proposed USEPA nutrient guidelines for Ecoregion III, 6.
- Catchment geology was the most influential factor on variability in water quality from natural areas.
- Catchments underlain by sedimentary rock generally produce higher constituent concentrations than those underlain by igneous rock.
- Other environmental factors such as catchment size, flow-related factors, rainfall, slope, and canopy cover as well as land cover did not significantly affect the variability of water quality in natural areas.
- This study produced regionally applicable flux estimates for natural catchments encompassing storm and non-storm conditions (Table ES-1).

The flux estimates generated from this study should be applicable for estimates of the contribution of natural areas to overall watershed load throughout the southern California region. Because the sampling sites are representative of the major geologic and natural land cover settings of the region, they can be used to estimate regional or watershed specific loading from natural areas. The concentration provided by this study can also be used to help calibrate watershed models that account for rainfall runoff rates and antecedent dry conditions. Such models can be used to simulate water quality loading under a range of antecedent and rainfall conditions, thereby providing managers with additional tools for evaluation of background water quality conditions.

Table ES-1. Estimated total annual fluxes of metals (kg/year km^2), nutrients (kg/year km^2), and solids (mt/year km^2) in natural catchments. No data available (-).

Annual Flux (kg/year km^2)									
	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Zinc
Arroyo Seco	0.31	0.06	0.58	0.36	189.50	0.19	0.20	0.13	1.11
Piru Creek	0.22	0.01	0.54	0.39	474.10	0.11	0.38	0.09	0.96
Sespe Creek	0.06	0.03	0.43	0.44	573.30	0.12	0.46	0.14	1.14
Santiago Creek [a]	0.16	0.05	0.13	0.21	65.70	0.05	0.22	0.54	0.67
Tenaja Creek [a]	0.03	0.01	0.07	0.05	77.10	0.03	0.03	0.02	0.29

Annual Flux (kg/year km^2)								
	Ammonia	Total Nitrogen	Dissolved Organic Carbon	Total Organic Carbon	Ortho-phosphate	Total Phosphorus	Total Dissolved Solids	Total Suspended Solids
Arroyo Seco	3	230	860	890	8	5	63	9
Piru Creek	3	190	620	1320	6	-	-	315
Sespe Creek	8	290	650	950	7	-	87	4059
Santiago Creek [a]	7	450	1710	1770	11	28	193	5
Tenaja Creek [a]	1	40	200	180	2	6	12	4

[a] Total fluxes are only for the eight months of the study from December 2005 through August 2006 during which the stream was flowing. No stream flow was present after August 2006 until the start of the next storm season.

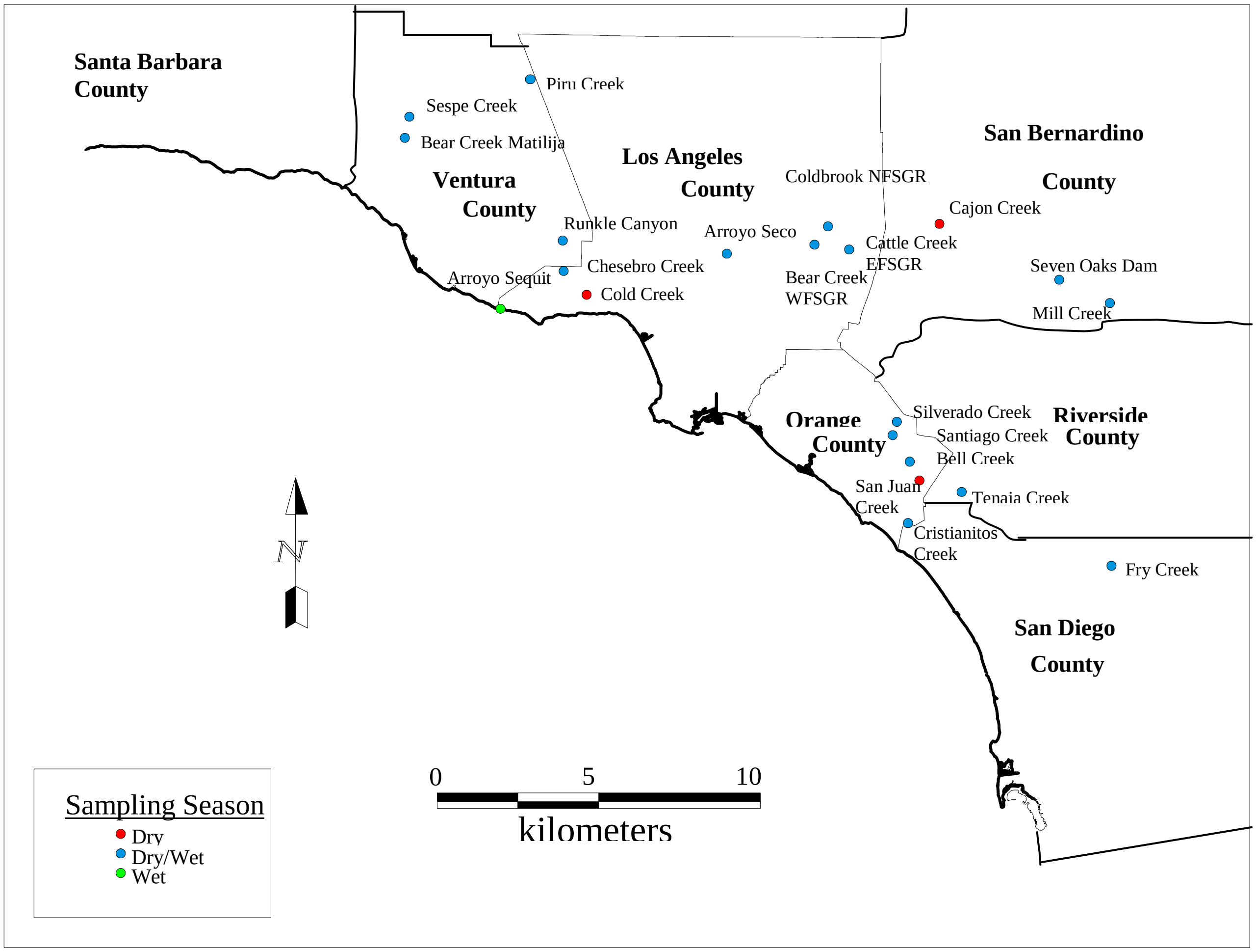

Figure ES-1. Study sites: red dots indicate sites sampled during dry weather only; blue dots indicate sites sampled in both dry and wet weather; and green dots indicate sites sampled during wet weather only.

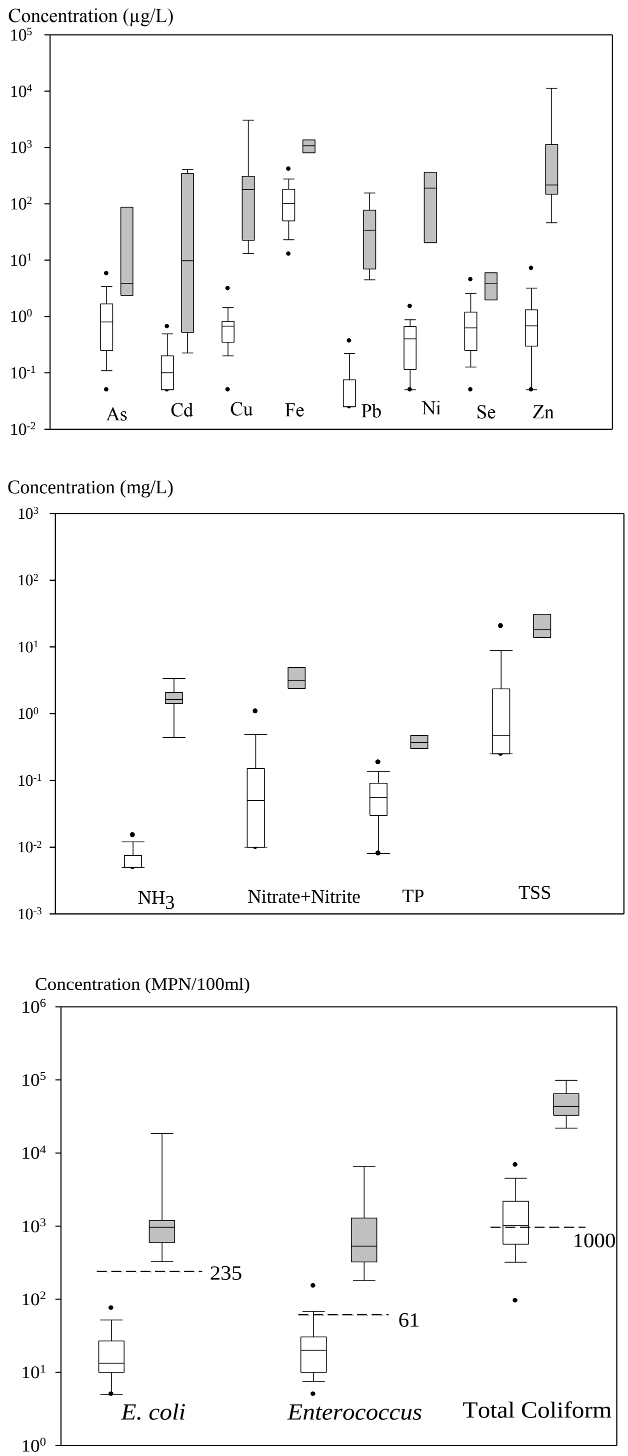

Figure ES-2. Comparison of dry weather concentrations of metals, nutrients, TSS, and bacteria between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. Solid lines within boxes indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots indicate 5th and 95th percentiles. The Y axis is in log scale. Dotted lines indicate Department of Health and Safety draft guidelines for freshwater recreation.

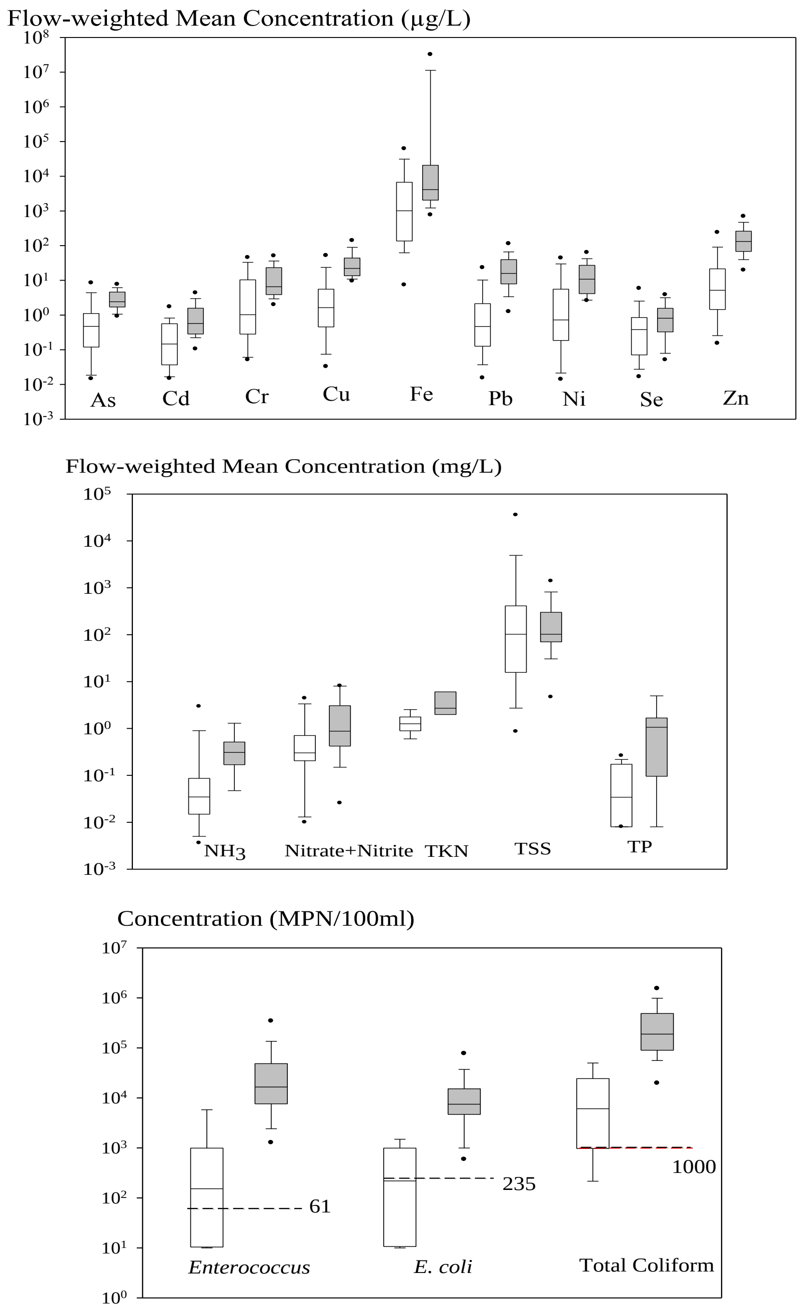

Figure ES-3. Comparison of wet weather concentrations of metals, nutrients, TSS, and bacteria between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. Solid lines within boxes indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots indicate 5th and 95th percentiles. The Y axis is in log scale. Dotted lines indicate Department of Health and Safety draft guidelines for freshwater recreation.

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INTRODUCTION

Background

More than 100 stream reaches in southern California's coastal watersheds are currently designated as impaired for water quality with respect to their designated beneficial uses. Consequently, they have been added to the US Environmental Protection Agency (USEPA) 303(d) list for a range of constituents including nutrients, algae, bacteria, and metals. In the Los Angeles Region of the Water Quality Control Board (LARWQCB) alone, Section 303(d) listings will result in the development of more than a dozen Total Maximum Daily Loads (TMDLs) in the Los Angeles, San Gabriel, Malibu, Ballona, and Santa Clara watersheds over the next several years. For most of the designated reaches, TMDLs will be developed and National Pollutant Discharge Elimination System (NPDES) permits will be issued that contain requirements intended to ensure that water quality standards are met and beneficial uses are protected. One of the important steps in TMDL development is to identify all sources of the constituent(s) of concern in order to accurately quantify loads and set appropriate standards and allocations.

One of the challenges in developing TMDLs and estimating loads from coastal watersheds is accounting for the natural contribution from undeveloped catchments. This natural contribution can be affected by natural land cover and the underlying geology in a watershed can directly affect constituent concentrations. Trace metals, which are a source of impairment in many watersheds, occur naturally in the environment (Turekian and Wedepohl 1961, Trefry and Metz 1985, Horowitz and Elrick 1987). In southern California, the metavolcanics that make up the transverse ranges are known to leach certain metals as they weather. This was documented by Schiff and Tiefenthaler (2000), who used an iron normalizing technique to assess the magnitude of anthropogenic enrichment of trace metals in suspended sediments of stormwater runoff in the Santa Ana Watershed and found that nearly all of the nickel and chromium emissions – and approximately two-thirds of the copper, lead, and zinc emission -- were of natural origin. Land cover/vegetation type can also affect total loadings in a watershed. Studies have also shown that land cover type may significantly impact water quality (Detenbeck *et al.* 1996, Johnes *et al.* 1996, Johnson *et al.* 1997, Gergel *et al.* 1999, Richards *et al.* 1996, Larsen *et al.* 1988). For example, grasslands (both native and non-native) have been shown to contribute relatively high loadings of nitrogen following rainfall events (Johnes et. al 1996). These loadings contribute to total nitrate and nitrite concentrations and may play a role in algal levels in streams and estuaries. Large portions of the total mass of metals in water are associated with sediments, including clay/silt particles and particulate organic carbon, which are influenced by land cover (Johnson *et al.* 1997, Gergel *et al.* 1999, Richards *et al.* 1996). Bacteria levels in water are also affected by other natural and anthropogenic conditions. Wildlife, including birds and mammals, may be sources of bacteria to natural streams. Grant *et al.* (2001) studied enterococci bacteria in a costal saltwater marsh and found that bacteria generated in the marsh had greater effect on coastal water quality than dry season urban runoff. The presumed sources of these bacteria were birds that used the tidal salt marsh as habitat. Ahn *et al.* (2005) also investigated sources of bacteria in urban stormwater in southern California and concluded that natural sources could be significant contributors to total bacteria levels. However, no studies have been found that attempt to quantify background (or reference) levels of bacteria, and little to no information is available on this issue.

To compensate for the lack of adequate information on natural sources of metals, nutrients, and bacteria, many TMDLs are written with load allocations based on data from other parts of the country or, worse yet, anecdotal data from previous time periods. As a result, these TMDLs may be developed with inefficient or overly stringent load allocations in order to meet numeric targets. The need for information on loading from undeveloped areas is amplified by the desire for many managers to use background concentrations or conditions as part of the numeric target for their TMDL. For example, the TMDL for bacteria for Santa Monica Bay beaches used a watershed that was comprised of entirely open land use as a benchmark for success. Urbanized watersheds were required to generate no more bacterial exceedence days than the open, benchmark watershed. Unfortunately, little is known about the bacterial dynamics or wet and dry weather contributions from the open land uses, making the efficacy of this requirement difficult to assess.

Goals of the study

The overall goal of this project is to evaluate the contributions and properties of stream reaches in undeveloped catchments throughout southern California in order to assist environmental managers establish load allocations and appropriate numeric targets. Specific questions that will be addressed are:

- What are the ranges of concentrations, loads and flux rates of various trace metals, nutrients, and solids associated with storm and non-stormwater runoff from natural areas?
- How do the ranges of constituent concentrations and loads associated with natural areas compare with those associated with urban (developed) areas and existing water quality standards?
- How do environmental characteristics of catchments influence constituent concentrations and loads from natural landscape?

This project begins to fill the existing gap in the understanding of loadings to streams from natural landscapes by characterizing the natural condition of flow, suspended solids, organic carbon, nutrients, metals, and bacteria, and relate these to watershed properties such as geology, soils, and vegetative cover. The results of this project provide valuable information for development of water quality standards, TMDL allocations, and regional nutrient criteria. Furthermore, this project will produce tools that managers and decision makers can use to better predict the impact of future land use on water quality and more accurately evaluate the effectiveness of management strategies.

STUDY DESIGN

The overall goal of this study was to characterize wet and dry weather water quality at a set of sites that is representative of existing natural conditions in southern California. This goal was accomplished in four phases. First, existing data was compiled and organized. Second, southern California watersheds were characterized in terms of geology and land cover and selected appropriate sites that represent the range of natural conditions found throughout the region. Third, both dry and wet weather sampling was conducted. Fourth, assessment tools including estimates of dry and wet weather ambient concentrations, flux rates, and expectations of beneficial use conditions were developed. The main phases of the study design are summarized below.

Compilation of existing data sources

The goal of Phase 1 was to compile and summarize existing data from natural sites to help inform the sampling design for subsequent phases of the project. The study's *a priori* hypothesis, based on existing literature, was that geology and land cover would be key features influencing variation in water quality from natural areas. In order to test this hypothesis, preliminary analysis of the existing data on water quality in natural areas of southern California was conducted using data from USEPA's Environmental Monitoring and Assessment Program (EMAP) and the State of California's Surface Water Ambient Monitoring Program (SWAMP). These data were used to investigate the effect of geology and land cover on natural loadings of selenium and zinc. The analysis of variance (ANOVA) showed the levels of selenium were significantly different in different land cover groups. The levels of selenium were also significantly different in different geology types. These results suggested that geology and land cover might influence the levels of several nutrients and metals in surface water. It also demonstrated that the effects of geology and land cover on surface water quality were appropriate factors for further investigation. The detailed results of the preliminary investigation are included in Appendix I. It is important to note that the existing data were too limited to adequately quantify regional background concentrations or to discern other factors that may influence these concentrations. However, they were useful in guiding development of the study design for this project.

Watershed characterization

The goal of Phase 2 was to characterize southern California watersheds in terms of their general features, geology, and land cover. Southern California's coastal watersheds occur in a variety of geologic and topographic settings, have a variety of soil types, and contain a variety of natural vegetation communities. These factors are known to influence natural loadings (Lakin and Byers 1941, Dunne and Leopold 1978, Ohlendorf *et al.* 1986, Larsen 1988, Ohlendorf *et al.* 1988, Ledin *et al.* 1989, Tracy *et al.* 1990, Tidball *et al.* 1991, Detenbeck *et al.* 1993, Presser *et al.* 1994, Hounslow 1995, Johnes *et al.* 1996, Richards *et al.* 1996, Johnson *et al.* 1997b, Gergel *et al.* 1999, Hibbs and Lee 2000). In addition, wildlife, including birds and mammals, may be sources of bacteria to natural streams. This phase characterized the major watersheds in terms of their physical and biological characteristics. The watershed and site characterizations were catalogued in GIS for use in later portions of the project to facilitate information transfer to other efforts that may use this data. Geologic and land cover type for the coastal watersheds in southern California were determined by plotting watershed boundaries over digitalized geology (California Division of Mines and Geology,1962) and land cover maps (National Oceanographic Administration (NOAA) Coastal Change Analysis Program (CCAP) 1999). The results of the analysis for this phase are provided in Appendix II.

Selection of sampling sites

The goal of Phase 3 was to select sampling sites that would represent the range of natural conditions throughout southern California. Using the watershed characterization and the list of data gaps produced under Phases 1 and 2, a series of potential sampling sites (i.e., stream reaches) were selected. Sites were selected that covered the range of factors that were assumed to affect variability in loadings from natural systems.

General framework for site selection

Review of existing data suggested that surficial geology and dominant land cover likely influenced water quality loading from minimally developed catchments. Consequently, this study's sampling design involved stratified sampling based on these two independent variables. The overall sampling framework for the project is shown in Table 1.

Geologic forms consist of a certain lithologic type or combination of types, including igneous, sedimentary, or metamorphic, which may be consolidated or divided into different classes (American Geological Institute 1984). Land cover types consist of forest, shrub, and grassland, which may also be consolidated and divided into different classes (National Oceanographic and Atmospheric Administration 2003). Due to resource constraints, priority was given to sites in areas representing the largest proportion of natural areas in the study region: sedimentary rocks-shrub group, igneous rocks-shrub group, sedimentary rocks-forest group, and igneous rocks-shrub group. This prioritization of geology/land use combinations encompassed the majority of natural area in the coastal watersheds of southern California.

Criteria for site selection

A series of criteria was developed to provide objective guidelines to classify catchments in various conditions and select appropriate natural sites for inclusion in the study. These criteria were established through literature survey and meetings with the project's technical advisory committee and stakeholders, after consulting various agencies involved in water quality management. The result was a consensus list of criteria that would ensure that sampling would capture natural conditions without influence from any land-based anthropogenic input[1] and be representative of the range of natural conditions that exist in southern California.

- Catchments draining to the sites should be natural and as close to pristine condition as possible. Contributing drainage area should be at least 95% undeveloped.
- Field reconnaissance should reveal no evidence of anthropogenic effects such as septic tanks, isolated residence, excessive wildlife or human use, or evidence of excessive channel erosion.
- Sites should be regionally distributed across southern California. To meet this criterion, sampling sites should be distributed across the six major southern California counties and include as many of the major watersheds draining to the Southern California Bight as possible.
- Sites should be representative of major geologic settings/land cover types and be relatively homogenous. For this study, sites screened with these general criteria were grouped in terms of representative geology and land cover for southern California (Table 1). The goal was to select a minimum of four to five sites representing each of the priority treatments in the sampling framework (i.e., locations with an "A" prioritization in Table 1).

[1] Aerial deposition of anthropogenic emissions may affect the surface water quality at the selected sampling sites. Due to the regional nature of this source, no attempt was made to exclude or control for effects of dry or wet aerial deposition.

- Sites should have either year-round or prolonged dry weather flow that allows sampling during both storm and non-storm conditions. A stream with prolonged dry weather flow can be defined as one that still flows one to two months after the end of the last storm, even if it dries up later in the season.
- Sites should be targeted toward 3rd -order watersheds in which streams have large enough catchments to reliably generate flow during both storm and non-storm conditions. This position in the watershed also allows selection of sites for which catchments are small enough to have homogenous contributing drainage areas. Sites at this position in the watershed are representative of the watershed position of many of the less pristine waterbodies to which data from this study will be compared.
- Sites should not be within catchments that have burned during the previous three years. According to a study on the impact of wildfire in the Santa Monica Mountains (Gamradt and Kats 1997), erosion following the 1993 wildfire produced major changes in stream morphology and composition. These fire-induced landslides and siltation eliminated pools and runs, and altered habitats. Thus, streams that were impacted by wildfires were excluded from this study[2].
- The stream reach being sampled should be ratable for flow to allow computation of mass loadings of water quality constituents.
- Sites should be located in an area where sampling can be conducted safely.
- Field crews should be able to access the sampling location after hours and on weekends.
- Property owners and other responsible parties must provide permission for site access and sampling.

Selected sampling sites

Candidate sites were selected based on a review of existing data from the SWAMP, EMAP, United States Geological Services (USGS) Hydrologic Benchmark Network, USGS National Water Quality Assessment, Heal The Bay, Malibu Creek Watershed Monitoring Program, Santa Barbara Coastal Long Term Ecological Research Project (SBC-LTER), and conversations with US Forest Service Resource staff officers, Counties of Ventura, Los Angeles, Orange, San Bernardino, San Diego, various stormwater agencies and the technical advisory committee for this project.

Forty-five candidate sites were identified using the criteria describe above. Following detailed office and field investigation, a total of 22 sites were selected for inclusion in the study. The sites were are located across six counties and twelve different watersheds: Arroyo Sequit, Los Angeles River, San Gabriel River, Malibu Creek, San Mateo Creek, San Juan Creek, Santa Ana River, San Luis Rey River, Santa Clara River, Ventura River, and Calleguas Creek, as shown in Figure 1 and listed in Table 2. Detailed information on each site is provided in Appendix III.

Dry and wet weather sampling

The goal of Phase 4 was to collect samples at selected sampling sites over the course of two years during both dry weather and wet weather conditions. These data were used to estimate the dry and wet weather metal concentrations, flux rates, and loads associated with natural areas.

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[2] Wildfires occur regularly in southern California and are natural elements of native habitats. In this study, however, the impact of wildfire was not investigated and only natural sites with no history of wildfire over the past 3 years were included in order to limit the number of variables that affected water quality.

Site characterization

Each catchment was characterized for its environmental settings: 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. Geologic and land cover type for the coastal watersheds in southern California were determined by plotting catchment boundaries over a digitized geology map (Strand 1962, Rogers 1965, 1967, Jennings and Strand 1969) and land cover map (NOAA CCAP 2003). The rest of catchment characteristics were assessed using ArcView GIS 3.2a (ESRI, Redlands, CA). Percent canopy cover was defined as a percent vegetation cover over the study reach based on field measurements using a spherical forest densitometer (Wildco, Buffalo, NY).

Dry weather sampling

Three dry weather sampling events were conducted: spring 2005, fall 2005, and spring 2006 (Table 3). Dry weather 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 minutes after completion of the initial water sampling. 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 dissolved oxygen (DO) were measured in the field using Orion 125 and Orion 810 field probes (Thermo Electron Corporation, Waltham, MA). Canopy cover was assessed using a spherical densitometer (Wildco, Buffalo, NY). 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 flow meter measured velocity using the Faraday law of electromagnetic induction. The velocity was measured at three points along each transect, and the values from three transects were integrated to estimate overall flow at each site. To estimate biomass of algae, percent cover of algae was assessed visually at each site using the defined algal protocol (Appendix IV) as modified from the EPA Rapid Bioassessment Protocol (Barbour *et al.* 1999). Percent algal cover was estimated separately for benthic algae, algae attached to rocks or vascular plants, and free floating algae. Algae were sampled for chlorophyll-a analysis along each transect with a periphyton sampler modeled on the sampler described by Davies & Gee (1993). Algal samples were immediately frozen on dry ice for subsequent analyses. Details of the method of algal sampling and percent cover assessment are described in Appendix IV.

Wet weather sampling

A total of 30 site-events were sampled during two wet seasons between December 2004 and April 2006, with each site being sampled during two to three storms (Table 4). A site was considered eligible for sampling if it had not received measurable rainfall for three consecutive days and flow was no more than 20% above baseflow. When rain was forecast, field crews were deployed and sampling was initiated when flows exceeded base flow by approximately 10 to 20%. Streams were sampled manually when safety and access restrictions permitted. In other cases, an automatic sampling method was used.

Stream discharge and rainfall were measured during each sampling event. Rainfall was measured using a standard tipping bucket that recorded in 0.025 cm increments. 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 prior to the onset of rain. Velocity was measured using an acoustic Doppler velocity (AV) meter. The AV meter was mounted to the invert of the stream channel, and velocity, stage, and instantaneous flow data were transmitted to a data logger/controller upon query commands found in the data logger software.

Manual sampling (pollutograph)

Manual sampling was used at streams where safety and access concerns permitted. Between 10 and 12 discrete grab samples were collected per storm at approximately 30 to 60 minutes intervals for each site-event, based on optimal sampling frequencies in southern California described by Leecaster *et al.* (2002). Samples were collected more frequently when flow rates were high or rapidly changing, and less frequently during lower flow periods. Samples were collected using peristaltic pumps with Teflon® tubing and stainless steel intakes fixed at the bottom of the channel pointed in the upstream direction in areas of undisturbed flow. After collection, the samples were stored in pre-cleaned glass bottles on ice with Teflon-lined caps until they were shipped to the laboratory for analysis. Streams were sampled until flow measurements indicated that flow had subsided to at least 50% of the peak flow. For prolonged events, water quality sampling was terminated after 24 hours. Even after the end of sampling periods, flow measurements often continued to reflect the prolonged descending tail of the hydrograph for several days.

Automatic sampling

When site accessibility and/or safety prohibited manual sampling, automatic samplers were used. Samplers were installed ahead of the storm 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. Intervals were determined based on expected duration of storm. If a storm was expected to last for several days, longer intervals were set. If a storm was expected to last for a short period of time, shorter intervals were set. In most cases, the four sample bottles were analyzed individually. In some cases two bottles were composited if analysis of the storm hydrograph revealed that they captured similar portions of the storm event. All sample tubing was triple purged with ambient and de-ionized water between samples. After collection, the samples were stored in pre-cleaned glass bottles on ice with Teflon®-lined caps until they were shipped to the laboratory for analysis.

Laboratory analysis

Water samples were analyzed for pH, hardness, conductivity, total recoverable metals, nutrients, DOC/TOC, TDS/TSS, and bacteria and algal samples were analyzed for chlorophyll a following protocols approved by the USEPA (1983) and standard methods approved by the American Public Health Association (Greenberg *et al.* 2000). Metals were prepared by digestion, followed by analysis using inductively coupled plasma-mass spectrometry (ICP-MS) to obtain total recoverable concentrations of arsenic, cadmium, copper, chromium, iron, lead, nickel, selenium, and zinc. In addition, samples of winter 2006 were analyzed for both dissolved and particulate concentrations for each metal. Total dissolved solids (TDS) were analyzed using a flow injection analyzer (Lachat Instruments model Quik Chem 8000). Total suspended solids (TSS) were analyzed by filtering a 10- to 100-ml aliquot of stormwater through a tarred 1.2 mm (micron) Whatman GF/C filter. The filters plus solids were dried at 60°C for 24 hours, cooled, and weighed. Nitrate and nitrite were analyzed using cadmium reduction method and ammonia was analyzed using distillation and automated phenate. Total Kjeldahl nitrogen (TKN) was analyzed using digesting/distilling and semi-automated digester. Total organic carbon (TOC) and dissolved organic carbon (DOC) were determined via high temperature catalytic combustion using a Shimadzu 5000 TOC Analyzer. Orthophosphate was analyzed using a titration method. Total phosphorus was persulfate-digested. Every analysis included QA/QC checkup with certified reference materials, duplicate analyses, matrix spike/ matrix spike duplicates, calibration standards traceable to the National Institute of Standards, and method blanks. Table 5 shows the list of analytes, along with minimum detection limits (MDLs) and applicable units for each analyte.

Data analysis

Dry weather

Three analyses were used to characterize dry weather water quality from natural areas. 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 as the product of flow and concentration for each sample (Equation 1):

$$\text{Load} = \sum F_i \cdot C_i \qquad (1)$$

where F_i was the mean flow at sampling site i, and C_i was the concentration at site i for individual constituents.

A mass loading was expressed as load/day instead of an event based load. Flux was calculated as the ratio of the mass loading per contributing catchment area. All data were analyzed to determine if they were normally distributed. For constituents that were not normally distributed, results were recorded as geometric means and upper and lower ends of 95% confidence intervals[3]. If the data were normally distributed, results were recorded as arithmetic means ± the 95% confidence interval.

Second, factors that impact variability in water quality of natural catchments were investigated. To explain variability in water quality among the natural catchments, relationships between environmental characteristics of the catchments and water quality constituent concentrations and fluxes were investigated using multivariate analyses. In this study, an ordination method, redundancy analysis (RDA) was used. 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); and a matrix of predictor variables (e.g., environmental variables, explanatory variables, or independent variables) is used to quantify variation in a matrix of response variables (e.g., water quality variables, response variables, or dependent variables). For this study, RDAs were performed using the program CANOCO 4.54 (ter Braak and Smilauer 1997). Water quality variables used in the RDA were concentrations of all constituents. Environmental variables were geologic types (igneous rock vs. sedimentary rock), land cover types (forest vs. shrub), latitude of site, catchment area (km^2), elevation of site (km), slope of catchment, mean flow (m^3/sec), and percent canopy cover. Dummy values were assigned for the categorical variables; such as geology and land cover types. For example, a sampling site within a catchment dominated by igneous rock was assigned the value of one for igneous rock and a value of zero for sedimentary rock.

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 constituents when adding a variable to the regression model. The variable with the largest extra fit was

[3] The confidence interval represents values for the population parameter for which the difference between the parameter and the observed estimate is not statistically significant at the 5% level.

then included, and the process was repeated until no variables remained that could significantly improve the fit of the model. 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 biplots that represent optimally the joint effect of the environmental variables on water quality variables in a single plane (ter Braak 1990). In addition, the entire water quality data set was grouped based on the most influential environmental variables. Subsequent analyses, such as analysis of variance, ANOVA (Sokal and Rohlf 1995), were carried out to examine the significance of differences among the groups with a significance level of $p < 0.05$.

Lastly, concentrations and fluxes in natural catchments were compared with data previously collected from developed catchments to determine if significant differences existed between the two groups. Data for developed catchments were obtained from Southern California Coastal Water Research Project (SCCWRP) 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, California (Ackerman and Schiff 2003, Stein and Tiefenthaler 2005, Stein and Ackerman 2007). The data from the SCCWRP dry weather studies were collected at the developed sites and processed in the same manner as the data from the natural sites. More information on selected developed sites is provided in Appendix V. Differences between natural and developed catchments were investigated by comparing median values using ANOVA, (Sokal and Rohlf 1995) with a significance of $p < 0.05$. Eight metals (arsenic, cadmium, copper, iron, lead, nickel, selenium, and zinc), three nutrients (ammonia, nitrate+nitrite, and total phosphorus), , three bacterial indicators, and TSS were examined. Mean concentration and flux data were log-transformed and compared. If data failed in normality test, a one-way ANOVA on ranks (Kruskall 1952, Kruskall and Wallis 1952) was performed to examine differences between the groups. The Kruskal-Wallis test is most commonly used when one attribute variable and one measurement variable exist, and the measurement variable does not meet the assumptions of an ANOVA: normality and homoscedasticity. It is the non-parametric analogue of a single-classification ANOVA. To determine how variability observed in natural catchments related to variability observed in developed catchments, the respective coefficient of variation (%CV) [4] for the two data sets was 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. In all cases non-detects were assigned values of ½ minimum detection limits.

Wet weather

Three analyses were used to characterize wet-weather 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 (FWM) concentrations, mass loadings, and flux rates were calculated for each site. Using only those samples for a single storm, the event FWM was calculated according to Equation 2:

[4] % CV = 100 x (standard deviation/mean)

$$FWM = \frac{\sum_{i=1}^{n} C_i \bullet F_i}{\sum_{i=1}^{n} F_i} \qquad (2)$$

where: *FWM* was the flow-weighted mean for a particular storm; *Ci* was the individual runoff sample concentration of i^{th} sample; *Fi* was the instantaneous flow at the time of i^{th} sample; and n was the number of samples per event.

Event mass loadings were calculated as the product of the FWM 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 analyzed to determine if they were normally distributed. For those constituents that were not normally distributed, results were recorded as geometric means and upper/lower 95% confidence intervals. If the data were normally distributed, results were recorded as arithmetic means ± the 95% confidence interval.

Second, factors that impact variability in water quality from the natural catchments were investigated. To explain variability in water quality among different natural catchments, relationships between environmental characteristics of the catchments and concentrations were investigated using multivariate analyses. Variability within a storm event was also examined in terms of first flush. Variability of constituent levels within a storm event and between seasons was examined. First, flows and concentrations within storm events were evaluated by examining the time-concentration series relative to the hydrograph using a pollutograph. A first flush in concentration from individual storm events, defined as a peak in concentration preceding the peak in flow, is often observed in small urban watersheds (Characklis and Wiesner 1997, Sansalone and Buchberger 1997, Buffleben *et al.* 2002, Stein *et al.* 2006). This observation was quantified using cumulative discharge plots for which 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 ≥75% of the mass being discharged in the first 25% of runoff volume. A moderate first flush was defined as ≥30% and ≤75% of the mass being 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. Second, changes in proportions of metals between particulate phase and dissolved phase over the course of storm were examined and compared with concentrations of TSS, TDS, and flow. The Pearson correlation analysis was conducted to test correlation of the ratios with flow. Lastly, ANOVA was conducted in order to test if constituent concentrations differed significantly among different seasons. The %CV for each constituent was compared among different seasons in order to estimate the degree of seasonal variability.

Relationships between catchment characteristics and constituent concentration were investigated using RDA. Water quality variables used in the RDA were flow-weighted concentrations (FWMC) of all measured water quality constituents. Environmental variables used were geologic setting (igneous vs. sedimentary), land cover type (forest vs. shrub), latitude, catchment area (km^2), elevation of sampling location (km), 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 (%). The RDA and subsequent analyses, such as ANOVA, were conducted in a similar manner to those of the dry weather data.

Concentrations and loads in natural catchments were compared with data previously collected from developed catchments to determine if significant differences existed between natural and developed areas. Stormwater data from developed catchments in the greater Los Angeles area were obtained from a previous SCCWRP study (Stein *et al.* 2007) and the Ventura County Watershed Protection District. The developed catchments included Los Angeles River, San Jose Creek, Ballona Creek, Coyote Creek, Walnut Creek, San Gabriel River, Pueblo Creek, and Calleguas Creek. Details of selected developed sites are provided in Appendix IV. Differences between natural and developed catchments were investigated using a one-way ANOVA (Sokal and Rohlf 1995) with a significance level of $p < 0.05$. Means for flow-weighted concentration and flux per each sampling event were estimated. Flow-weighted mean concentration and flux data were log-transformed prior to comparison. If data failed in the equal variance test, a Kruskal-Wallis ANOVA on ranks was performed to examine difference between the groups. To determine how the variability observed in natural catchments related to that observed in developed catchments, respective %CV of the two data sets were compared.

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.

Estimation of annual loadings from natural landscapes

Annual loadings of metals, nutrients, and solids from natural streams in southern California were estimated, and storm-originated load and non-storm-originated load estimates were compared. Year-round flow data that were necessary to estimate annual loads were not available at all natural sites. Thus, 5 out of 22 natural sites were selected to represent the diversity in the catchment size, geologic setting, land cover type, and flow conditions in southern California (Figure 19). The study sites included three perennial streams (Arroyo Seco, Sespe Creek, and Piru Creek) and two intermittent streams (Santiago Creek and Tenaja Creek) with catchment sizes ranging from 17 to 318 km^2, respectively (Table 6). The USGS daily flow data were available for the perennial sites. For the intermittent sites, water pressure sensors to monitor flow were installed.

Flow data from USGS gauging stations

For the three gauged systems, daily average flows for the 1994-2004 water years were downloaded from the USGS website (http://waterdata.usgs.gov/ca/nwis/sw). This ten-year period contains dry, wet, and moderate years, and is, therefore, representative of the expected range of rainfall conditions. Flow data was unavailable for the 2004 water year for Piru Creek and the 1998 and 2001 water years for Sespe Creek. Flow data for the 2005 and 2006 water years were not available due to incomplete data quality check by USGS.

Flow monitoring using water level loggers

At the two ungauged intermittent streams, pressure transducers to measure water surface elevation (i.e., water level) were installed. Water level was monitored every 15 minutes during the 8-month study period from December 2005 through July 2006 using Hobo® model U20-001-01 water level logger (Onset Computer, Bourne, MA). Two water level loggers were deployed at each site. One was installed above the water level to measure atmospheric pressure and the other was installed under water level to measure combined pressure of atmospheric and water pressures. The water pressure was computed by subtracting the atmospheric pressure from the combined pressure. Water level was estimated based on the temperature that was logged with the pressure. Water level data were converted to flow data using flow-rating curves that were obtained from previous sampling events conducted during the dry and wet seasons of 2004 through 2006. Separate rating curves for dry and wet weather flows were obtained. A rating curve with the highest correlation coefficient among possible linear or non-linear regressions was selected to convert a water level into flow for each site.

Storm flow *separation from non-*storm flow

Storm flow was separated from non-storm flow based on rainfall data for the sites monitored with the Hobo water level loggers. For the USGS gauged sites long-term rainfall data were not available, thus, storm flow was separated from non-storms flow using the following steps: First, ΔX_i, the difference of flow between two data points was computed according to Equation 3:

$$X_i - X_{i-1} = \Delta X_i \qquad (3)$$

where X_i was flow at time *i*.

Second, the beginning of each storm event was defined for a time when ΔX_i changed from zero or a negative value to a positive value with ΔX_i that is more than 60% of X_i. The 60% criterion was set to exclude the increase of flow due to the natural fluctuation of base flow (Hatje *et al*. 2001). Third, a peak flow point was identified as a time just before ΔX_i turned negative. Next, the end of each storm event was defined as T_i after the peak flow occurred, when the ΔX_i was negative and the flow reduced to 50% of peak flow. If ΔX_i became zero or positive before it dropped to the 50% of peak flow, a time of the last negative ΔX_i was assigned as the end of the storm event. Storm flows and non-storm flows were summed separately for each water year.

Estimation of loads and fluxes

Annual load for each water quality constituent was estimated according to Equation 4:

$$W = \sum_j Cm \bullet \mathrm{Qj} \bullet K \qquad (4)$$

where *W* was the load (mt or kg); *Cm* was the FWM for storm flow or mean concentration for non-storm flow (mg/L or µg/L); Q_j was the total discharge volume of flow ($Q_{\text{storm flow}}$ = mean daily storm flow days with storm flow/year; $Q_{non\text{-storm flow}}$ was the mean daily non-storm flow days with non-storm flow/year); and *K* was the unit conversion factor of 10^6.

Loadings were calculated separately for storm vs. non-storm discharge volume. Loading estimates were based on the product of the mean concentration determined by this study and mean volume over the period of record. Implicit in this approach is the assumption that the concentration values determined during the two years of this study are representative of typical concentrations in natural areas. The total annual load for each water year was obtained by summing the storm load and non-storm load. In order to account for differences in catchment size, an annual flux for each site was computed as load divided by the size of drainage area.

Table 1. Sampling framework. **Highest priority (A) and Lowest priority (C).**

Land Cover	**Dominant Geology**		
	Sedimentary Rocks	Metamorphic Rocks	Igneous Rocks
Forest	A	C	A
Shrub	A	C	A
Grassland	B	C	B

Table 2. Study site locations, characteristics, and sampling conditions.

Site Name	Watershed	Sampling Conditions	Geology	Land Cover	Latitude	Longitude
Arroyo Seco	LA River	Dry/Wet	Igneous	Forest	34.2124	-118.1780
Bear Creek WFSGR	San Gabriel	Dry/Wet	Igneous	Forest	34.2408	-117.8840
Cattle Creek EFSGR	San Gabriel	Dry/Wet	Igneous	Shrub	34.2283	-117.7670
Coldbrook NFSGR	San Gabriel	Dry/Wet	Igneous	Forest	34.2922	-117.8390
Chesebro Creek	Malibu Creek	Dry/Wet	Sedimentary	Forest	34.1557	-118.7260
Cold Creek	Malibu Creek	Dry	Sedimentary	Shrub	34.0902	-118.6470
Cristianitos Creek	San Mateo	Dry/Wet	Sedimentary	Shrub	33.4621	-117.5610
San Juan Creek	San Juan	Dry	Sedimentary	Shrub	33.5819	-117.5240
Santiago Creek	Santa Ana	Dry/Wet	Sedimentary	Shrub	33.7086	-117.6150
Bell Creek	San Juan	Dry/Wet	Sedimentary	Shrub	33.6347	-117.5570
Silverado Creek	Santa Ana	Dry/Wet	Sedimentary	Shrub	33.7461	-117.6010
Seven Oaks Dam	Santa Ana	Dry/Wet	Igneous	Shrub	34.1477	-117.0600
Cajon Creek	Santa Ana	Dry	Igneous	Shrub	34.3023	-117.4640
Mill Creek	Santa Ana	Dry/Wet	Igneous	Shrub	34.0822	-116.8890
Fry Creek	San Luis Rey	Dry/Wet	Igneous	Forest	33.3445	-116.8830
Piru Creek	Santa Clara River	Dry/Wet	Sedimentary	Shrub	34.6911	-118.8510
Sespe Creek	Santa Clara River	Dry/Wet	Sedimentary	Shrub	34.5782	-119.2580
Bear Creek Matilija	Ventura River	Dry/Wet	Sedimentary	Forest	34.5184	-119.2710
Runkle Canyon	Calleguas	Dry/Wet	Sedimentary	Shrub	34.2408	-118.7310
Tenaja Creek	San Mateo	Dry/Wet	Igneous	Shrub	33.5508	-117.3833
Arroyo Sequit	Arroyo Sequit	Wet	Sedimentary	Shrub	34.0458	-118.9347

Table 3. Dry weather sampling events: Shaded boxes indicate sampling events occurred at the site; unshaded boxes indicate no sampling due to lack of flow during the season.

Site Name	Spring 2005	Fall 2005	Spring 2006
Arroyo Seco			
Bear Creek WFSGR			
Cattle Creek EFSGR			
Coldbrook NFSGR			
Chesebro Creek		-	-
Cold Creek			
Cristianitos Creek		-	-
San Juan Creek			
Santiago Creek			
Bell Creek			
Silverado Creek			
Santa Ana River at Seven Oaks Dam			
Cajon Creek			
Mill Creek			
Fry Creek		-	
Piru Creek			
Sespe Creek			
Bear Creek Matilija			
Tenaja Creek		-	

Table 4. Wet-weather sampling events. Shaded boxes indicate sampling events occurred at the site; unshaded boxes indicate no sampling due to lack of flow during the season. Automatic sampling (Auto); Manual grab sampling (Pol). Numbers in parenthesis indicate the number of composite samples collected.

Site Name	7-Dec-04	28-Dec-04	7-Jan-05	11-Feb-05	17-Mar-05	29-Apr-05	2-Jan-06	28-Feb-06	11-Mar-06	28-Mar-06	4-Apr-06
Arroyo Seco					Auto (4)			Auto (8)			
West Fork San Gabriel River					Auto (4)						Auto (8)
Cattle Creek, a tributary to EFSGR						Auto (4)	Auto (4)				Auto (8)
Coldbrook NFSGR						Auto (4)	Auto (4)				
Chesebro Creek			Pol								Auto (4)
Cristianitos Creek at Cristianitos Rd			Auto (4)								
Santiago Creek on Modjesko Canyon				Auto (5)			Auto (4)		Auto (4)		
Bell Canyon Creek			Pol				Pol				
Silverado Creek				Auto (4)			Auto (4)				
Santa Ana River at Seven Oaks Dam											
Mill Creek										Auto(8)	
Fry Creek				Pol						Pol	
Piru Creek at Arizona Crossing								Auto (8)			
Sespe Creek at Sespe Gorge	Auto (1)							Auto (8)			
Bear Creek North Fork Matilija	Auto (1)							Pol			
Runkle Canyon		Auto (4)	Auto (4)								
Tenaja Creek						Auto (4)		Auto (8)			
Arroyo Sequit						Pol					

Table 5. Comparison of minimum detection limits (MDLs) for constituents analyzed.

Analyte	Minimum Detection Limit	Analytical Method
pH	0.1 pH unit	SM4500H+B
Conductance	0.1 micromhos	SM2510B
DO	0.01 mg/L	SM4500OG
Temperature	0.01 °C	SM2550B
Hardness	1.0 mg/L	SM2340A EDTA titration
Nutrients		
NH_3	0.01 mg/L	SM 4500-NH3F
TKN	0.14 mg/L	EPA 351.2
Nitrate+Nitrite	0.02 mg/L	SM 4500-NO3/-NO2
TP/OP	0.016 mg/L	SM 4500-P C
TSS	0.5 mg/L	SM 2540-D
TDS	0.1 mg/L	SM 2540-C
TOC	0.5 mg/L	EPA 451.1
DOC	0.5 mg/L	EPA 451.1
Metals		
Arsenic	0.1 µg/L	EPA 200.8
Cadmium	0.1 µg/L	EPA 200.8
Chromium	0.1 µg/L	EPA 200.8
Copper	0.1 µg/L	EPA 200.8
Iron	1.0 µg/L	EPA 200.8
Lead	0.05 µg/L	EPA 200.8
Nickel	0.1 µg/L	EPA 200.8
Selenium	0.1 µg/L	EPA 200.8
Zinc	0.1 µg/L	EPA 200.8
Bacteria		
Total Coliform	10 MPN/100 ml	Idexx Quantitray
E. coli	10 MPN/100 ml	Idexx Quantitray
Enterococcus	10 MPN/100 ml	Idexx Quantitray
Algae		
Chlorophyll a	0.005 mg/L	EPA 446.0

Dissolved oxygen (DO); ammonia (NH_3); total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC); total Kjeldahl nitrogen (TKN); total phosphorus (TP); and orthophosphate (OP).

Table 6. Study site characteristics, including catchment size.

Site Name	Stream Type	Catchment Size (km^2)	County	Watershed	Geologic Type	Land Cover Type	Method of Collecting Flow Data
Santiago Creek	Intermittent	17.02	Orange	Santa Ana	Sedimentary	Shrub	Hobo water level logger
Arroyo Seco	Perennial	41.50	Los Angeles	Los Angeles River	Igneous	Forest	USGS11098000*
Tenaja Creek	Intermittent	42.47	Riverside	San Mateo	Igneous	Shrub	Hobo water level logger
Sespe Creek	Perennial	128.46	Ventura	Santa Clara River	Sedimentary	Shrub	USGS 11111500*
Piru Creek	Perennial	318.65	Ventura	Santa Clara River	Sedimentary	Shrub	USGS 11109375*

*USGS gauging station numbers.

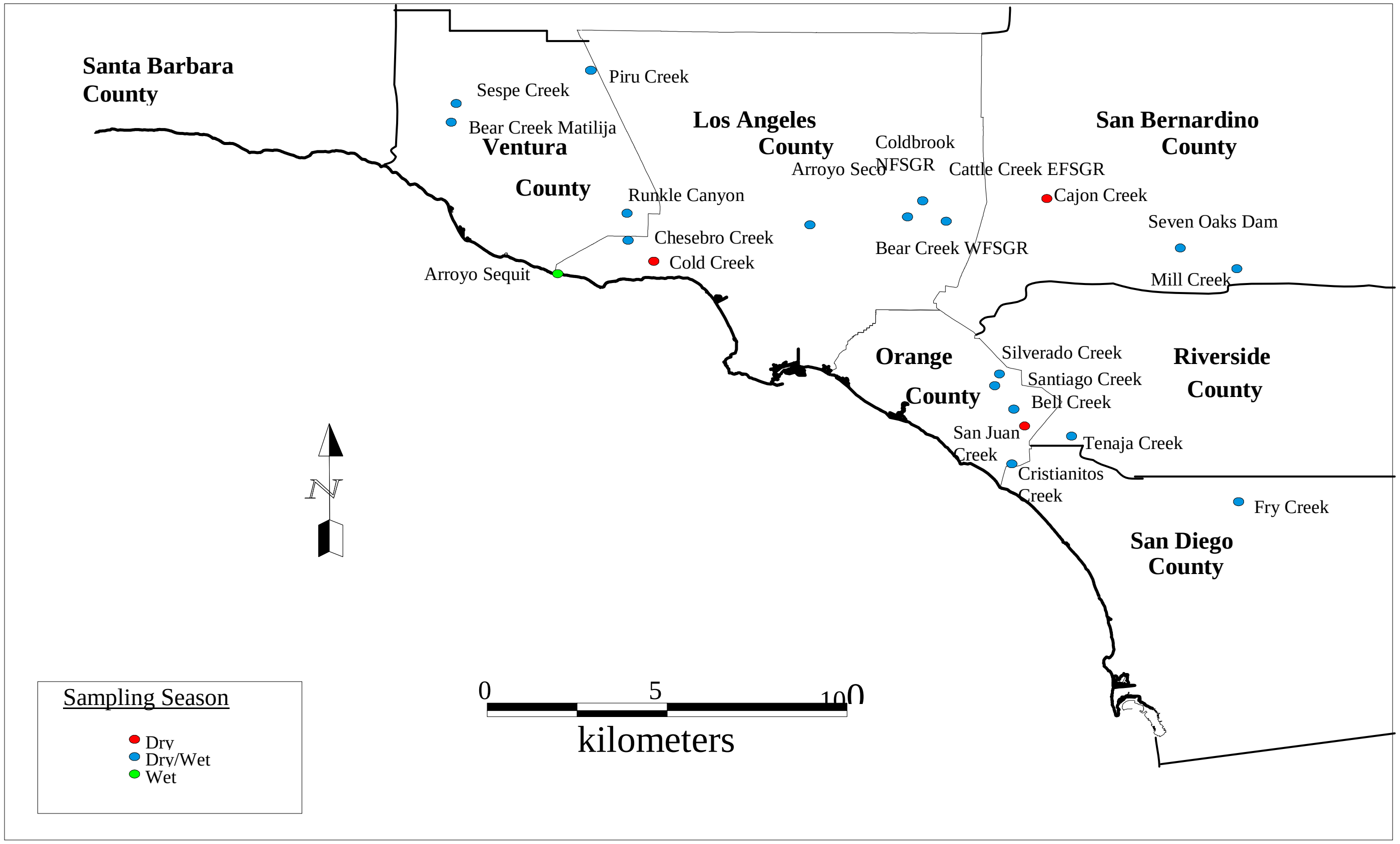

Figure 1. Study sites: red dots indicate sites sampled during dry weather only; blue dots indicate sites sampled in both dry and wet weather; and green dots indicate sites sampled during wet weather only.

DRY WEATHER

Background

Over the last decade, efforts to manage water quality have concentrated mainly on stormwater, which is perceived to be the largest source of pollutant loading (Driscoll *et al.* 1990, Lau *et al.* 1994, Wong *et al.* 1997, Noble *et al.* 2000, Schiff 2000, Ackerman and Schiff 2003). However, dry weather pollutant loadings may also constitute a significant impact to water quality in terms of both concentration and load (McPherson *et al.* 2002, McPherson *et al.* 2005, Stein and Tiefenthaler 2005). For instance, in six urban watersheds in the Los Angeles region, dry weather loading accounted for 20 to 50% of the total annual load of metals depending on the year's rainfall (Stein and Ackerman 2007); Table 7). In southern California, which is characterized by a dry Mediterranean climate with limited annual precipitation, the majority of rainfall occurs in the winter, with an average of only 37 rainfall days per year (Ackerman and Weisberg 2003, Nezlin and Stein 2005). Thus, dry weather flow can constitute a significant portion of total annual flow, particularly during dry years. Although concentrations of pollutants in dry weather flow might be relatively low (Mizell and French 1995, Duke *et al.* 1999), dry weather flow can be a chronic source of pollution and may impose threats to aquatic life because of its consistent contribution (Bay and Greenstein 1996, Stein and Tiefenthaler 2005, Stein and Ackerman 2007, Ackerman *et al.* 2003). This section provides dry weather concentration and flux estimates for natural areas.

Flow and field measurements

Seven of the nineteen streams sampled were intermittent, while the rest were perennial; intermittent streams included Chesebro Creek, Cristianitos Creek, San Juan Creek, Santiago Creek, Bell Creek, Fry Creek, and Tenaja Creek. Mean flow ranged from 0 to 0.72 m^3/sec with a mean of 0.33 m^3/sec. 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 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 over a period of months. Review of monthly average flow data from USGS (USGS National Water Information System: Web Interface, http://waterdata.usgs.gov/ca/nwis) showed that base flow in perennial streams varied over one order of magnitude, with the highest flows occurring in May and the lowest occurring in September.

Concentrations, loads, and fluxes ranges

Nutrients, except TOC and total phosphorus (TP), were neither normally nor log-normally distributed. Metals were mostly log-normally distributed. Bacteria were log-normally distributed. Thus, statistical summaries of all constituents were performed based on the assumption of the lognormal distribution. In all cases, concentrations, loads, and fluxes observed from the natural sites exhibited a great deal of variability, as indicated by large 95% confidence intervals (CI; Table 8). For example, the geometric mean of total dissolved solids was 274.4 mg/L and the 95% CI ranged from 183.0 mg/L to 411.5 mg/L.

No significant difference among sampling events in spring 2005, fall 2005, and spring 2006 was observed for most of constituents. The exceptions were concentrations of DOC, TOC, cadmium (Cd), and orthophosphate (OP), which showed significant differences among sampling events.

Mean concentration of DOC in fall 2005 was more than two times greater than that in spring 2005 and spring 2006. However, no consistent or systematic differences where one sampling event had higher concentrations for all four constituents were observed. Mean flows of sampling sites were significantly lower in fall 2005 than spring 2005 and spring 2006. Concentrations. Loads, and fluxes for each study site are shown in Appendix VII.

Algal levels at natural catchments

Algal abundance varied among seasons and years. Algae were observed at most of sampling sites in spring and fall 2005 except Mill Creek where the flow was too fast to safely access the stream for sampling. In contrast, algae were seldom observed during sampling events in fall 2006. In spring, stream algae were dominated by the green filamentous algae *Cladophora* spp. In addition, *Nostoc* spp., which have gelatinous bodies and grow attached to hard substrates, were observed, but constituted a minor component of the total algal community. Observations during the fall of 2005 suggest a shift in the community type as flows decreased, with *Nostoc* spp. becoming the dominant algae, and *Cladophora* spp. being rarely observed. This trend, however, was not repeated in 2006. *Nostoc* spp. was rarely observed during sampling events in 2006. Mean chlorophyll-a concentrations were 439 mg/m^2 for benthic algae, 0.48 mg/m^2 for attached algae, and 0.034 mg/m^2 for free floating algae (Table 8). The total chlorophyll-a concentration was 440 mg/m^2. The geometric mean of percent cover for each algae type were 23.6% for benthic algae, 6.4% for attached algae, and 2.6% for free floating algae (Table 8).

Effect of environmental characteristics on dry weather water quality in natural catchments

Geologic type (sedimentary rock and igneous rock) and slope were the main sources of variance in the dry weather water quality data. The stepwise selection in RDA resulted in these variables significantly increasing the overall model fitness (Table 9). The remaining six variables 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%, compared to 20.3% for the model that included all nine variables (Table 10).

The predominant source of variability 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 10 and 11). Among the variables retained in the RDA model, slope contributed least to variation along the first axis and most along the second axis (Table 11). This indicates that geologic setting is a more important factor in defining dry weather water quality of natural catchments than the other environmental factors tested here.

Correlations between water quality and environmental variables are explained in the biplot (Figure 2). 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 correlated with igneous rock. Arsenic was positively correlated with slope. Other constituents exhibited no strong correlation with any of the environmental variables.

Concentrations of several constituents exhibited significant differences between the different geology groups. Results of the ANOVA indicate that copper, iron, nickel, selenium, OP, and TDS concentrations were significantly higher in natural catchments underlain by sedimentary rock than those underlain by igneous rock ($p < 0.05$). Other constituents did not exhibit any significant differences between the geologic groups.

Comparison with developed catchments

Concentrations and fluxes differed significantly between the natural and developed catchments for all constituents ($p < 0.005$; Figure 3a, 4a, 5, 6, and 7). Metal concentrations at the natural catchments were two to three orders of magnitude lower than concentrations observed in the developed catchments (Figure 3a). For example, the geometric mean for copper was 0.56 µg/L in the natural catchments and 132.40 µg/L in the developed catchments. 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; for example, the geometric mean concentration of ammonia was 6.05 mg/L in the developed areas and 0.061 mg/L in the natural areas. Similarly, the geometric mean flux of ammonia was 896g/ km^2 day in the developed areas and 3g/km^2 day in the natural areas (Figure 4a). Bacteria concentrations were approximately two orders of magnitude lower at natural sites than in the developed Ballona Creek watershed (Figure 7). These differences were statistically significant ($p = <0.001$) for all three bacteria indicators.

Concentrations of metals, nutrients, and solids at the natural catchments were separated for igneous and sedimentary geology types; concentrations at each geology type were then compared with concentrations at the developed catchments. Concentrations at natural sites underlain by sedimentary and igneous rock were both significantly lower than concentrations at the developed catchments (Figure 3b and 4b).

In all cases, the variability observed in the natural areas was substantially higher than that observed in developed areas (Table 12). The %CVs of copper, lead, and zinc in the natural areas were more than two orders of magnitude greater than those in the developed areas. The greater %CVs in the natural catchments resulted from the larger geometric standard deviations compared with the geometric mean values.

Discussion

Dry weather concentrations of metals, nutrients, solids, and bacteria from natural catchments in the southern California Costal region were lower than those from developed catchments. Furthermore, dry weather concentrations documented in this study were one to three orders of magnitude lower than concentrations for reference sites in existing ambient monitoring programs such as EMAP and SWAMP (Table 13). These differences likely results from the fact that EMAP and SWAMP use a broad definition of “natural” and assign sites probabilistically based on general catchment land use. In some cases, there may be low levels of rural residential, ranching, or agricultural (e.g., orchards) land uses upstream of the sampling sites, even though the reference sites are far from major urban developments and meets the general definition of “natural” (NOAA CCAP 2003). Conversely, in this study sites were rigorously selected to exclude any potential effects of non-natural land use or land cover.

Dry weather concentrations 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; Table 14a). There are currently no established nutrient standards available for comparison to data collected from the natural catchments. However, in December 2000, USEPA proposed standards for TKN, nitrate+nitrite, total nitrogen (TN), and TP, respectively, for Ecoregion III, 6, which includes southern California (USEPA 2000; Table 14b). Although these proposed standards have not been approved, they provide a reasonable basis of comparison to levels of potential environmental concern. The geometric means of all nutrients were below or similar to the proposed USEPA regional nutrient criteria. 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 averaged on the 25th percentiles of concentrations from four seasons that include wet and dry weather. As shown in this study, levels of nutrients can vary considerably between dry and wet weather. Therefore, it is important to consider storm and non-storm conditions separately in future criteria development.

Median bacteria levels at the natural sites were lower than the Department of Health and Safety (DHS) draft guideline for freshwater recreation for *E. coli* and enterococci but higher for total coliforms (Figure 7). Instances of exceedance of the standards were not correlated with the runoff volume or with catchment size ($p > 0.05$).

There are no established water quality criteria for algae. Thus, the algal levels in this study were compared with literature values typically associated with eutrophic conditions. The mean algal biomass of 147 mg/m^2 at the natural sites was slightly lower than the algal nuisance threshold of 150 mg/m^2 stated in USEPA's Nutrient Criteria Technical Guidance Manual for Rivers and Streams (2000), but was higher than the 84 mg/m^2 suggested as a 50th percentile concentration of chlorophyll-a for eutrophic streams by Biggs and Thomsen (1995). Similarly, the total percent cover of three algal types of 32.6% was higher than the 30% cover suggested as a 50th percentile condition for eutrophic streams by Biggs and Thomsen (1995). However, algal biomass was substantially lower than values at developed sites reported by Welch *et al.* (1988) and Dodds *et al.* (1998).

Neither chlorophyll-a concentration nor algal percent cover was significantly correlated with any nutrient concentrations. The lack of correlation may be due to the narrow range of low values observed for both algae and nutrients at the natural sites. Alternatively, algal levels may be more related to levels of organic nutrients or to physical factors, such as flow or canopy cover, as suggested by Biggs and Thomsen (1995). In addition, the results of this study with respect to algal types and biomass are limited by the number of sampling events conducted during the dry weather. More frequent and continuous sampling/survey throughout the year is necessary to assess more representative changes in algal community and biomass. The lack of correlation between algal biomass and nutrients may also be partly due to this limitation.

The contribution of atmospheric deposition was not accounted for in this study. Therefore, concentration and flux data presented here include contributions from both natural loading and atmospheric deposition to the catchment and subsequent washoff. Prior studies show that rates of atmospheric nitrogen deposition can be quite high in xeric regions, such as those that include the majority of coastal catchments in southern California (Clark *et al.* 2000). Smith *et al.* (2003) showed that estimates of annual loading of TN and TP could be 16 to 30% lower when corrected for atmospheric deposition rates. In addition, mountainous areas within the South Coast air basin, within the greater Los Angeles area, receive the highest nitrogen deposition rates in the country (Fenn and Kiefer 1999, Fenn *et al.* 2003). In addition, Bytnerowicz and Fenn found thatdry deposition[5] of nitrogen over large areas of California was of greater magnitude than wet

[5] The removal of atmospheric particles that, in the absence of water in the atmosphere (i.e.,, rain), settle to the ground as particulate matter.

deposition[6] due to the arid climate (Bytnerowicz and Fenn 1996). Finally, Fenn *et al.* found that the contribution of atmospheric deposition could be even higher in late summer when fog occurs with unusually high atmospheric NO_3^- and NH_4^+ (Fenn *et al.* 2002). These findings imply that the dry weather concentrations of nutrients derived solely from natural sources may be even lower than values presented in this study.

This study showed that concentrations of metals, nutrients, and solids from natural catchments are highly variable. This may result from numerous factors, such as temporal and spatial variability and methods of data analysis. One factor that may influence data variability is treatment of non-detects (NDs). In this study, the percent of NDs for a given constituent ranged from 1.8% for TSS to 59.6% for TP (Table 15). 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, samples were assigned a value of one-half the MDL to ND samples used in this study. Use of the MDL instead of one-half 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, OP, and TSS, which would have increased by 12, 18, 30, and 8%, respectively.

Environmental settings such as geology and land cover have been shown to affect water quality in natural catchments (Lakin and Byers 1941, Dunne and Leopold 1978, Ohlendorf *et al.* 1986, Larsen 1988, Ledin *et al.* 1989, Tracy *et al.* 1990, Tidball *et al.* 1991, Detenbeck *et al.* 1993, Presser *et al.* 1994, Hounslow 1995, Johnes *et al.* 1996, Richards *et al.* 1996, Johnson *et al.* 1997a, Gergel *et al.* 1999, Hibbs and Lee 2000). In this study, geology was the primary factor in determining dry weather water quality in natural catchments. Levels of TDS and other constituents were generally higher in streams draining sedimentary catchments than those draining igneous catchments. This difference can be explained by the higher erodibility of sedimentary rock resulting in the increased release of sediment and associated constituents into the water. Differences in constituent concentrations based on geologic setting were most pronounced for compounds that are typically associated with particles, such as copper, zinc, and nickel. 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. The likely mechanism for this effect is an increase in erosion and washoff associated with steeper watersheds (Naslas *et al.* 1994). Overall, the effect of both slope and geology was less pronounced for dry weather conditions than for wet weather conditions, most likely due to a lower amount of overland (surface) runoff.

Land cover did not have a significant effect on dry weather water quality in this study. However, other studies have documented the importance of land cover on water quality (Nolan and Hitt 2003, Willett *et al.* 2004). Binkley *et al.* (2004) reported phosphorus levels in hardwood-forested streams that were more than two orders of magnitude higher than the concentrations found in this study. In our study, forested catchments did not show significantly higher levels for any phosphorus-related constituents than shrub catchments. This highlights the importance of considering regional differences. The soils of hardwood forests typically include well-developed O-horizons and are subject to relatively long periods of saturation. These factors contribute to leaching of nutrients from decaying organic matter in the O-horizon to the streams draining the catchments. In contrast, forested areas in southern California are characterized by young sandy soils with little to no O-horizon and generally low organic matter. These soils are not

[6] The removal of atmospheric particles to the earth's surface by rain or snow (SRA 2003).

substantially different than those found in scrub-shrub areas; hence, differences in nutrient loading were not expected.

Table 7. Means of dry weather and wet-weather concentrations for metals (total recoverable), nutrients, and solids. Data not available ('- ').

Constituent	Arroyo Seco		Piru Creek		Santiago Creek		Sespe Creek		Tenaja Creek		Unit
	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	Dry	Wet	
Arsenic	2.17	0.89	2.01	0.47	0.49	0.22	0.46	0.36	1.38	0.73	µg/L
Cadmium	0.28	0.37	0.08	0.04	0.08	0.11	0.26	0.20	0.08	0.34	µg/L
Chromium	0.12	6.97	0.23	8.94	0.22	0.25	0.08	5.40	0.31	2.82	µg/L
Copper	0.58	3.63	0.73	5.51	0.42	0.38	0.95	4.83	0.13	2.33	µg/L
Iron	37.86	2264.78	154.69	7962.21	131.83	121.22	108.86	7253.36	200.50	3322.19	µg/L
Lead	0.03	2.26	0.07	1.85	0.03	0.11	0.03	1.54	0.12	1.44	µg/L
Nickel	0.16	2.20	0.53	5.76	0.80	0.27	0.73	5.36	0.62	1.21	µg/L
Selenium	0.77	0.52	0.66	0.53	0.97	1.04	1.45	0.69	0.72	0.50	µg/L
Zinc	0.70	12.64	0.32	16.11	0.75	1.46	0.37	14.35	0.94	12.50	µg/L
Ammonia	0.01	0.03	0.01	0.03	0.00	0.02	0.01	0.09	0.01	0.06	mg/L
Total Nitrogen	0.43	2.23	0.54	2.35	0.41	1.01	0.55	3.32	0.24	1.56	mg/L
Dissolved Organic Carbon	2.82	6.75	3.07	5.80	3.13	3.28	3.50	5.53	5.23	6.24	mg/L
Total Organic Carbon	3.18	6.53	9.97	6.71	3.65	3.22	6.92	6.66	4.43	6.01	mg/L
Total Phosphorus	0.04	0.01	-	-	0.05	0.06	-	-	0.18	0.18	mg/L
Orthophosphate	0.02	0.08	0.03	0.06	0.04	0.01	0.05	0.06	0.00	0.11	mg/L
Total Dissolved Solids	269.83	401.52	-	-	439.72	334.96	869.67	417.54	399.50	349.11	mg/L
Total Suspended Solids	0.29	107.03	2.55	5454.92	0.96	13.97	0.38	51969.43	2.38	184.15	mg/L

Table 8. Dry weather geometric means (Geomean), along with upper and lower limits of 95% confidence interval (CI) for concentrations, mass load, and flux.

Metals	Concentration (μg/L)			Mass Load (g/day)			Flux (g/km^2 day)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Arsenic	0.66	0.94	0.47	7.90	13.72	4.55	0.33	0.51	0.21
Cadmium	0.11	0.15	0.09	1.34	2.20	0.81	0.06	0.10	0.03
Chromium	0.17	0.22	0.13	2.03	3.22	1.28	0.08	0.14	0.05
Copper	0.56	0.72	0.43	6.64	10.59	4.16	0.28	0.43	0.18
Iron	83.90	109.83	64.10	997.79	1628.97	611.18	41.37	69.19	24.73
Lead	0.05	0.06	0.03	0.55	0.89	0.34	0.02	0.04	0.01
Nickel	0.30	0.41	0.22	3.56	6.03	2.10	0.15	0.24	0.09
Selenium	0.58	0.84	0.41	6.95	11.84	4.08	0.29	0.49	0.17
Zinc	0.56	0.82	0.39	6.70	10.52	4.27	0.28	0.50	0.16
Nutrients	**Concentration (mg/L)**			**Mass Load (kg/day)**			**Flux (kg/km^2day)**		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Ammonia	0.01	0.01	0.01	0.07	0.11	0.05	0.003	0.005	0.002
Nitrate+Nitrite	0.05	0.08	0.03	0.58	1.08	0.31	0.02	0.05	0.01
Total Kjeldahl Nitrogen	0.28	0.31	0.25	3.29	5.07	2.14	0.14	0.22	0.09
Dissolved Organic Carbon	2.68	3.39	2.12	31.87	49.86	20.37	1.32	2.17	0.80
Total Organic Carbon	2.85	3.37	2.41	33.88	51.18	22.43	1.40	2.18	0.91
Orthophosphate	0.02	0.02	0.01	0.20	0.33	0.13	0.008	0.014	0.005
Total Phosphorus	0.05	0.06	0.04	0.57	0.89	0.36	0.02	0.04	0.01
Solids	**Concentration (mg/L)**			**Mass Load (kg/day)**			**Flux (kg/km^2)**		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Total Dissolved Solids	274.43	411.49	183.02	3132.46	5804.84	1690.37	137.86	250.53	75.87
Total Suspended Solids	0.85	1.27	0.57	10.12	17.80	5.76	0.42	0.78	0.23

Microbes	Concentration (MPN/100ml)			Algae*	Percent Cover (%)			Chlorophyll-a (mg/m^2)		
	Geomean	Upper CI	Lower CI		Mean	Min	Max	Mean	Min	Max
E. coli	15.83	20.11	12.46	Benthic	23.60	0.00	100.00	439.20	0.00	6946.20
Enterococcus	19.84	25.49	15.45	Attached	6.40	0.00	38.10	0.48	0.00	2.30
Total Coliform	1047.83	1429.96	767.82	Free floating	2.60	0.00	37.20	0.03	0.00	0.21

* Algal data were normally distributed and arithmetic means, minimums and maximums were computed.

Table 9. Dry weather results of stepwise selection of environmental variables using redundancy analysis (RDA)[a].

Environmental Variables	Extra Fit	Cumulative Fit	Significance (p value)
Igneous Rock	0.073	0.073	0.005
Sedimentary Rock	0.073	0.146	0.005
Slope	0.040	0.186	0.04
Mean Flow	0.039	0.225	>0.05
Elevation	0.034	0.259	>0.05
Catchment Size	0.032	0.291	>0.05
Canopy Cover	0.032	0.323	>0.05
Latitude	0.025	0.348	>0.05
Forest	0.023	0.371	>0.05
Shrub	0.023	0.395	>0.05

[a] 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: 1006. Total number of water quality variables: 18. Significance was determined by Monte Carlo permutation using 199 random permutations.

Table 10. Statistical summary of RDA for dry weather water quality.

		Axes			
		1	2	3	4
Eigenvalues		0.075	0.038	0.22	0.11
Water Quality Environment Correlations		0.65	0.65	0.00	0.00
Cumulative Percentage variance	Water Quality Data	7.50	11.00	33.00	45.00
	Water Quality-Environment Relation	66.00	100.00	0.00	0.00

Table 11. Canonical coefficients of environmental variables with the first two axes of RDA for dry weather concentrations of metals, nutrients, and solids.

	Water Quality Constituent Axes	
Environmental Variables	1	2
Sedimentary Rock	-0.63	-0.15
Igneous Rock	0.63	0.15
Slope	0.16	0.64

Table 12. Comparison of percent coefficient of variation (%CV) between natural sites and developed sites for metals, nutrients, and solids in the dry weather condition. Data were not available ('-').

Metal	Natural			Developed		
	Sample Size	Concentration %CV	Flux %CV	Sample Size	Concentration %CV	Flux %CV
Arsenic	51	530	1500	4	81	950
Cadmium	51	2300	13000	4	980	14000
Chromium	51	1400	7600	8	41.30	200
Copper	51	460	1800	11	4.40	72
Iron	51	3.20	16	8	0.14	1.20
Lead	51	6100	28000	10	15.10	200
Nickel	50	1000	4300	8	5.00	29
Selenium	51	650	2400	8	52	380
Zinc	51	710	3000	11	1.7	23
Ammonia	51	24000	190000	10	320	720
Nitrate+Nitrite	51	8500	37000	8	97	550
Total Kjeldahl Nitrogen	50	540	3900	0	-	-
Dissolved Organic Carbon	51	88	460	0	-	-
Total Organic Carbon	51	65	350	0	-	-
Orthophosphate	51	25000	91000	0	-	-
Total Phosphorus	49	5100	25000	8	350	3400
Total Dissolved Solids	51	1.60	6.30	0	NA	NA
Total Suspended Solids	50	500	2300	8	11	53
E. coli	52	29	-	12	0.28	-
Enterococcus	52	20	-	12	0.45	-
Total Coliform	52	0.50	-	12	0.0036	-

Table 13. Comparison of dry weather geometric means of concentration of the natural catchments with geometric means from reference sites of the existing ambient monitoring programs (EMAP and SWAMP).

Metal	Existing Ambient Monitoring Programs	Natural Loadings
Selenium (µg/L)	13.70	0.58
Zinc (µg/L)	5.25	0.56
Ammonia (mg/L)	1.47	0.01
Dissolved Organic Carbon (mg/L)	1.67	2.68
Total Phosphorus (mg/L)	1.99	0.05
Total Nitrogen (mg/L)	301	0.32
Total Suspended Solids (mg/L)	495	0.85

Table 14a. Water quality standards for metals. Standards are from the California Toxics Rule (CTR) – Inland surface waters for freshwater aquatic life protection. Standards for hardness-dependent metals shown here are those at 100 mg/L. Four-day criteria are used for the comparison of the dry weather water quality.

Metal	Continuous Concentration (µg/L) Four-day Average	Hardness Standard
Arsenic	150	Independent
Cadmium	2.20	Dependent
Chromium (III)	180	
Copper	9.00	
Nickel	52	
Lead	2.50	
Selenium	5.00	Independent
Zinc	120	Dependent

Table 14b. Comparison of EPA proposed nutrient criteria for rivers and streams for Ecoregion III, 6 (central and southern California) with dry weather geometric means.

Nutrient	Ecoregion III, 6	Natural Catchments in Dry Weather Geometric Mean
Total Kjeldahl Nitrogen (mg/L)	0.36	0.28
Nitrate+Nitrite (mg/L)	0.16	0.05
Total Nitrogen (mg/L)	0.52	0.33
Total Phosphorus (mg/L)	0.03	0.05

Table 15. Percent non-detects (%ND) of the dry weather data. Constituents not shown did not have NDs.

Constituent	No of ND	No of Sample	%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
Dissolved Organic Carbon	67	115	58.3
Nitrate	4	104	3.8
Nitrite	24	120	20.0
Orthophosphate	64	119	53.8
Total Kjeldahl Nitrogen	32	108	29.6
Total Phosphorus	62	104	59.6
Total Dissolved Solids	21	108	19.4
Total Suspended Solids	2	109	1.8

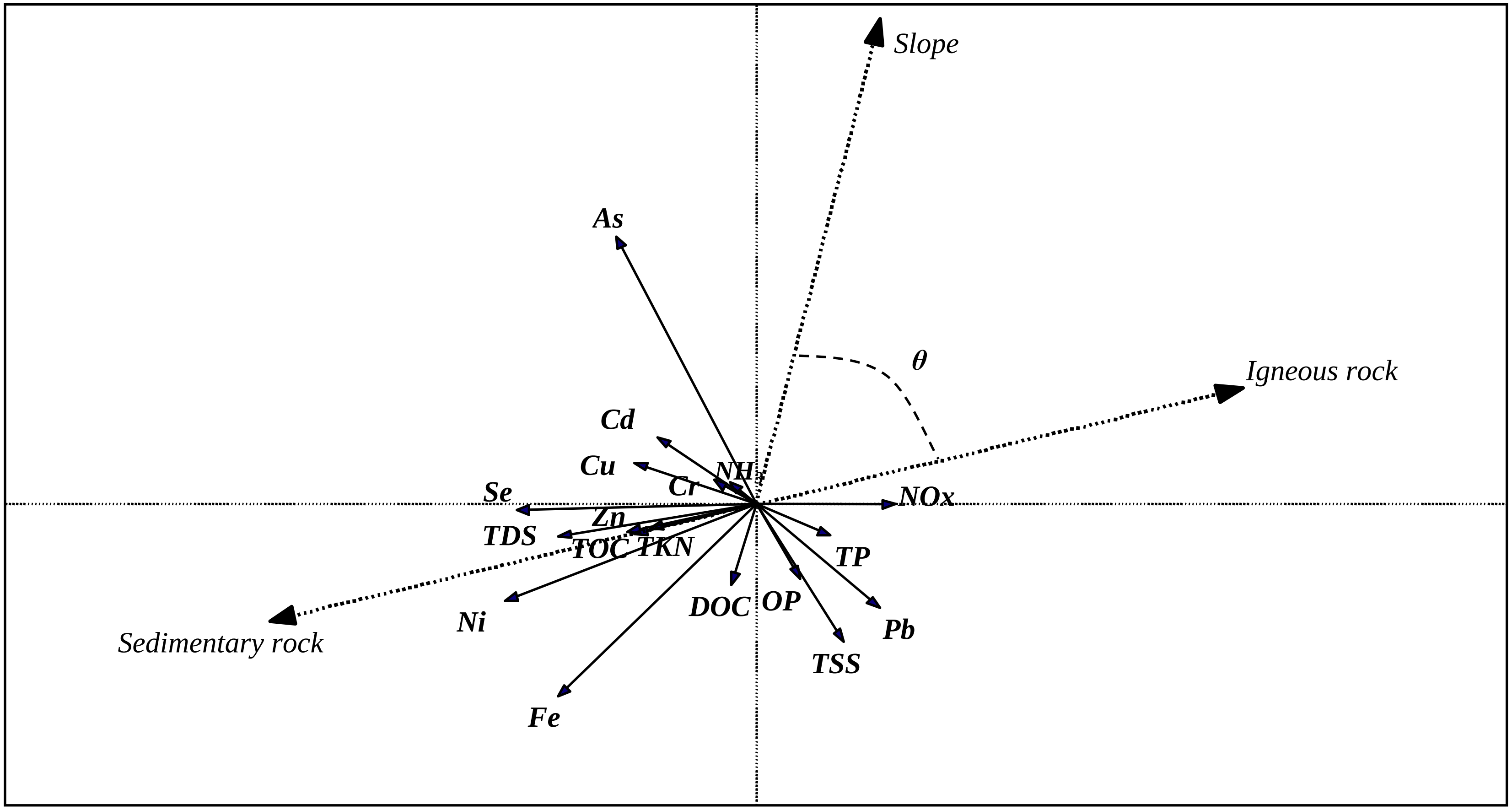

Figure 2. Correlation biplots showing relations between dry weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigen values: 0.151 and 0.0280 for the first (horizontal) and second (vertical). cos θ ≈ correlation coefficient between two variables (arrows). Longer arrows indicate which factor is more important in generating variability (Ter Braak, 1995). 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); and Nitrate+Nitrite (NOx).

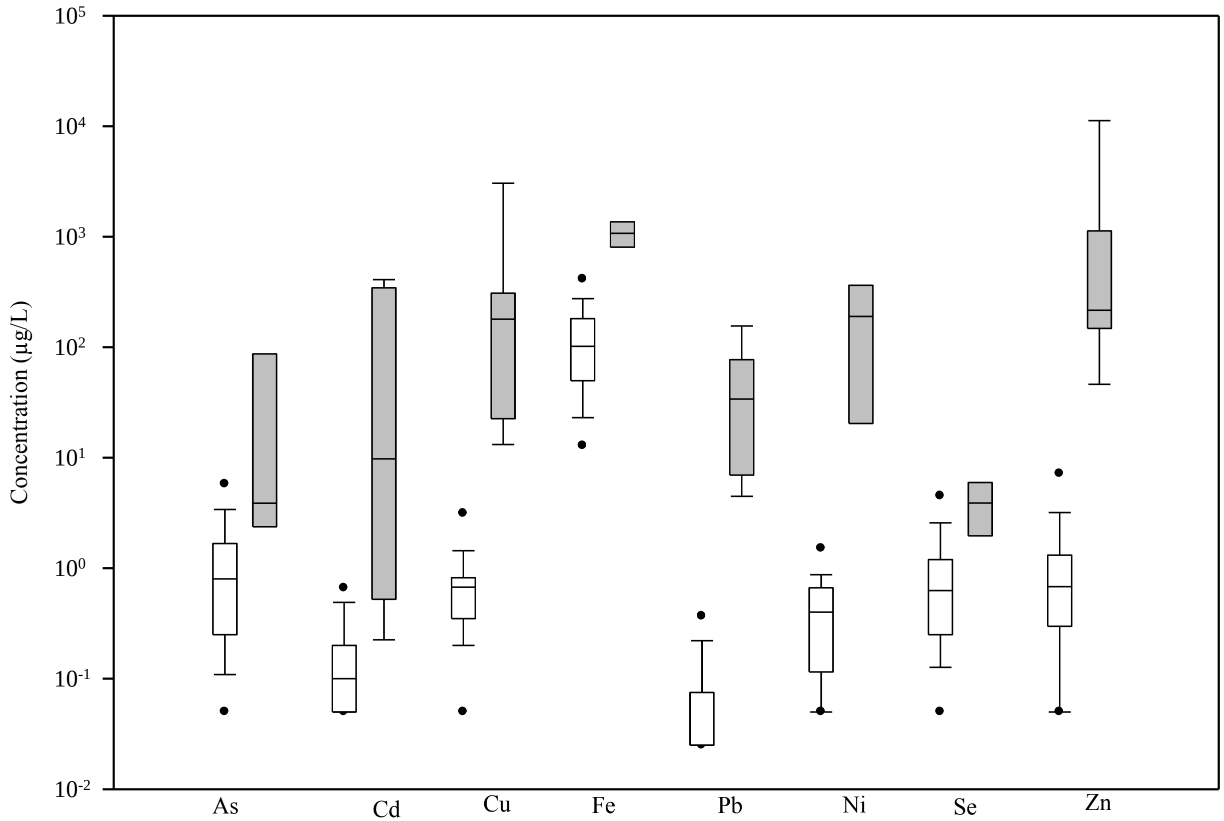

Figure 3a. Comparison of dry weather concentrations of metals between natural and developed catchments. White boxes represent natural sites, and gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles.. The Y axis is in log scale.

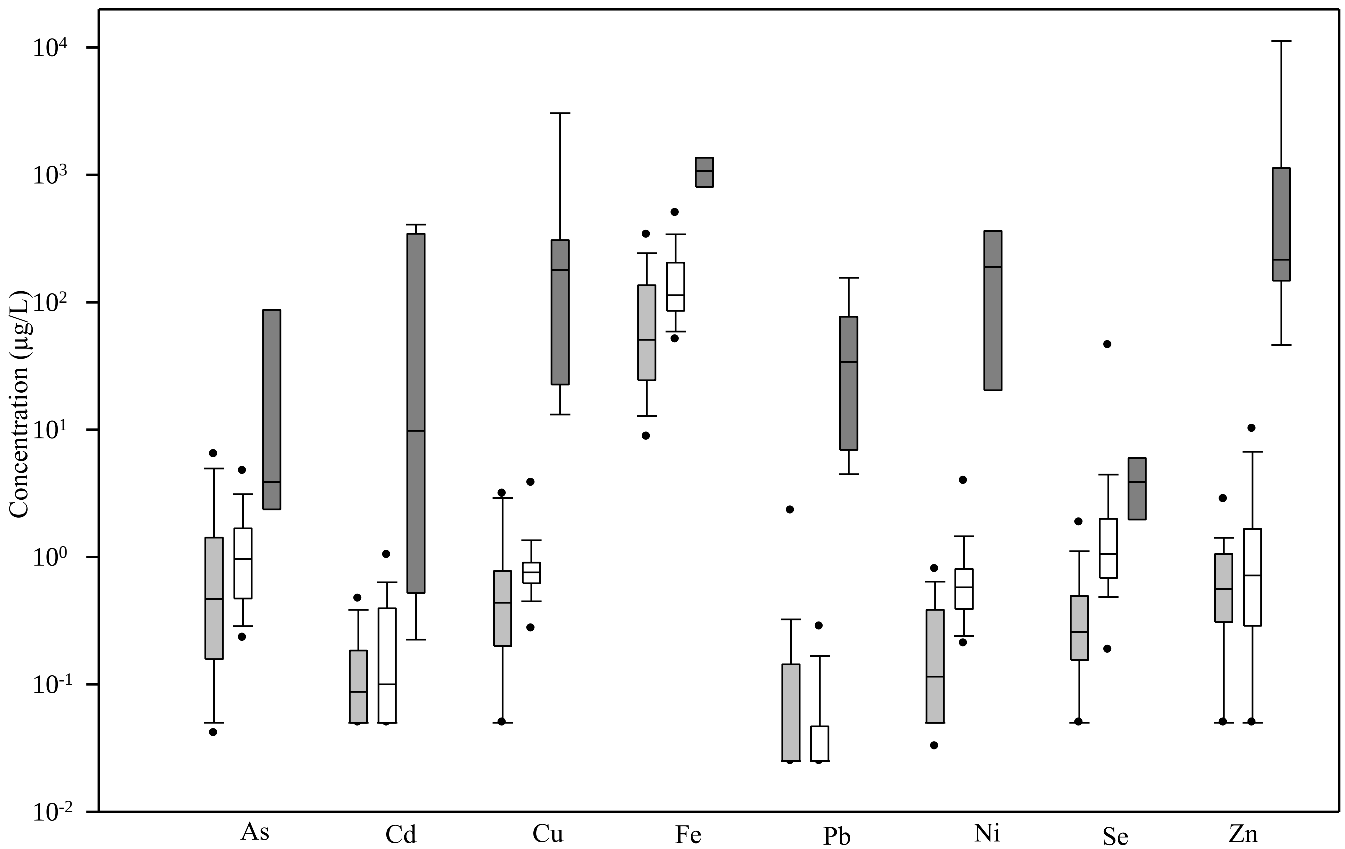

Figure 3b. Comparison of dry weather concentrations of metals between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock; white boxes represent natural sites underlain by sedimentary rock; and dark gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.

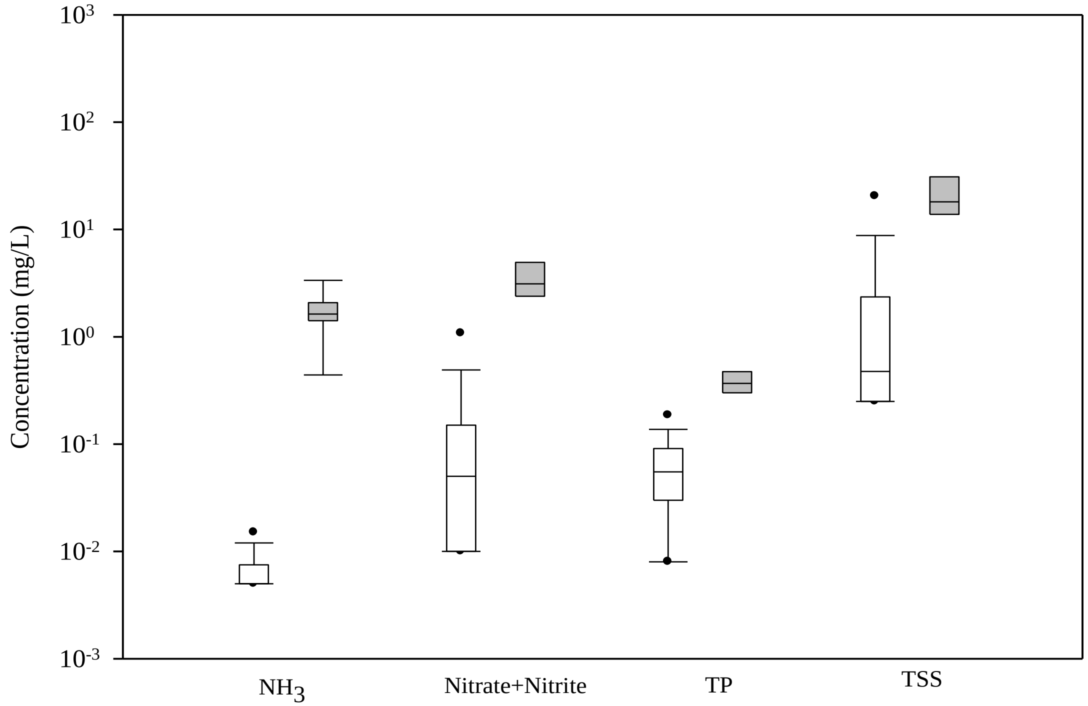

Figure 4a. Comparison of dry weather concentrations of ammonia (NH_3), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural sites, and gray boxes represent developed sites. The Y axis is in log scale.

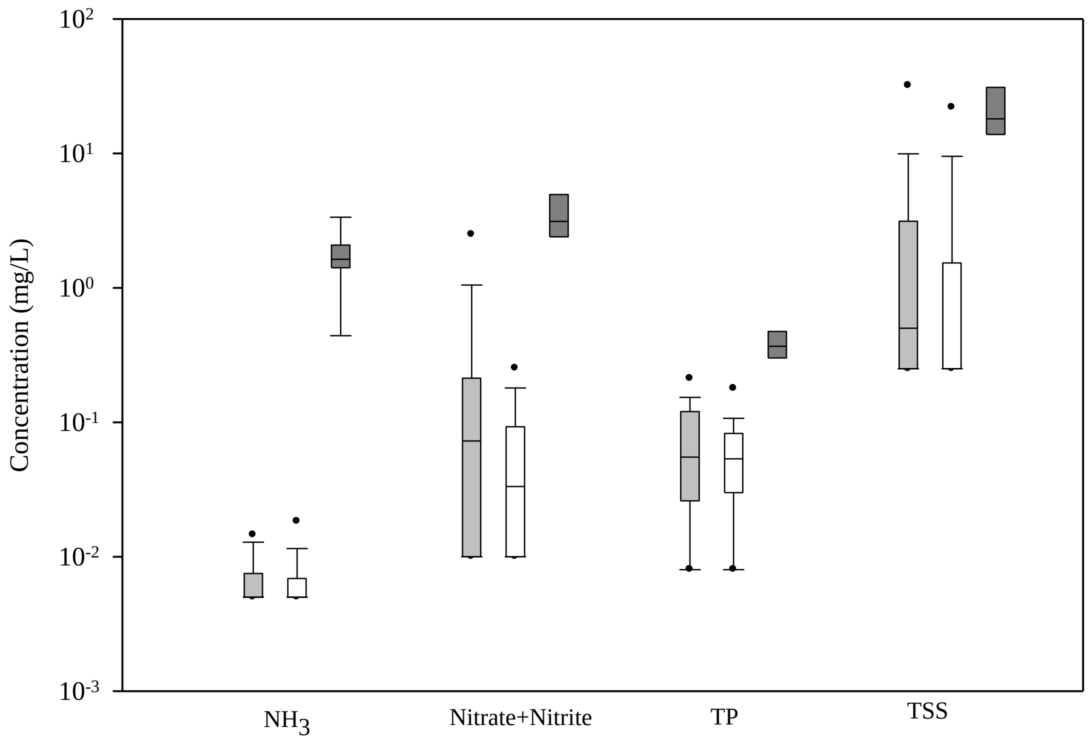

Figure 4b. Comparison of dry weather concentrations of ammonia (NH_3), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. The Y axis is in log scale.

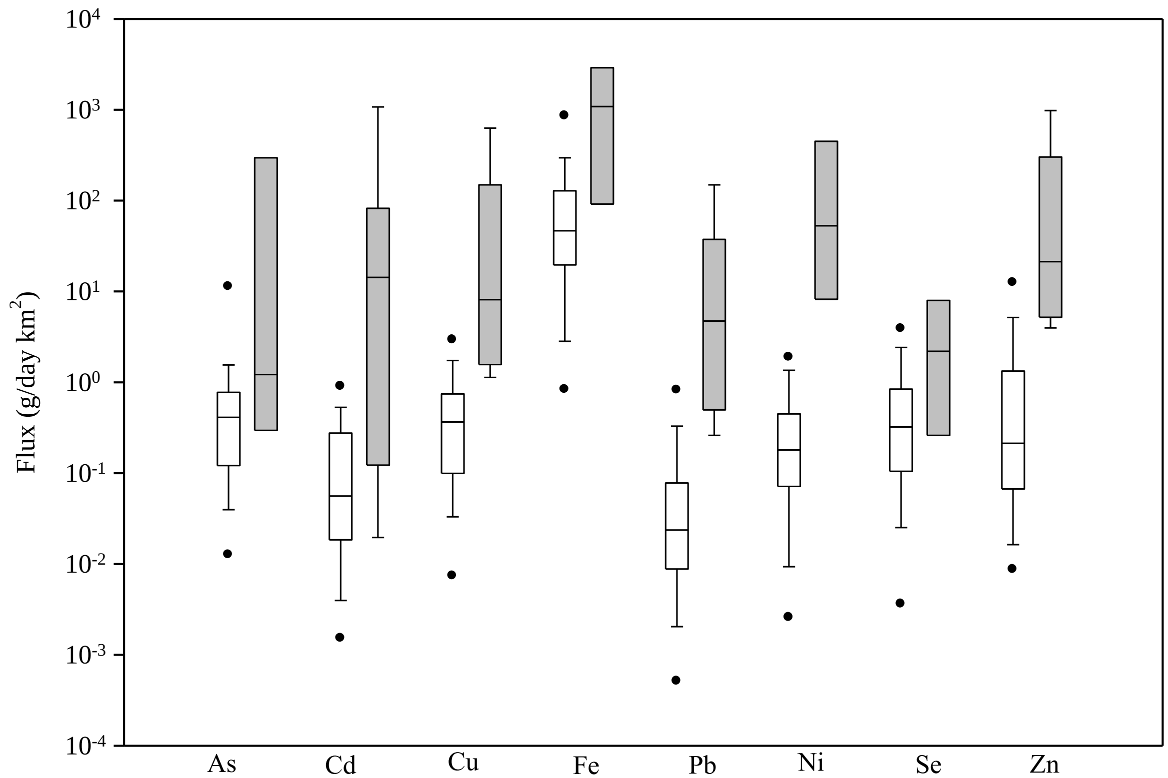

Figure 5. Comparison of dry weather fluxes of metals between natural and developed catchments. White boxes represent natural sites, while gray boxes represent developed sites. The Y axis is in log scale.

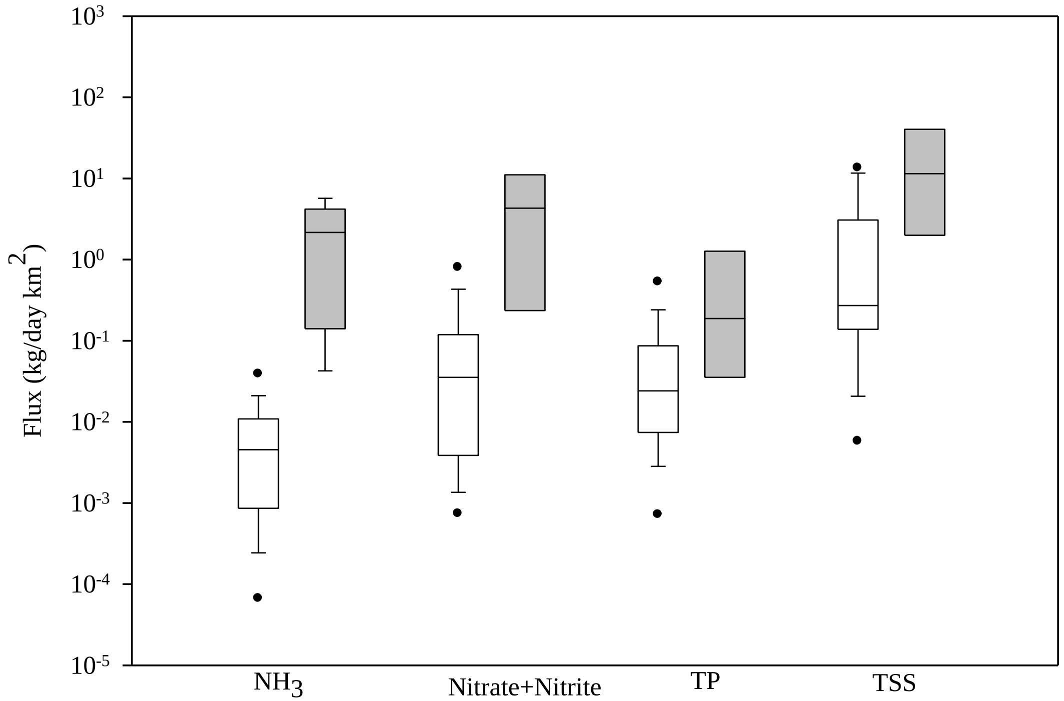

Figure 6. Comparison of dry weather fluxes of ammonia (NH_3), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural sites, while gray boxes represent developed sites. The Y axis is in log scale.

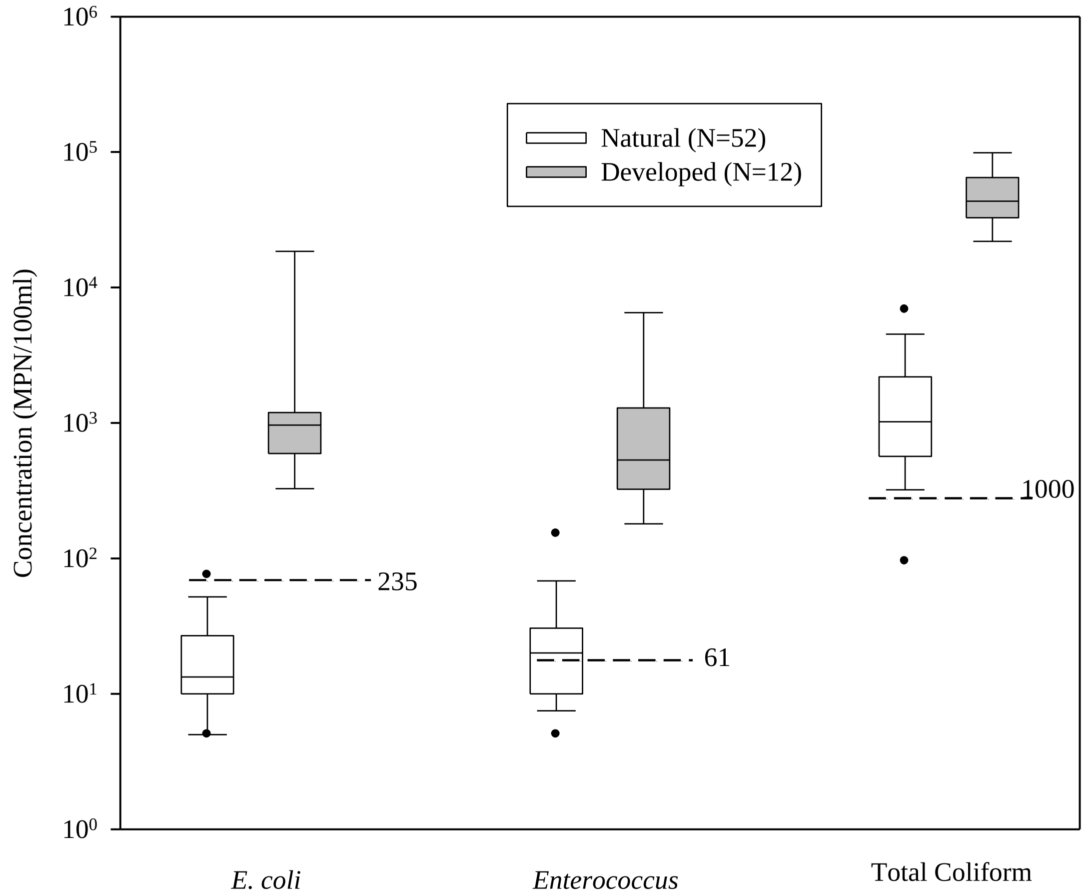

Figure 7. Comparison of dry weather bacteria concentrations between undeveloped and developed catchments. Blue boxes represent natural catchments, and yellow boxes represent developed catchments. The Y axis is in log scale. N is the number of samples per catchment type. Dotted lines are Department of Health and Safety draft guideline for freshwater recreation.

WET WEATHER

Background

Stormwater runoff has been recognized as a major source of pollution to many of the nations waterways (Characklis and Wiesner 1997, Davis *et al.* 2001). In southern California, pollutants associated with stormwater have been shown to result in significant ecological effects in local receiving waters of the Southern California Bight (Bay and Greenstein 1996, Noble *et al.* 2000, Schiff 2000). Consequently, much effort and resources have been devoted to the evaluation and management of stormwater (USEPA 1995, Wong *et al.* 1997, Ackerman and Schiff 2003, Ahn *et al.* 2005). One of the challenges associated with stormwater management is accounting for the impact of biogenic inputs, or the natural contribution from undeveloped areas (natural loadings) on overall water quality.

Unlike man-made compounds, such as Polychlorinated Biphenyls (PCBs), many constituents found in stormwater, such as metals, nutrients, and solids, can originate from natural, as well as anthropogenic, sources (Turekian and Wedepohl 1961, Dickert 1966, Trefry and Metz 1985, Horowitz and Elrick 1987, Seiler *et al.* 1999). Therefore, high levels of these constituents may not directly indicate a water quality problem, and it may be difficult to differentiate anthropogenic effects and natural variability in the system.

Existing ambient monitoring programs typically include a few reference streams in relatively undeveloped areas, but mainly focus on dry weather water quality and devote little, if any, resources for characterizing reference conditions for stormwater runoff. To compensate for the lack of data on natural stormwater loadings, water quality standards, such as TMDLs, are often written using load allocations based on data from other parts of the country or, with anecdotal data from previous time periods. As a result, these standards may be ineffective or overly stringent. Quantification of stormwater loads from natural areas in southern California (presented in this section) would help remedy this situation.

Rainfall and flow

Annual rainfall during the study period (2004 to2006) was compared to the average annual rainfall from 1872 to 2006 (Figure 8; Los Angeles County Department of Public Works (LADPW) rain gage station #716 at Ducommun St., Los Angeles, CA - http://ladpw.org/wrd/Precip/index.cfm). Rainfall for the 2004-2005 storm season was significantly above the long-term average annual rainfall of 40 cm. In contrast, annual rainfall during 2006 was approximately two-thirds of the average. Therefore the two study years represented an unusually wet year and a below-average rainfall year.

Event rainfall over the study period ranged from 0.81 to 17.20 cm. Mean storm flow was 1.39 ± 2.31 m^3/sec and flow varied from 1.51×10^{-2} to 9.76 m^3/sec. Peak flows ranged from 6.88×10^{-2} to 53.72 m^3/sec with the 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 2004-2005, mean rainfall was 7.3 cm/storm event, while in 2005-2006 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 2004-2005 vs. 8.1$\pm$ 15.3(m^3/sec) in 2005-2006.

Ranges of concentrations, loads, fluxes for metals, nutrients, and solids

Geometric means ranged from 0.3 to 5 μg/L for metals except iron (962 μg/L) and from 0.04 to 6 mg/L for nutrients. Geometric means of TDS and TSS were 98 and 251 mg/L, respectively, and those of bacteria ranged from 123 to 4467 MPN/100ml. Concentrations, loads and fluxes for each constituent are summarized as geometric means and upper and lower 95% CI in Table 16. In all cases, concentrations and loads observed from the natural catchments exhibited a great deal of variability, as indicated by large 95% CI; concentrations, loads, and fluxes generally varied over one order of magnitude. Concentrations. Loads, and fluxes for each study site are shown in Appendix VIII.

Temporal variability in concentration and load

No first flush was observed in stormwater runoff from the natural catchments as indicated by the cumulative mass loading plots. 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 9). 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 typically observed in developed catchments, where peak concentrations occur during the rising limb of the hydrograph. An example of the pollutograph for Piru Creek shows that the peak concentration of copper occurred on the decreasing limb of the hydrograph (Figure 10), and the pollutograph was more spread out in natural areas than typically observed in developed watersheds.

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

Levels of constituents varied between among storm seasons. The range of variability in data was larger during the wetter 2004 storm season than during the drier 2005 storm season. Variability among different storm events in 2004 was significantly larger than variability in 2005, for all constituents except TDS (Appendix VI - Table 1). For example, the %CV for TSS in 2004 was approximately three times larger than that in 2005: 1,154 and 393, respectively. Geometric means for all constituents except DOC and TP were higher in 2004 than those in 2005 (Appendix VI – Table 2).

Particulate vs. dissolved concentrations of metals in storm runoff

Ratios of particulate to dissolved metals concentrations changed over the course of storms. Particulate metals increased with increased flow, and were significantly associated with an increase in the concentration for TSS ($p < 0.05$). Figure 11 shows an example of this pattern from a storm event at Bear Creek. The concentration of TSS sharply increased with the increase in rainfall and flow, while the concentration of TDS dropped, primarily due to dilution by increased runoff. 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 11). The pattern of TSS concentration was synchronized with the increase in particulate metals and inversely related to TDS concentrations. Although this pattern was consistent among all metals, the ratio of particulate to dissolved concentration varied by metal. Arsenic (As) and selenium (Se) exist 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 (Figure 11). At peak flow, the ratio of particulate over dissolved metals for As and Se increased by approximately two orders of magnitude coincident with an increase in TSS. Copper (Cu), lead (Pb), and zinc (Zn) existed primarily in the dissolved phase during baseflow conditions. However, during peak flow particulate metals increased by three orders of magnitude and the majority of metals in storm runoff occur in the particulate phase. Increased particulate metal concentrations persisted long after flow subsided; the ratio of particulate to dissolved metals did not return back to the pre-storm levels for two days following peak flow.

Environmental factors that influence variability in constituent concentrations

The influence of environmental variables on water quality data was examined in a two-step process. First, RDA was used to identify the variables that accounted for the majority of variance in the data set as a whole. Second, the entire water quality data set was grouped based on the environmental variables identified by the RDA model. The data were log-transformed and the significance of differences between the groups was analyzed using ANOVA.

Geologic setting (sedimentary vs. igneous) and elevation were the main determinants of variance in the wet-weather water quality data. According to the RDA stepwise selection, geology and elevation showed higher extra fit than the other eleven variables tested and significantly increased the fitness of the model (Table 17). Because sedimentary geologic setting, igneous geologic setting, and elevation were the only variables that significantly contributed to the fitness of the RDA model ($p < 0.05$), subsequent RDA analysis was conducted using only these three environmental variables, thereby maximizing the ability of the model to resolve differences between environmental classes.

The RDA model with three environmental variables explains 66.6% of variance in water quality data (Table 18). In contrast, the model that included all fourteen environmental variables explained only 44.3% of variance. The first axis of the RDA model was determined by the two geologica setting variables. This axis had a canonical coefficient of ±0.5167 and explained 84.5% of total model variance relating water quality to environmental variables; the second axis of the RDA model was determined by elevation, had a canonical coefficient of 0.3777, and explained 15.5% of total model variance (Tables 19 and 20).

Most metals, TSS, and a few nutrients were correlated with geology variables as shown in the biplot (Figure 12). Total suspended solids and metals (except arsenic) were positively correlated with sedimentary rock. Dissolved organic carbon and TOC were negatively correlated with sedimentary rock and positively correlated with igneous rock. Total Kjeldahl nitrogen was strongly positive-correlated with elevation. Arsenic, OP and TDS were negatively correlated with elevation. Other constituents exhibited no strong correlation with any of the environmental variables. The correlations suggested by the RDA results were reconfirmed by regression analysis.

Concentrations of several constituents exhibited significant differences between the two geologic types. Results of the ANOVA indicate that Cu, Ni, Se, Zn, NH_3, and TSS, concentrations were significantly higher in runoff from natural catchments underlain by sedimentary rock than those underlain by igneous rock ($p < 0.05$). Other constituents did not exhibit any significant differences between the geologic types.

Comparison with developed catchments

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 response to increased rainfall in developed catchments (Figure 13a.). Ratios of mean flow and total runoff volume to catchment size also increased less sharply in response to increase of rainfall in natural catchments than in response to increased rainfall in developed catchments. This difference between natural catchments and developed catchments was likely due to difference in the amount of impervious surface in the 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 storms at the natural sties were distributed above the average total rainfall per storm event at Los Angeles DPW station #716 at Ducommun St., Los Angeles, CA, between 1997 and 2003 (Figure 13b). This is primarily because most of natural sites are located at upper portions of the watershed, while most of developed sites are located at lower portions of the watershed. The natural sites in mountainous areas of higher altitude are more likely to have more frequent and higher precipitation than the developed sites.

Flow-weighted mean concentrations (FWMCs) from the natural catchments were significantly different ($p < 0.05$) from those of developed catchments in southern California for all constituents examined except TSS. Comparisons were conducted for a total of nine metals (As, Cd, Cr, Cu, Fe, Pb, Ni, Se, and Zn), four nutrients (NH_3, TKN, TP, and nitrate+nitrite), and TSS. Among them, Cd, Se, NH_3, TKN, and TSS passed both normality and equivariance tests and were analyzed using ANOVA. Constituents that failed the normality test were examined using one-way ANOVA on ranks. Metal concentrations at the natural catchments were approximately one to two orders of magnitude lower than concentrations observed in the developed areas (Figures 14a and 14b). Concentrations of NH_3, nitrate+nitrite, and TKN for the natural catchments were about one order of magnitude lower than those for the developed catchments; conversely, TSS concentrations showed no significant difference between geologic setting (Figures 15a and 15b). Comparison of fluxes (i.e., mass loading per unit area) between the natural and the developed catchments showed that fluxes for As, Cu, Fe, Pb, Ni, Zn were one order of magnitude lower in natural catchments (Figure 16); NH_3 concentrations were also one order of magnitude lower for natural catchments than for developed catchments (Figure 17).

Wet weather bacteria levels in the Los Angeles River were higher than those from natural sites, although the differences were not as great as during dry weather (Figure 7). Stormwater bacteria levels at the natural catchments were approximately two to three orders of magnitude lower than those at developed sites in Los Angeles River watershed (Figure 18). Kruskal-Wallis ANOVA on ranks showed that differences between wet weather bacteria levels were significant. It should be noted that bacteria monitoring in the Los Angles River included fecal coliforms instead of *E. coli*, precluding a direct comparison with the natural sites. However, based on an assumption that *E. coli* levels typically equal 80% of fecal coliforms, median *E. coli* levels in the Los Angeles River were almost 20 times higher than those observed at the natural sites.

In all cases, the variability observed in the natural catchments was substantially larger than that observed in the developed catchments both in terms of FWMCs and fluxes based on %CV (Table 20). For example, in the developed catchments, the geometric mean of FWMCs for Fe was 9,729 µg/L and the geometric standard deviation was 18. Comparatively, the geometric mean for iron was 962 µg/L and the geometric standard deviation was 11 in the natural catchments. Greater %CVs in the natural catchments resulted from the larger geometric standard deviation compared with the geometric value.

Discussion

Constituent concentrations from natural areas were generally one order of magnitude lower than those from the developed catchments, with the exception of TSS. Both FWMC and flux of TSS in the natural catchments were similar to those in the developed catchments, indicating that natural areas may be a substantial source of TSS to downstream areas. Previous studies on developed catchments have reported a strong correlation between particle-bound pollutant load and TSS, particularly for metals (Characklis and Wiesner 1997, Stenstrom *et al*. 1997). However, as shown in this study, high TSS from natural catchments does not automatically correspond to 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 differ 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 transport and deposition patterns.

Metal concentrations were compared with the California Toxics Rules (CTR) acute toxicity standards for inland surface waters (freshwater aquatic life protection standards; Table 21a). Concentrations were consistently below the CTR standards for all metals except for a few isolated exceedances for copper. When compared to the CTR criteria, total copper concentrations from individual samples exceeded the standard in 15 out of a total of 133 samples analyzed, while none of the FWMC values exceeded CTR standards (Figure 19a). However, when dissolved concentrations of copper[7] were compared with the CTR standard, only one out of 133 values exceeded CTR standard (Figure 19b).

The CTR criteria are based on dissolved concentrations; hence the CTR provides a simple matrix for the conversion of total to dissolved concentrations. However, as shown in this study, the ratio of particulate to dissolved metal concentrations varies over the course of a storm. Therefore, it is difficult to infer toxicity from an instantaneous sample. Bioavailability, and thus toxicity, will be affected by numerous factors, including partitioning between particulate and dissolved phases, pH, conductivity and concentration of DOC (Paulson and Amy 1993). Therefore, estimates of metal toxicity should be based on direct measure of dissolved concentrations.

There are no established nutrient standards available for comparison to data collected from the natural catchments in this study. However, in December 2000, USEPA proposed guidelines of 0.363 mg/L, 0.155 mg/L, 0.518 mg/L, and 0.030 mg/L for TKN, nitrate+nitrite, TN, and TP, respectively for Ecoregion III, 6, which includes southern California (USEPA 2000; Table 21b). The geometric means of flow-weighted concentrations of TKN and TP in the natural catchments were similar or below the proposed standards; however, the geometric means of nitrate+nitrite and TN were above the proposed levels. Higher levels of nitrate+nitrite, which lead to high TN (TN = TKN+ nitrate+nitrite) in the natural areas, suggest that wet weather natural background levels for nutrients in southern California may exceed currently proposed USEPA guidelines. This may be because the USEPA guidelines are not specific for the wet weather only, but based on the lower quartile of all existing nutrient data, including data from both wet and dry conditions. Thus, the USEPA guidelines for wet weather may underestimate actual natural background nutrient levels.

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[7] Dissolved concentrations of metals were analyzed separately from particulate concentrations only for stormwater samples collected in the winter of 2005/2006.

In addition to exceeding the proposed USEPA guideline, wet-weather TN level measured in this study were close to levels considered eutrophic by Dodds *et al.* (Dodds *et al.* 1998). Dodds *et al.* classified 100 temperate streams in the United States and defined eutrophic condition as the upper one-third of observed nutrient levels. This discrepancy implies that natural streams in southern California may be substantial sources of nitrogen to downstream waterbodies that have the potential to contribute to nitrogen levels with associated algal growth in receiving waters.

Several factors could have influenced the estimates of natural concentrations and fluxes provided by this study. First, the treatment of NDs, which occur fairly frequently given the inherently low concentrations of constituents in natural catchments can significantly impact concentration estimates (Table 22). However, the assignment of a value of one-half of the detection limit to NDs are not expected to change the findings of this study. This can be illustrated by examining the nutrient data, which had a higher incidence of NDs than metals due to higher MDLs (Table 5). In this study's data, 53% of the total phosphorous samples were ND. If a value equal to the detection limit (instead of one-half of the detection limit) had been assigned to these samples, the overall geometric mean concentration would have increased by only 0.05%, primarily due to the large fluctuation of concentrations over the course of each storm event. Because several high concentrations during a storm event greatly influence the FWMC, the value assigned to a few samples at lower concentrations does not substantially affect the mean. Concentrations of TP in the natural catchments typically exhibited a change of five to six orders of magnitude during a storm event. If the NDs occurred during low flow, the change of the NDs was not likely to affect the FWMCs.

The role of aerial deposition, which was not accounted for in this study, is another factor that could have influenced the this study's estimates. If aerial deposition had been considered, the natural background levels estimated by this study would have been even lower. Atmospheric deposition can be a significant factor that affects loadings in natural areas. For example, in Midwestern and Northeastern streams, atmospheric deposition of nitrogen can account for nearly all downstream nitrogen loads (Smith *et al.* 1987, Puckett 1995). Studies show that rates of atmospheric nitrogen deposition were high in the xeric wet region, which includes a majority of coastal catchments in southern California (Clark *et al.* 2000). The study by Smith *et al.* (2003) reported that loadings of TN and TP could be 16 to 30% lower when corrected with atmospheric deposition rate. This suggests that the nutrient levels in the natural catchments could be lower than values presented in this study. Sabin *et al.* (2005) showed that atmospheric deposition potentially accounted for as much as 57 to 100% of the total trace metal stormwater loads to 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 and Kiefer 1999, 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 controlled most variability in among natural catchments. In this study, land cover did not significantly impact water quality. This result differs from previous studies which have reported that land use and land cover types have a significant impact on water quality (Larsen 1988, Detenbeck *et al.* 1993, Johnes *et al.* 1996, Richards *et al.* 1996, Johnson *et al.* 1997a, Gergel *et al.* 1999). 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 types of natural land cover on water quality has not been extensively examined prior to this study. Our ANOVA results showed that levels of constituents were not significantly different between two different land cover groups (forest and shrub). This suggests that any differences that might occur due to different types of natural land cover are subtle, and not a key deterministic factor in water quality, unlike the relatively dramatic differences between natural vs. developed land cover previously investigated. However, Miller *et al.*' study (2005) addressed the importance of land cover on natural water quality, indicating that the ecosystem 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 (one-order of magnitude) than maximum values for developed land uses observed in southern California coastal catchments (Ackerman and Schiff 2003). Values from Miller *et al.* were one to two orders of magnitude higher than the upper ends of 95% CI values for nutrients presented in this study. Miller *et al.* suggested that nutrients that were driven from mature organic horizons (O-horizons[8]) might have had little contact with mineral soil or root zone where strong retention and/or uptake of these ions would be expected. The major difference in nutrient levels between the Sierran catchments and the natural catchments examined in this study may be due to difference in abundance of O-horizon. 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)). The Lake Tahoe region and the southern California mountainous areas are located in California, but they are categorized as different ecoregions[9] and the nutrient levels vary by up to two orders of magnitudes. This highlights the importance of identifying region-specific background water quality and potentially significant impact of land cover on water quality.

Other environmental factors, such as catchment size, flow-related factors, rainfall, slope, and canopy cover, as well as land cover, did not significantly affect the variability of water quality. This suggests that the findings of this study may be extrapolated as natural background water quality to the southern California's coastal region. For example, natural catchments in this study were relatively small because few large undeveloped watersheds exist in the coastal region of southern California. 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. This allows extrapolation of this study's findings to natural background water quality for other larger or smaller developed watersheds.

Temporal patterns (within and between storm variability) were different in natural catchments than those 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. The

[8] O-horizon: At the top of the profile is the O horizon. The O horizon is primarily composed of organic matter. Fresh litter is found at the surface, while at depth all signs of vegetation structure has been destroyed by decomposition. The decomposed organic matter, or humus, enriches the soil with nutrients (nitrogen, potassium, etc.), aids soil structure (acts to bind particles), and enhances soil moisture retention.

[9] Ecoregions denote areas of general similarity in ecosystems and in the type, quality, and quantity of environmental resources. They are designed to serve as a spatial framework for the research, assessment, management, and monitoring of ecosystems and ecosystem components. By recognizing the spatial differences in the capacities and potentials of ecosystems, ecoregions stratify the environment by its probable response to disturbance. These general purpose regions are critical for structuring and implementing ecosystem management strategies across federal agencies, state agencies, and nongovernmental organizations that are responsible for different types of resources within the same geographical areas (http://www.epa.gov/wed/pages/ecoregions.htm).

observation of 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 first flush can occur up to several hours prior than the peak flow during a storm (Hoffman *et al.* 1984, Smith *et al.* 2000, Stein *et al.* 2006). The existence of first flush should not be assumed in all cases. Intensive monitoring of stormwater runoff from some (usually larger) catchments has failed to observe this phenomenon, mainly due to the complex commingling of flows from different areas within a large catchment (New South Wales Environment Protection Authority 2005). The lack of first flush in the natural catchments may be explained by the fact that first flush is generally seen only where the supply of pollutants is limited (New South Wales Environment Protection Authority 2005). For example, in natural catchments, sediment, as well as and associated bound pollutants, generated from soil erosion will 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 of TSS-correlated constituents, especially metals, during storms, as indicated by the spread observed in the pollutograph of natural areas. This may partially explain the comparability of TSS FWMC for natural and developed areas. Differences in pollutant delivery timing for natural areas compared to developed areas may provide some ability to segregate downstream loads that are anthropogenic in origin and most prevalent in the early part of storms, from those that are natural in origin and most prevalent later in the storm. This should be investigated further through additional empirical and modeling analysis.

Table 16. Wet weather geometric means (Geomean), upper and lower ends of 95% confidence interval (CI) for flow-weighted mean concentrations (FWMC), mass loads (mass load per storm event), and fluxes (mass load per unit area); loads and fluxes are per storm event.

Metals	FWMC (μg/L)			Mass Load (g)			Flux (g/km^2)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Arsenic	0.39	0.71	0.21	17.40	44.63	6.78	0.87	1.91	0.40
Cadmium	0.14	0.24	0.08	6.26	15.46	2.53	0.31	0.73	0.14
Chromium	1.40	3.09	0.63	62.59	188.88	20.74	3.13	7.98	1.23
Copper	1.54	3.17	0.75	68.84	201.07	23.57	3.45	8.68	1.37
Iron	962	2313	400	43100	139746	13293	2158	6160	756
Lead	0.51	1.06	0.24	22.80	64.84	8.02	1.14	2.94	0.44
Nickel	1.03	2.46	0.43	46.24	152.10	14.06	2.32	6.36	0.84
Selenium	0.33	0.60	0.18	14.93	41.22	5.41	0.75	1.85	0.30
Zinc	5.32	11.16	2.54	238.44	680.97	83.49	11.94	31.52	4.52
Nutrients	**FWMC (mg/L)**			**Mass Load (kg)**			**Flux (kg/km^2)**		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Ammonia	0.04	0.08	0.02	1.91	4.68	0.78	0.10	0.21	0.04
Dissolved Organic Carbon	6.26	9.54	4.11	338.67	915.76	125.25	11.83	30.35	4.61
Nitrate+Nitrite	0.34	0.58	0.19	15.01	36.20	6.22	0.75	1.54	0.37
Orthophosphate	0.04	0.06	0.02	1.91	4.35	0.84	0.10	0.20	0.05
Total Kjeldahl nitrogen	1.21	1.55	0.95	70.74	255.66	19.58	2.63	7.18	0.96
Total Organic Carbon	6.28	9.91	3.98	339.54	935.81	123.20	11.86	31.31	4.49
Total Phosphorus	0.12	0.21	0.07	1.12	4.54	0.28	0.09	0.55	0.02
Solids	**FWMC (mg/L)**			**Mass Load (kg)**			**Flux (kg/km^2)**		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Total Dissolved Solids	251	338	187	11200	25300	4990	637	1260	320
Total Suspended Solids	98.12	280.84	34.28	5069.70	20983.90	1224.84	257.25	854.39	77.46
Microbes	**Concentration (MPN/100ml)**								
	Geomean	Upper CI	Lower CI						
E. coli	125	399	39.70						
Enterococcus	140	511	38.80						
Total coliform	4460	13100	1510						

Table 17. Wet weather results of stepwise selection of environmental variables using redundancy analysis (RDA)[a].

Environmental Variable	Extra Fit	Cumulative Fit	Significance (p value)
Sedimentary Rock	0.119	0.119	0.025
Igneous Rock	0.119	0.239	0.025
Elevation	0.094	0.333	0.105
Peak Flow	0.055	0.388	0.390
Mean Flow	0.047	0.435	0.200
Catchment Size	0.044	0.479	0.890
Canopy Cover	0.044	0.522	0.080
Total Runoff Volume	0.040	0.562	0.305
Latitude	0.039	0.601	0.190
Baseline Flow	0.031	0.632	0.905
Total Rainfall	0.027	0.660	0.220
Shrub	0.023	0.683	0.445
Forest	0.023	0.706	0.445
Slope	0.017	0.723	0.165

[a]Variables are given in the order of inclusion. The extra and cumulative fits are given as %ages relative to the total sum of squares over all water quality variables (comparable to the % explained variance in univariate regression). Number of observations: 472; total number of water quality variables: 18. Significance was determined by Monte Carlo permutation using 199 random permutations.

Table 18. Statistical summary of RDA for wet weather water quality.

		Axes			
		1	2	3	4
Eigenvalues		0.15	0.03	0.37	0.12
Water quality Environment correlations		0.60	0.56	0.00	0.00
Cumulative Percentage Variance	Water Quality Data	15.10	17.90	55.00	66.60
	Water Quality Environment Relation	84.50	100	0.00	0.00

Table 19. Canonical coefficients of environmental variables with the first two axes of RDA for wet weather concentrations of metals, nutrients, and solids.

Environmental Variables	Water Quality Constituent Axes	
	1	2
Igneous Rock	0.52	-0.28
Sedimentary Rock	-0.52	0.28
Elevation	0.44	0.38

Table 20. Comparison of percent coefficient of variation (%CV) between natural and developed catchments. for metals, nutrients, and solids in the wet weather condition. Data not available ('-').

Metal	**Natural**			**Developed**		
	Sample Size	Concentration %CV	Flux %CV	Sample Size	Concentration %CV	Flux %CV
Arsenic	29	1355	996	36	71	115
Cadmium	29	3088	3205	36	437	618
Chromium	29	636	416	36	32	49
Copper	29	474	367	36	8	15
Iron	29	1.20	0.80	32	0.20	0.02
Lead	29	1476	1175	36	22	36
Nickel	29	1054	693	36	26	38
Selenium	29	1537	1620	20	520	369
Zinc	29	143	121	36	2.00	3.40
Ammonia	29	13566	8809	9	885	230
Dissolved Organic Carbon	19	41	69	0	-	-
Nitrate+Nitrite	29	1357	949	19	460	542
Orthophosphate	27	9095	7009	0	-	-
Total Kjeldahl Nitrogen	15	133	278	6	57	88
Total Organic Carbon	19	44	73	0	-	-
Total Phosphorus	21	12264	12753	13	3336	2174
Total Dissolved Solids	26	0.90	0.90	0	-	-
Total Suspended Solids	26	16	9	36	4	4
E. coli	-	-	-	26	-	-
Enterococcus	12	5.00	-	26	0.03	-
Total Coliform	12	0.07	-	26	0.00	-

Table 21a. Water quality standards for metals using the California Toxics Rule (CTR) – Inland surface waters for freshwater aquatic life protection. Standards for hardness dependency based on the hardness of 100 mg/L.

Metal	Maximum Concentration (µg/L) One-hour Average	Hardness
Arsenic	340	Independent
Cadmium	4.52	Dependent
Chromium	550	
Copper	14.00	
Nickel	469.17	Dependent
Lead	81.65	
Selenium	19.34	Independent
Zinc	119.82	Dependent

Table 21b. Comparison of USEPA proposed nutrient criteria for rivers and streams for Ecoregion III, 6 (Central and southern California) with wet weather geometric means.

Nutrient	Ecoregion III, 6 (mg/L)	Natural Catchments in Wet Weather Geometric Mean (mg/L)
Total Kjeldahl Nitrogen	0.36	0.34
Nitrate+Nitrite	0.16	1.21
Total Nitrogen	0.52	1.55
Total Phosphorus	0.03	0.03

Table 22. Percent non-detects (%ND) for wet weather data. Constituents not shown did not have NDs.

Constituent	No of ND	No of Sample	%ND
Arsenic	62	355	17.5
Cadmium	96	355	27.0
Chromium	11	355	3.1
Copper	9	254	3.5
Lead	76	355	21.4
Nickel	21	355	5.9
Selenium	56	355	15.8
Ammonia	73	216	33.8
Nitrate	44	220	20.0
Nitrite	93	218	42.7
Orthophosphate	41	210	19.5
Total Phosphorus	112	212	52.8
Total Suspended Solids	34	213	16.0

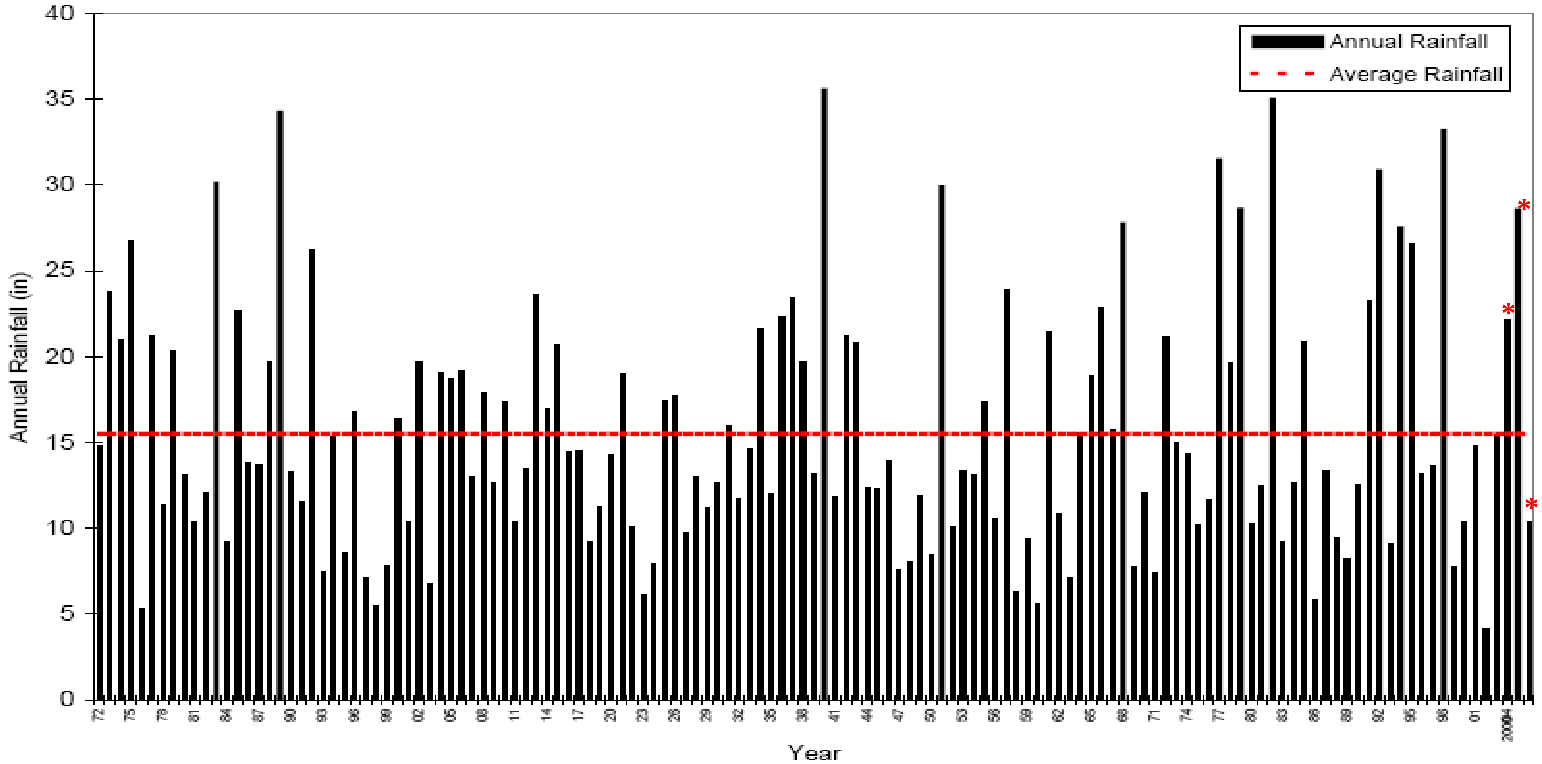

Figure. 8. Comparison of annual rainfall (wet season) at LADPW station #716, Ducommun St., Los Angeles in 2004, 2005, and 2006 with the average rainfall over 135 years. Red dotted line indicates the average annual rainfall of 135 years. * indicates the period of this study from 2004 through 2006.

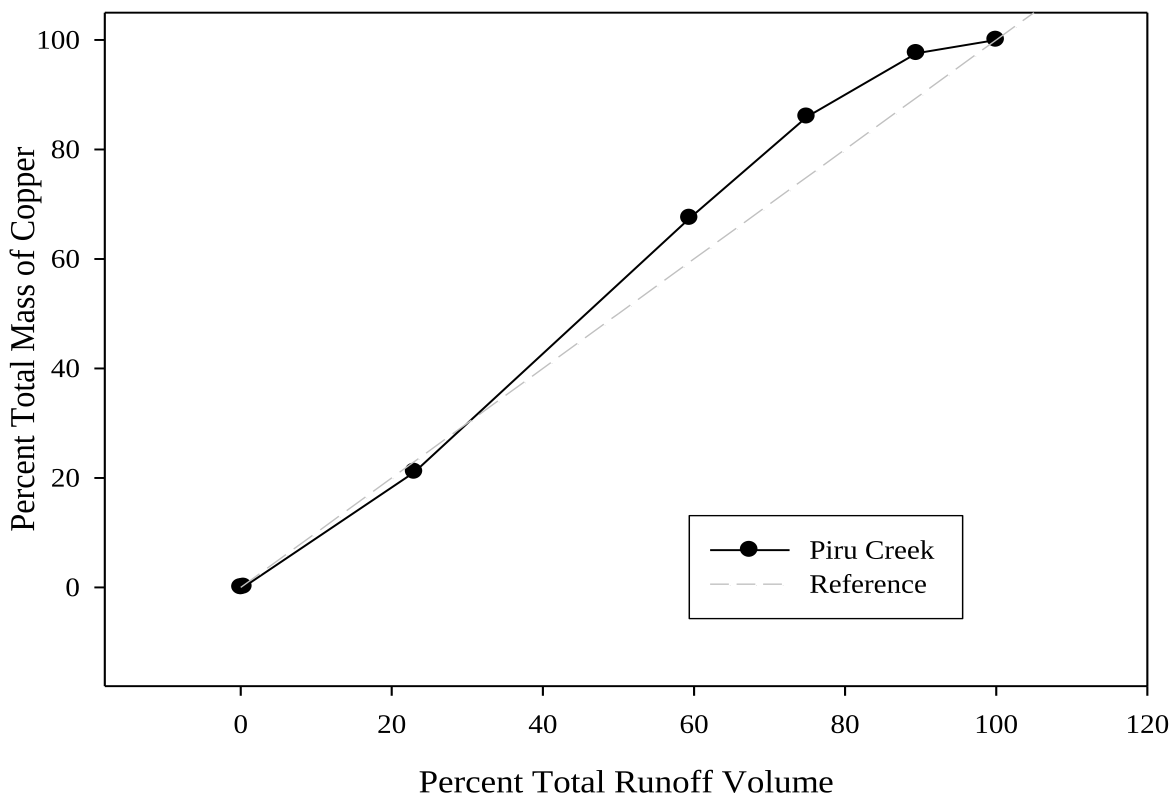

Figure 9. Cumulative copper mass loads for a storm (February 27 through March 1, 2006) at Piru Creek. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume.

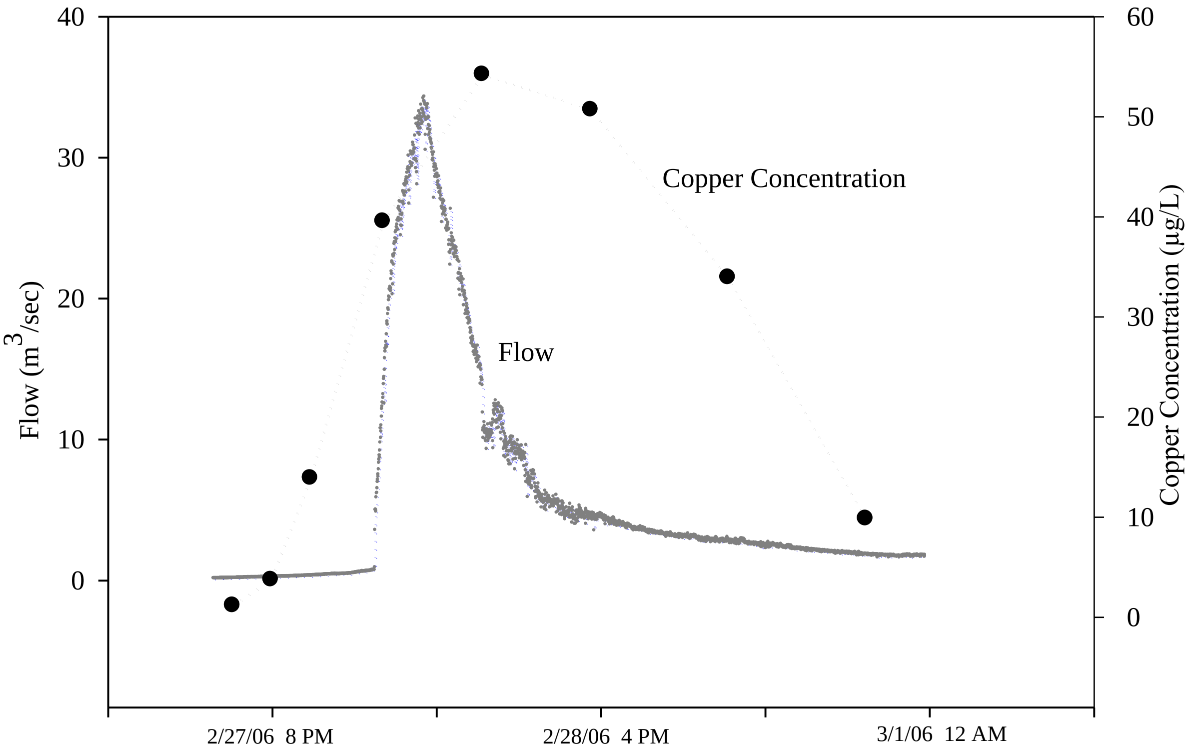

Figure 10. Variation in total copper concentrations with time for storm event in Piru Creek from February 27 through March 1, 2006.

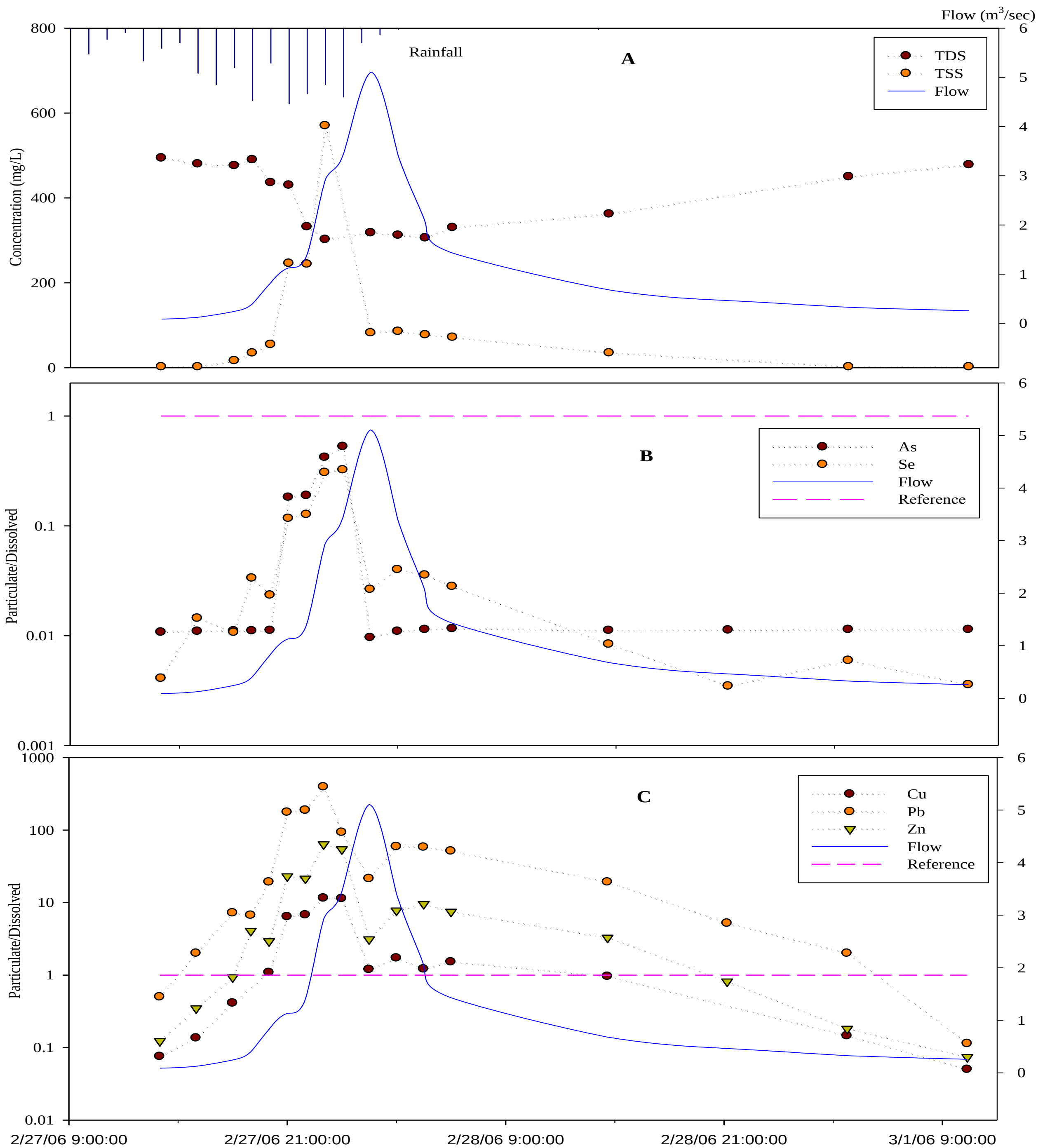

Figure 11. Change in the ratio of particulate metals over dissolved metals over the course of a storm event at Bear Creek, a tributary to North Fork Matilija, CA.

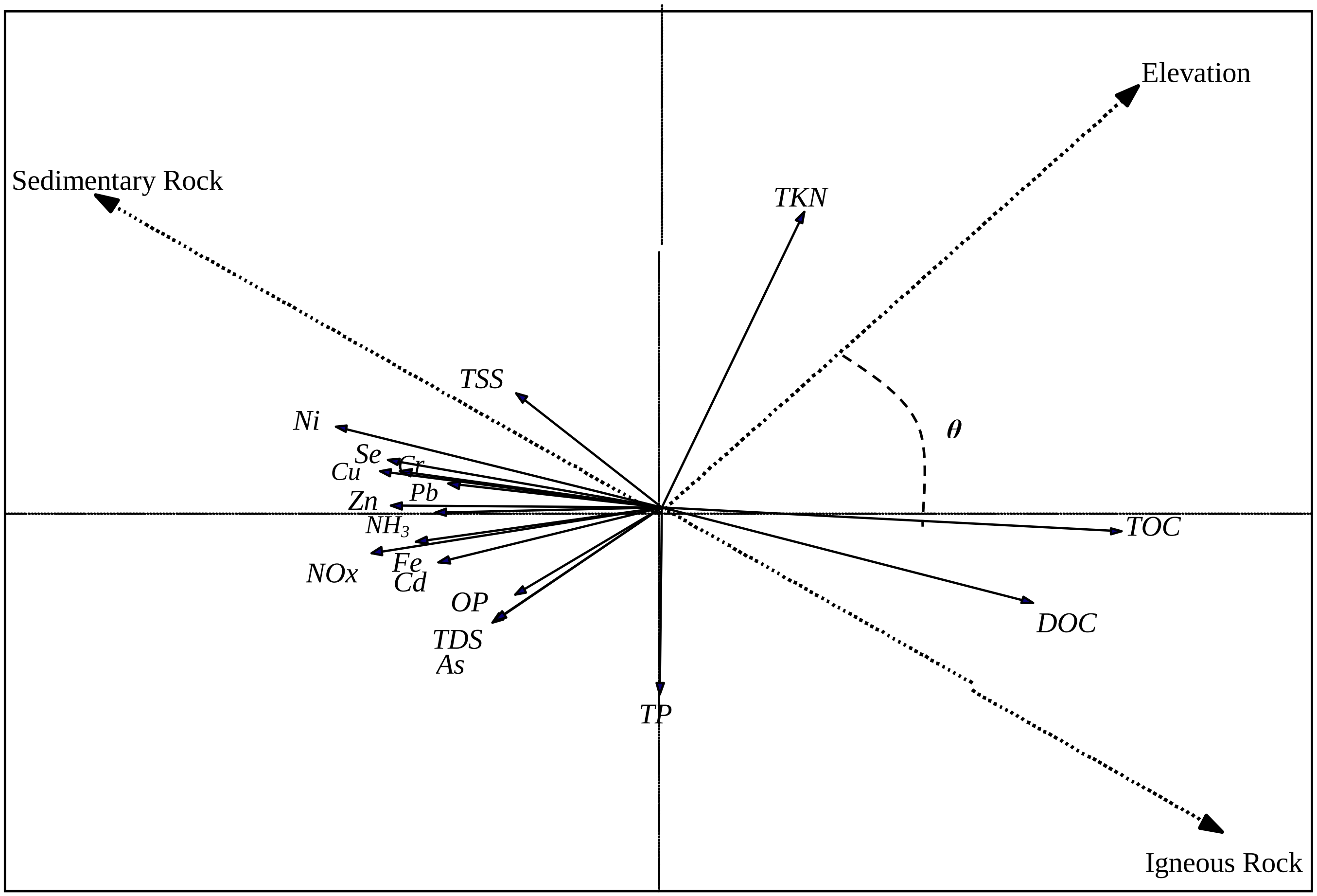

Figure 12. Correlation biplots showing the relations between wet weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigenvalues: 0.151 and 0.0280 for the first (horizontal) and second (vertical) axes. *cos θ ≈* correlation coefficient between two variables (arrows). Longer arrow indicates which factor is more important in generating variability. 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); and Nitrate+Nitrite (NOx).

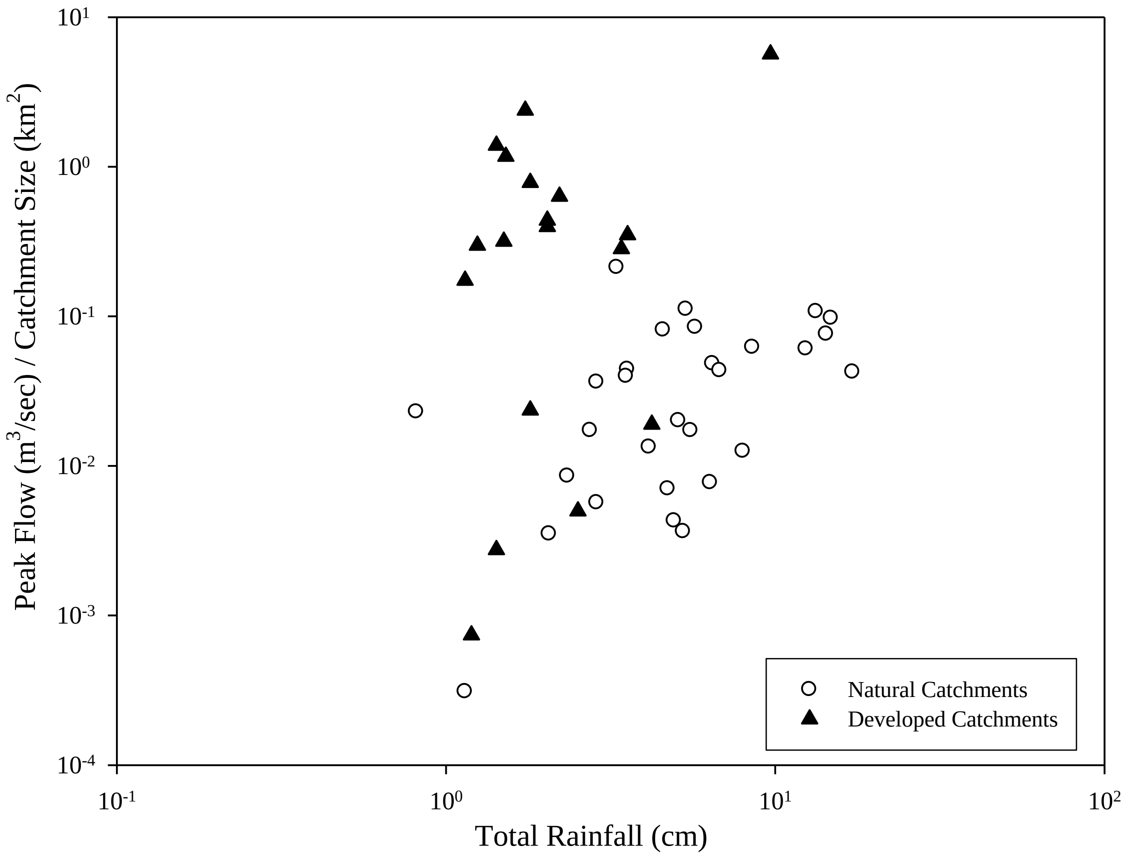

Figure 13a. Comparison of peak flow over catchment size vs. rainfall between natural catchments and developed catchments; X and Y axes are in log scale.

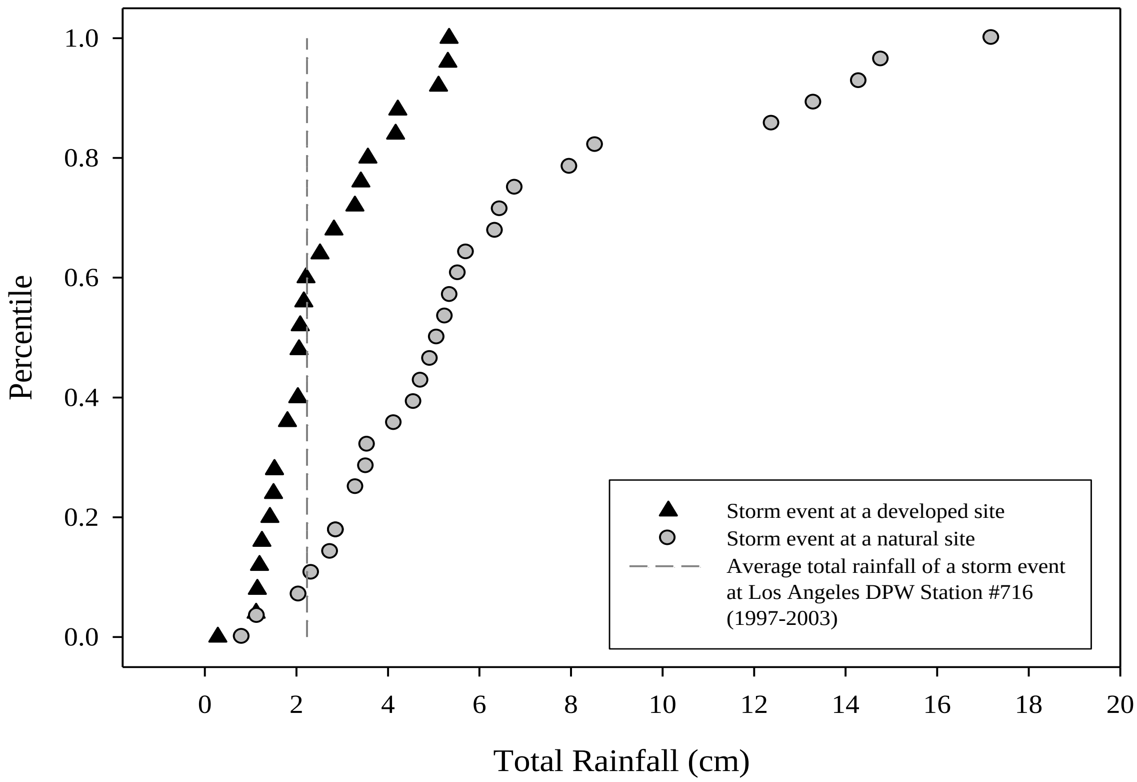

Figure 13b. Distribution of storm events in terms of total rainfall per storm event.

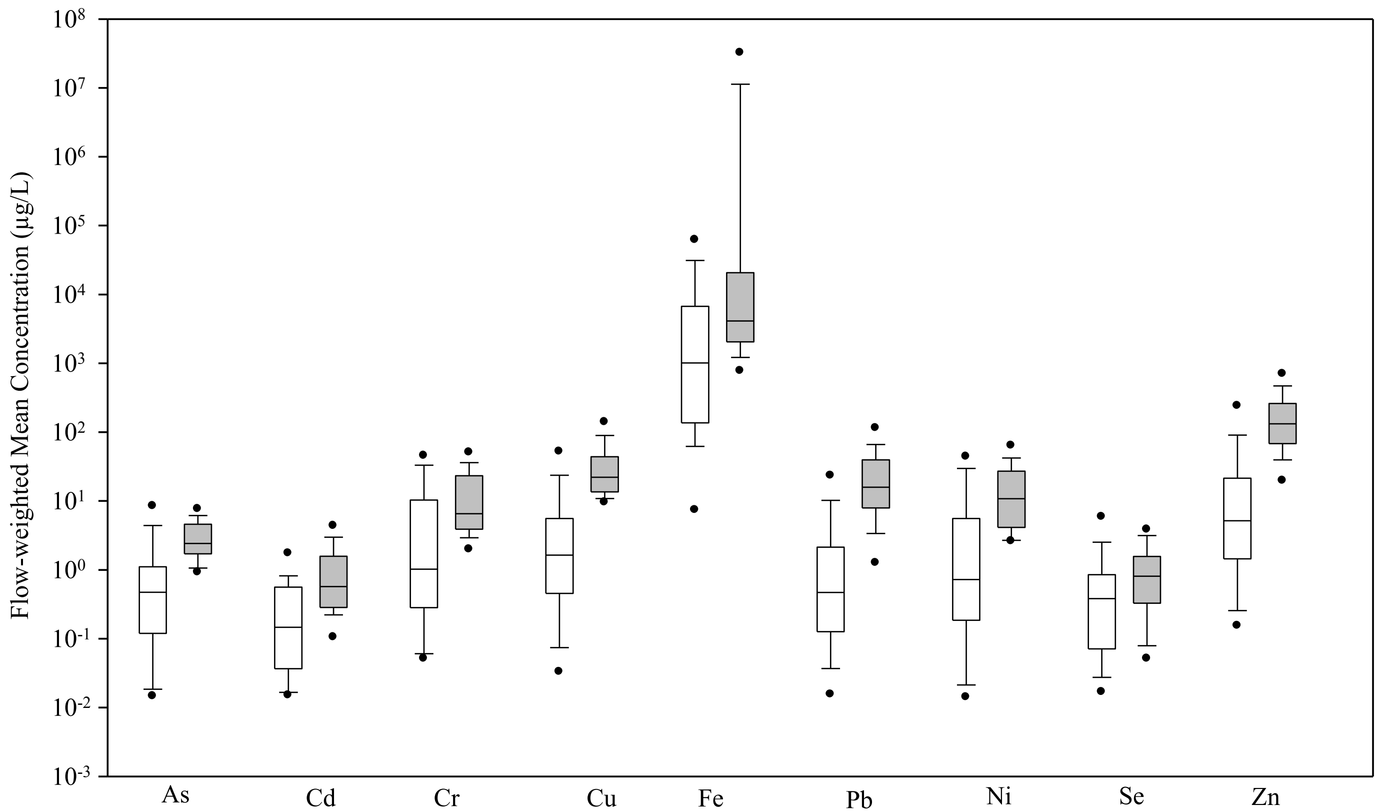

Figure 14a. Comparison of wet weather flow-weighted concentrations of metals between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.

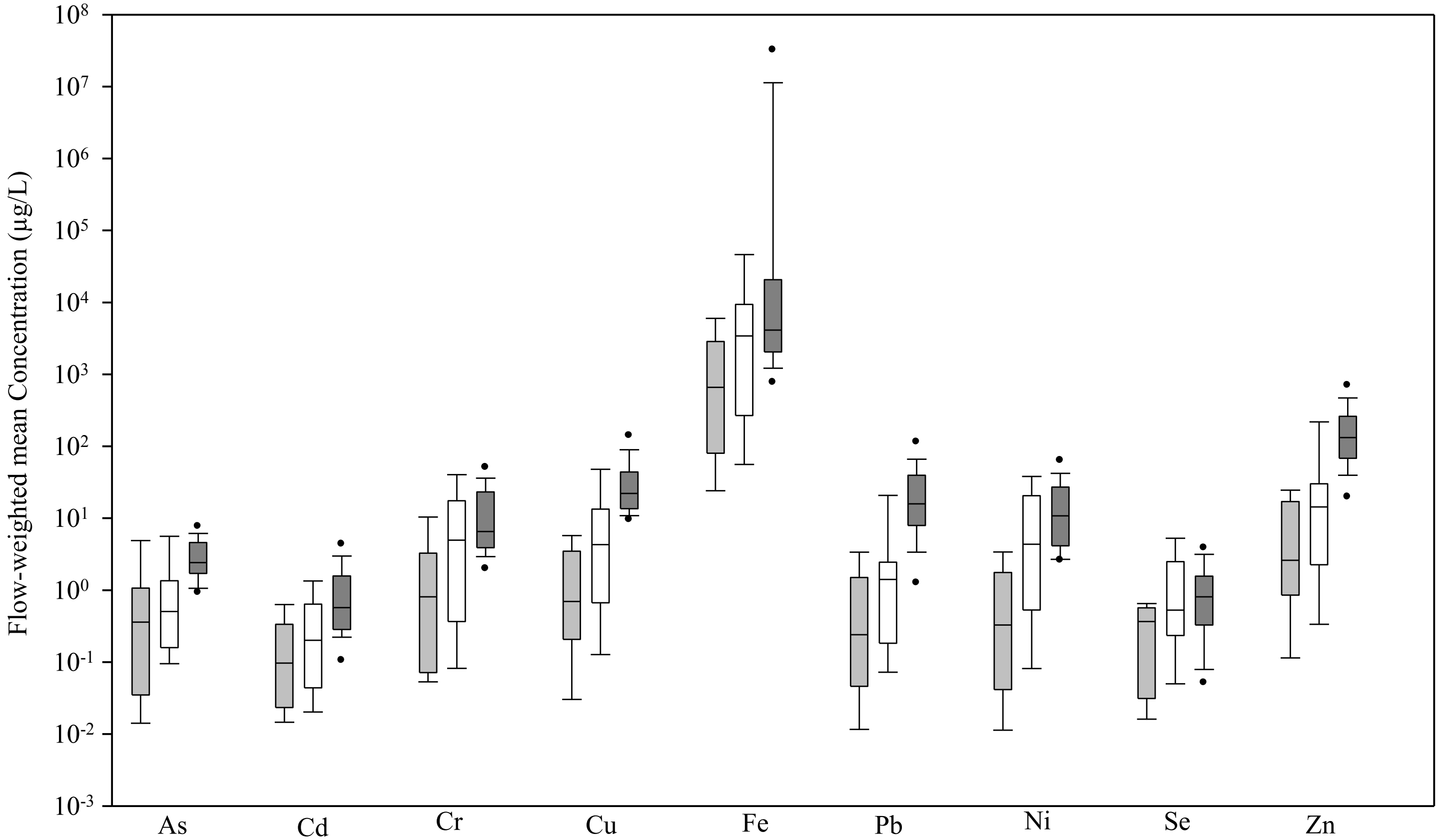

Figure 14b. Comparison of wet weather flow-weighted concentrations of metals between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.

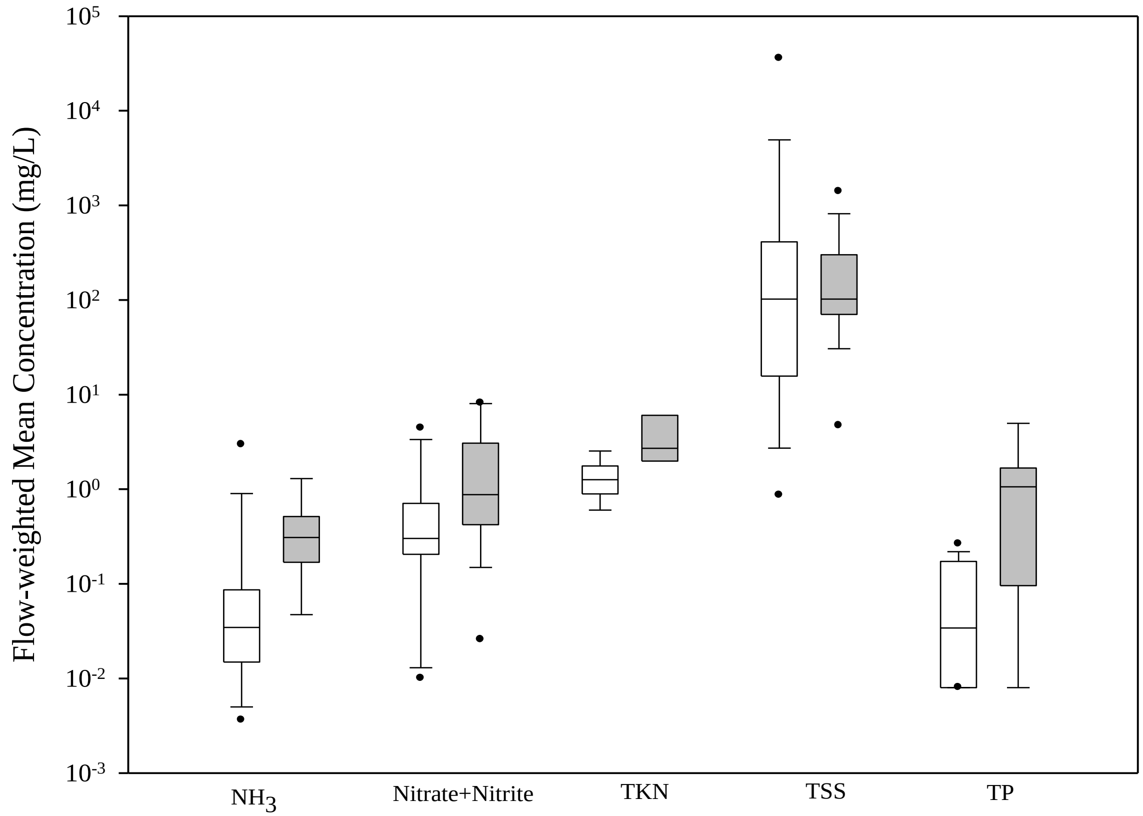

Figure 15a. Comparison of wet weather flow-weighted concentrations of ammonia (NH_3), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total suspended solids (TSS), and total phosphorous (TP) between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. The Y axis is in log scale.

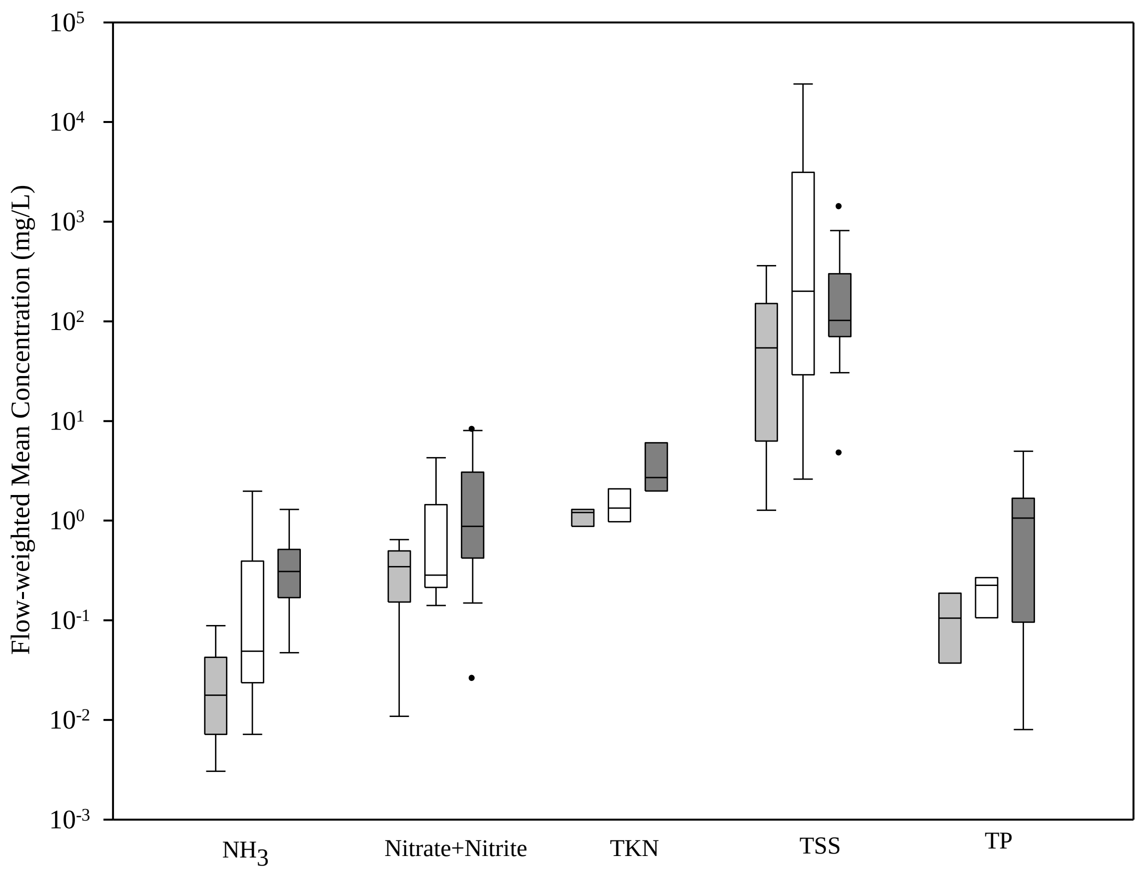

Figure 15b. Comparison of wet weather flow-weighted concentrations of ammonia (NH_3), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total suspended solids (TSS), and total phosphorous (TP) between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. Y axis is in log scale.

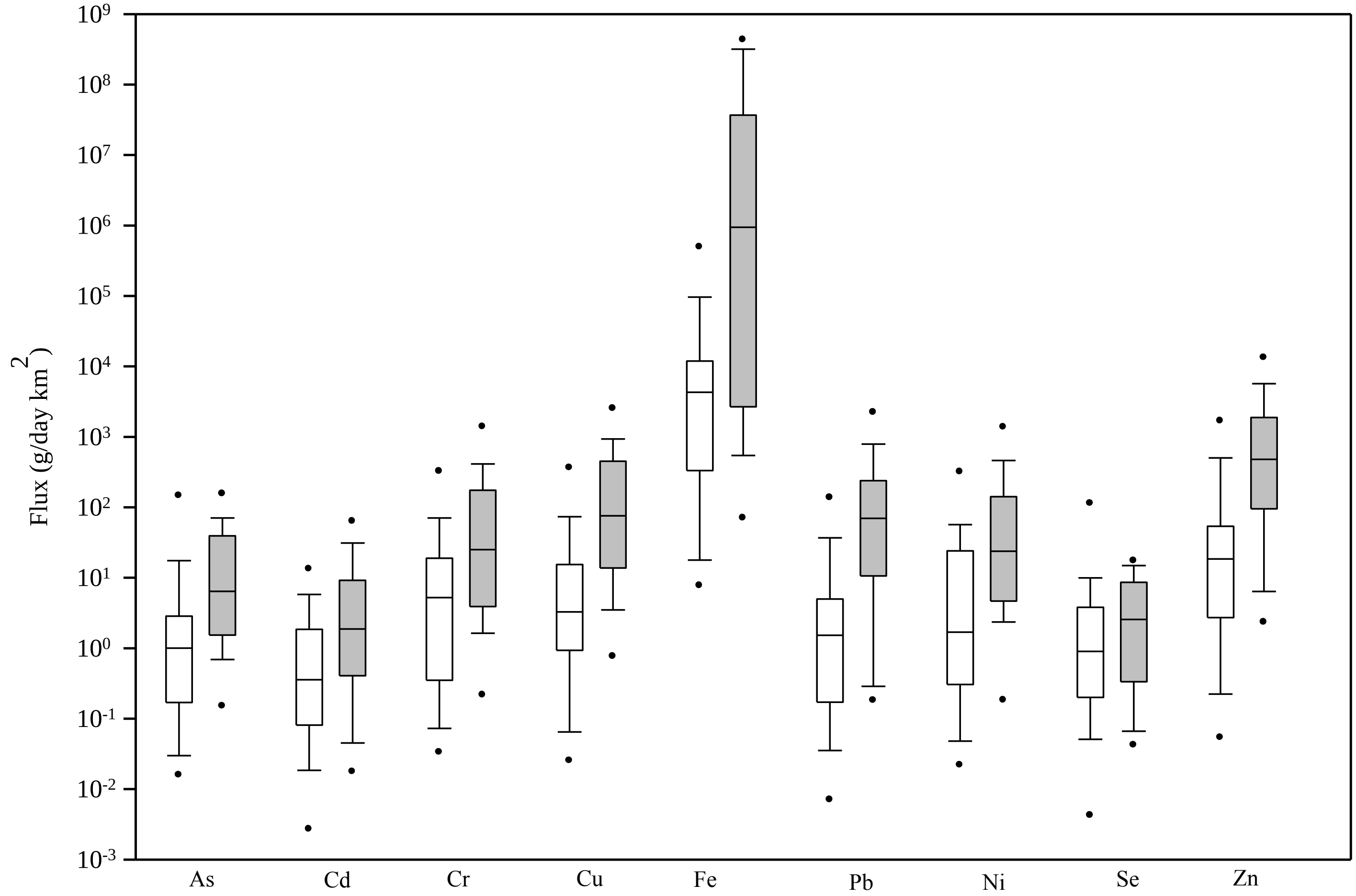

Figure 16. Comparison of wet weather fluxes of metals between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. Y axis is in log scale

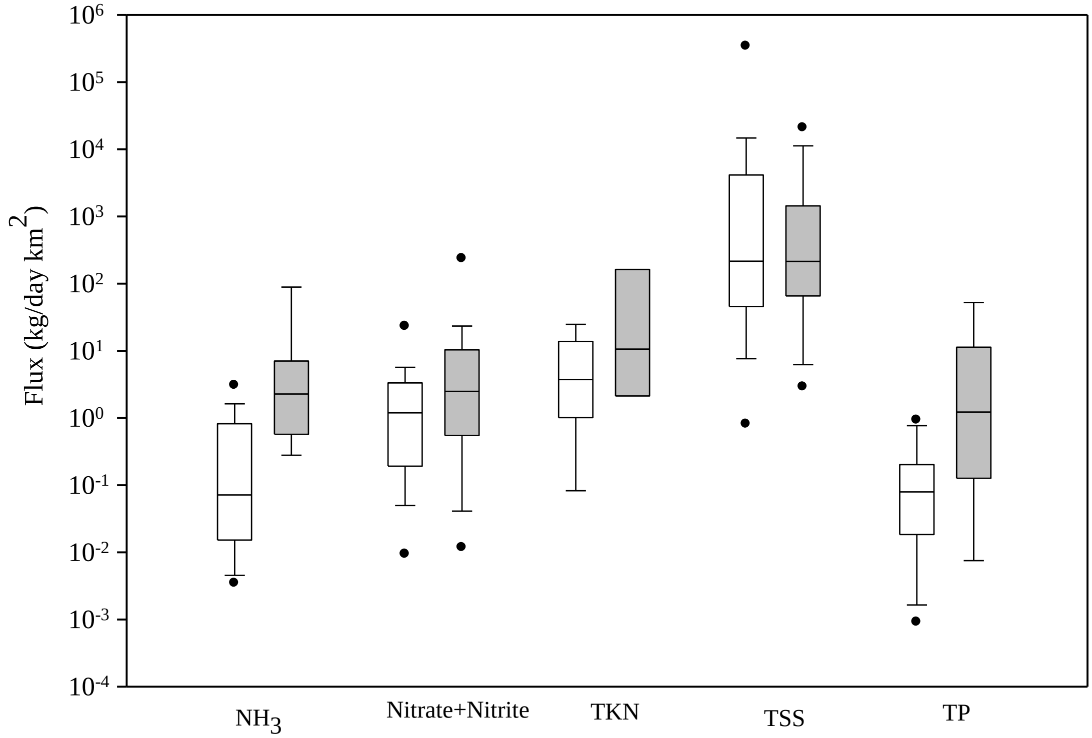

Figure 17. Comparison of wetweather fluxes of ammonia (NH_3), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. All fluxes are expressed in kg/day km^2. Y axis is in log scale.

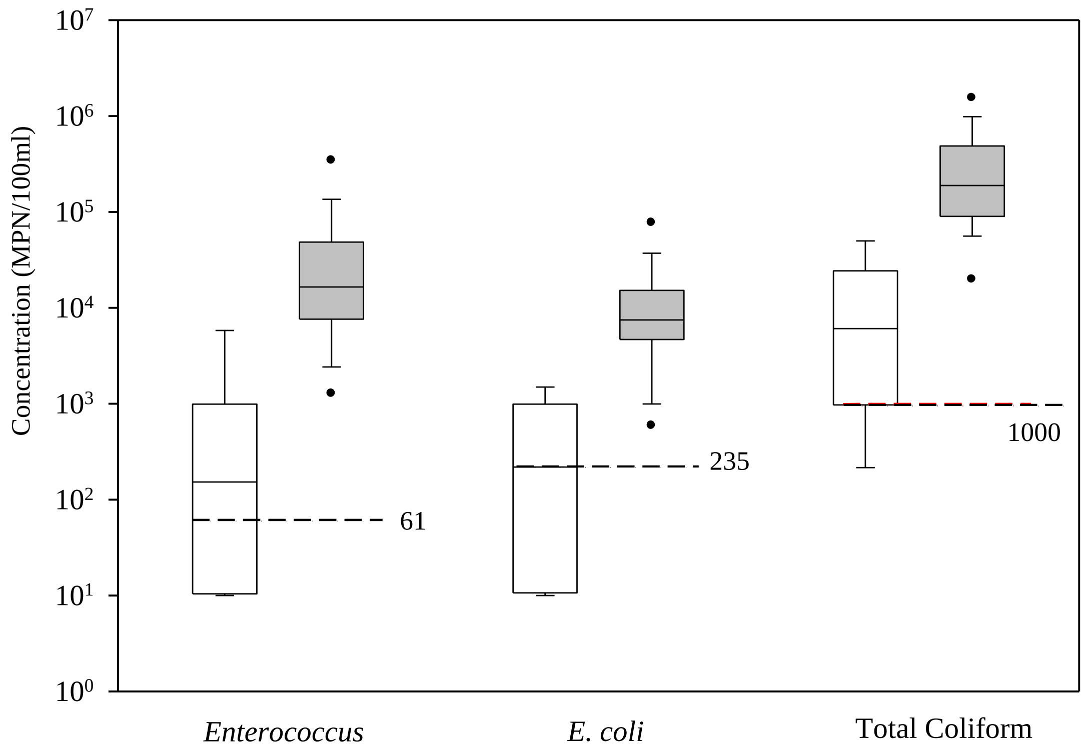

Figure 18. Comparison of wet weather flow-weighted concentrations of bacteria between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. .Y axis is in log scale. Dotted lines represent Department of Health and Safety draft guideline for freshwater recreation.

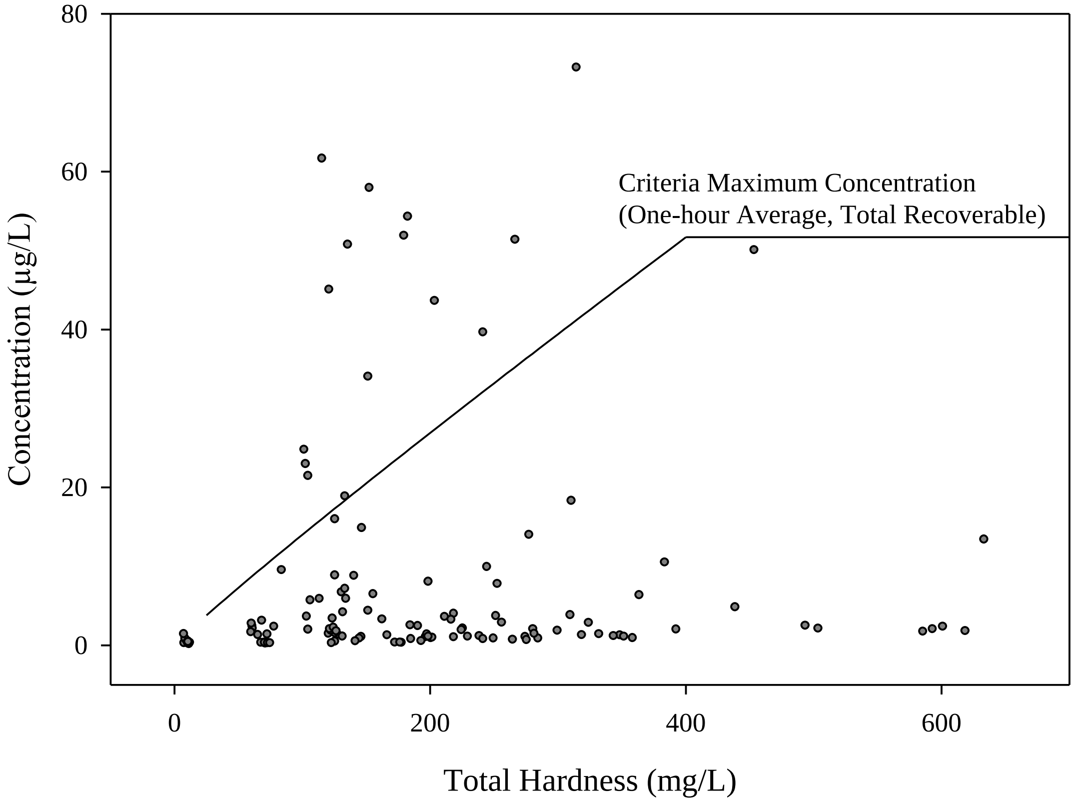

Figure 19a. Copper concentrations at natural catchments compared with the hardness-adjusted standard under the California Toxics Rule (CTR). The stormwater concentrations are compared with the acute standard.

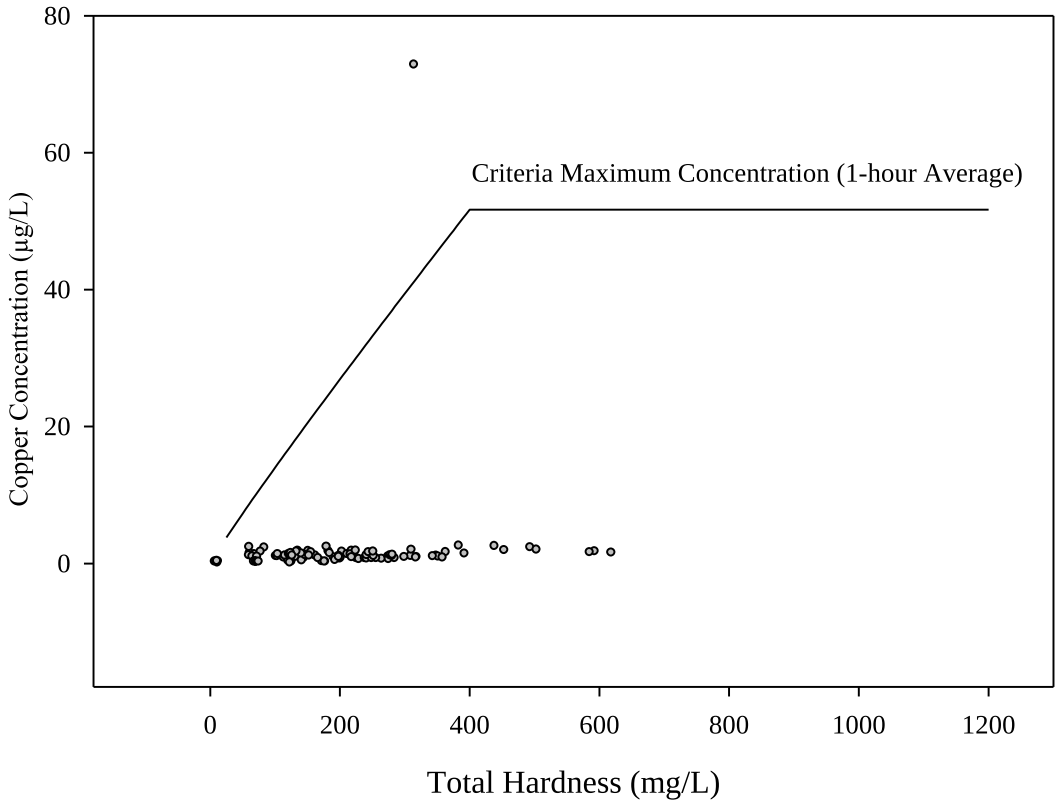

Figure 19b. Wet weather dissolved copper concentrations at natural catchments compared with the hardness-adjusted standard under the California Toxics Rule (CTR). The stormwater concentrations are compared with the acute standard.

ESTIMATION OF ANNUAL LOADS

Background

Constituent concentration ranges from natural areas that were documented in prior sections of this discussion provide valuable understanding of natural background water quality in southern California's costal watersheds (Figure 20). However, estimates of watershed loadings are required for many regulatory and management programs. For example, a number of water quality regulations (e.g., TMDLs) are based on daily or annual pollutant loads, rather than on concentration. Furthermore, evaluation of the overall contribution from natural areas to total watershed loading requires estimates of annual loadings based on measured concentrations from natural areas combined with long-term flow data.

Annual loading estimates should account for constituent contributions during both wet (storm) and dry (non-storm) periods. Unfortunately, existing ambient water quality monitoring studies often collect concentration data from natural areas only during dry weather. Seldom are there sufficient flow and water chemistry data available for both wet and dry seasons to fully estimate annual loading. Lack of distinct wet and dry weather data is particularly problematic in areas with semi-arid climates, such as southern California. Previous studies indicate that constituent concentrations from natural areas during wet and dry weather conditions might be within the same order of magnitude. However, non-storm flow can constitute a significant portion of the total annual flow, especially during years with low rainfall. Consequently, dry weather loading has the potential to be a substantial component of the total annual constituent load. In southern California's developed watersheds, dry weather metal load has been shown to constitute minor to appreciable portions of the total annual load (McPherson *et al.* 2002, Stein *et al.* 2003, Stein and Tiefenthaler 2005). For example, McPherson *et al.* (2002) reported that dry weather load contributed 8 to 42% of the total annual trace metal load in the Ballona Creek watershed near Los Angeles, CA. Past studies of the relative contributions of dry vs. wet weather load have focused solely on developed/urban watersheds (Duke *et al.* 1999, McPherson *et al.* 2002, McPherson *et al.* 2005). These prior studies lack information on wet and dry weather concentrations and sufficient flow data to fully estimate loading from natural areas. This section provides estimates of annual load from natural areas during both wet and dry weather conditions.

Flow

Three of the six streams studied were perennial (flowed all year): Arroyo Seco, Sespe Creek, and Piru Creek. The remaining streams were intermittent (flowing until mid-July or mid-August 2006 before drying up). Rating curves used for the conversion of water level into flows at the water level logged sites are shown in Figures 21a and 21b. The average storm flow in the perennial streams was 10.27 m^3/sec, which was two orders of magnitude greater than the average non-storm flow at the perennial streams (Table 23).

The relative volume discharged during the storm vs. non-storm periods varied based perennial or intermittent stream type. The annual discharge volume of non-storm flow was larger than the annual discharge volume of storm flow over the ten-year period at the perennially flowing Arroyo Seco and Piru Creek. The storm and non-storm volumes were similar at Sespe Creek except for the 1995 water year (Figure 22). The annual storm discharge at the intermittent streams (Santiago Creek and Tenaja Creek) was more than double the annual non-storm discharge due to the discontinuity of flow from late summer through fall. For example, the annual storm discharge volume at Santiago Creek was 6.5×10^6 m^3 and the annual non-storm discharge volume was 2.5×10^6 m^3.

Percent differences between storm and non-storm discharge volumes at perennial streams were greater in years with less overall discharge, which were dry years (1999 to2004; Figure 22). This implies that the contribution of the non-storm flow to annual discharge volume becomes more important in dry years.

Ranges of annual fluxes and the contribution of non-storm flow to the fluxes

Annual fluxes for metals (except Fe) ranged from tens to hundreds of grams per year km^2. Nutrient fluxes varied largely among constituents and streams. Ammonia ranged from one to eight kilograms per year·km^2, OP and TP ranged from kilograms to tens of kilograms per year km^2, and other nutrients ranged from ten to thousands of kilograms per year·km^2. For example ammonia was found to be 3 kilograms per year km^2 at Arroyo Seco, and total organic carbon was found to be 1,320 kilograms per year km^2. Total suspended solids ranged from 4.2 to 4,059 metric ton per year km^2. The median, minimum, and maximum values for each constituent are summarized in Table 24.

Storm flow contributed the majority of annual fluxes for constituents except As, nutrients, TOC, and TDS (Figure 23). Total suspended solids were almost entirely derived from storm runoff. However, between 40 and 60% of As, Cd, and Se were derived from non-storm flow.

Loading in perennial vs. intermittent streams

In the intermittent streams, storm flow was a major source of most metals, all nutrients, and solids (Tables 25 and 26). More than 97% of the TSS load was contributed by storm flow. In perennial streams, even though the annual non-storm discharge accounted for more than one-half of the total annual discharge, a greater portion of the annual load was contributed by high constituent concentrations in the storm flow (Table 25s and 26). Non-storm flow contributed more to annual metal loads at perennial streams than at the intermittent streams. For example, the non-storm flow contributed 51 to 78% for Cd at the perennial streams, while the non-storm flow contributed 10 to 21% for Cd at the intermittent streams.

Annual flux was generally lower at the intermittent streams than at the perennial streams (Table 27). This mainly resulted from differences in the total annual discharge volume. In addition, the annual fluxes at Santiago Creek and Tenaja Creek were derived from the annual loads of only eight months, December 2005 through July 2006, because the streams dried up in July 2006. Yet, the annual fluxes at the perennial streams -- Arroyo Seco, Piru Creek, and Sespe Creek -- were derived from the annual loads of the entire 12 months, December 2005 through December 2006.

Discussion

Annual flux rates were significantly lower in natural catchments than in developed catchments in southern California (Table 27). This difference can be illustrated by comparing this study's results to data from Ballona Creek, which is located in southern California and includes a significant portion of the City of Los Angeles, California. Approximately 85% of the 330 km^2 catchment is charactarized by urban land uses (Wong *et al.* 1997). Annual fluxes of Cr, Cu, Pb, Ni, Zn, and TSS for Ballona Creek were based on the load values presented in studies by McPherson *et al.* (2005) and Tiefenthaler *et al.* (in review). Annual fluxes of Cr, Cu, Pb, Ni, and Zn were one to two orders of magnitude higher at Ballona Creek than at natural streams. In contrast, fluxes of TSS was two to three orders of magnitude higher at Piru Creek and Sespe Creek than that at Ballona Creek. This is expected due to storm-induced erosion of soil from open areas in the natural catchments. Unlike urban catchments with larger impervious area and concrete-bottom channels, the five natural catchments are mainly open lands that can contribute large volumes of sediment (and hence TSS). In addition, in-channel erosion of natural streams, which can be a substantial source of TSS (Trimble 1997, Pons 2003) does not occur in concrete lined channels, such as Ballona Creek.

In the overall context, natural catchments contribute proportionately less of the total annual load to the receiving waters than would be expected based solely on catchment area. For example, approximately 2,300 kg of Cu, 1,150 kg of Pb, 11,550 kg of Zn are discharged from the Los Angeles River watershed annually (Tiefenthaler *et al.* in review). Arroyo Seco, a natural subwatershed of the Los Angeles River, occupies approximately 2% of the Los Angeles River catchment area, but contributes less than 1% of the total annual load of Cu, Pb, and Zn. This contribution drops to less than 0.6% for the dry weather load.

Watershed geology has been shown to be a major factor that influences constituent concentrations (and hence loads) from natural catchments. This difference is illustrated by patterns of TSS flux. Flux of TSS from Sespe and Piru Creeks were two to three orders of magnitude larger than those at other streams. The dominant geologic type of both Piru Creek and Sespe Creek is a sedimentary rock, which can be more easily eroded and can discharge more suspended solids into the water than igneous rock. The flux of TSS at Arroyo Seco, which is underlain by igneous rock, was only 8 mt/year km^2, less than 0.2% of the flux at Sespe Creek. In addition to the effect of geologic type, the magnitude of storm flow at Sespe and Piru Creeks were five times larger than that at Arroyo Seco.

The combined effect of geology and hydrology may also explain the higher nutrient fluxes observed in the natural streams in this study compared to nation-wide averages reported from a study by Clark *et al.* (2000). Clark reported total annual loading of nutrients from 85 natural stream basins across the United States, with a median annual basin flux of ammonia, total nitrogen, orthophosphate, and total phosphorus of 8.1, 86, 2.8, and 8.5kg/km^2, respectively (Table 27). At four of the five sites from this study, nutrient flux was three to four time greater than the basin median value reported by Clark *et al.* The higher phosphorus loadings at the natural streams may have resulted from mineral weathering of phosphorus-enriched sediments. For example, the TP loadings at Santiago Creek, where the dominant geologic type is a marine sedimentary rock, were three times higher than the values recorded in the Clark *et al.* (2000) stream basin study.

The contribution of dry weather load was proportionately smaller in natural areas than in developed watersheds. According to McPherson *et al.*, dry season loads in the urbanized Ballona Creek watershed accounted for 54, 19, 33, and 44% of Cr, Cu, Pb, and Ni loadings, respectively (McPherson *et al.* 2002). In contrast, dry season loads in the natural streams accounted for 8, 16, 4, and 21% of total annual Cr, Cu, Pb, and Ni loadings, respectively. Considering the relatively smaller contribution of the dry weather flow to the total annual discharge volume in Ballona Creek, which ranged from 9 to 25%, the proportional contribution of dry weather loadings in Ballona Creek was considerably higher than that in the natural streams, where more than half of the total volume discharged was derived from the non-storm flow. This difference likely results from the fact that dry weather flow (and loading) in Ballona Creek in comprised almost entirely of urban runoff that continually washes pollutants off of developed surfaces. In contrast, dry weather flow in natural streams is a combination of ground water discharge, and residual interflow, neither one of which typically has high constituent concentrations.

Estimated differences between storm and non-storm flux at natural areas could be influenced by two factors. First, the estimation of storm loading is directly dependent on the method used to separate storm flow from non-storm flow. The storm flow separation is in turn directly dependent on how to treat the prolonged tail part of storm hydrographs in the natural streams, which may persist for days or weeks after the cessation of rain. For this study, the end of a storm was defined as the point in time where flow was 50% that of the peak flow. The degree to which the choice of the 50% criterion influences general conclusions about the annual loadings was examined by estimating storm loadings using a cutoff of 25% of the peak flow. Using this cutoff, the mean total annual days with storm flow increased from 12, 19, and 20 days to 16, 37, and 43 days at Sespe Creek, Piru Creek, and Arroyo Seco, respectively. The change in the number of storm-days is more dramatic in wet years such as 1994 and 1998 due to their prolonged high flow during the spring and the summer. For instance, the application of the 25% criterion increased the storm flow days for the water year of 1998 at Arroyo Seco more than 100% from 46 to 104 days. This increase of the storm flow days translated to an increase of the total annual discharge volume of storm flow by 46, 25, and 9% at Arroyo Seco, Piru Creek, and Sespe Creek, respectively. In terms of changes in loading, storm flow loads of TN increased from 43 to 54 mt/year and TSS from 100,453 to 124,948 mt/year in Piru Creek. Constituents that were mainly contributed by the non-storm flow decreased due to the decrease of the total discharge volume of the non-storm flow. The non-storm load of TP at Arroyo Seco decreased from 40 kg/year to 27 kg/year with the 25% criterion.

Second, distribution of constituents between the dissolved and particulate phase may also influence differences in loadings between storm flow and non-storm flow. More than 60% of the annual load for cadmium and selenium were derived from the non-storm flow at the perennial streams. The higher occurrence of these metals in the non-storm flow may be correlated with the distribution of the metals between a dissolved phase and a particulate phase. Arsenic, cadmium, and selenium exist mainly in the dissolved phase in storm flow (Figure 24). A considerable number of samples show more than 100 times higher dissolved concentrations than particulate concentrations for these metals. This indicates that loading of arsenic, cadmium, and selenium depends less on levels of total suspended solids, and can occur at relatively high levels in non-storm flow. Other metals exist either mainly in particulate phase or in both phases in storm flows. Thus, the level of total suspended solids directly affects the levels of these particle-bound metals and partially determines the contribution of the non-storm flow to the total annual loadings. For example, lead and zinc were found mostly in particulate phase in the storm flow, which contributed 85 to 98% of the annual load. The contribution of storm flow to zinc load mirrors the high level of total suspended solids. In addition, higher particle-bound constituents are more easily mobilized during storms; therefore, a high proportion of particulate-bound metals occur during storms.

In this study, the distribution of metals between dissolved and particulate phases in non-storm flow was not measured. However, metals in urban non-storm flow occur predominantly in the dissolved phase, partially due to low total suspended solids concentrations (McPherson *et al.* 2002, Stein and Ackerman 2007). Preliminary data collected in the San Gabriel Watershed (Bernstein *et al.* in prep) suggests that this pattern is also true in natural streams. Therefore, it is reasonable to assume that the distribution of metals loading between storm and non-storm conditions in natural systems is largely a function of the particle dynamics of each particular metal. The particle dynamics and associated constituent loading should be a focus of future investigation.

Table 23. Means of storm and non-storm flows (m^3/sec) in intermittent and perennial streams.

Stream Type	Site Name	Non-storm Flow Mean	Storm Flow Mean
Intermittent	Santiago Creek	0.19	0.92
	Tenaja Creek	0.03	1.81
	Mean	0.11	1.37
Perennial	Arroyo Seco	0.16	2.04
	Piru Creek	1.00	10.73
	Sespe Creek	0.26	9.81
	Mean	0.63	10.27

Table 24. Ranges of annual fluxes for metals, nutrients, and solids in natural streams.

	Unit	Median	Minimum	Maximum
Arsenic	g/year km^2	160	30	310
Cadmium		30	10	60
Chromium		430	70	580
Copper		360	50	440
Iron		190000	65000	570000
Lead		110	30	190
Nickel		220	30	460
Selenium		130	20	540
Zinc		160	30	310
Ammonia	kg/year km^2	3.0	1.0	8.0
Total Nitrogen		230	40	450
Dissolved Organic Carbon		650	200	1700
Total Organic Carbon		950	180	1800
Orthophosphate		7.0	2.0	11
Total Phosphorus		6.0	5.0	28
Total Dissolved Solids	mt/year km^2	74.7	12	190
Total Suspended Solids		8.7	4.2	4100

Table 25. Annual load estimation of metals and the contribution of the dry weather loads in the annual loads.

Stream Type	Site Name	Contribution Type	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Zinc
Perennial	Arroyo Seco	Annual Storm Load (kg)	3.05	1.28	23.90	12.40	7780.00	7.75	7.56	1.78	43.40
		Annual Non-storm Load (kg)	10.10	1.33	0.54	2.71	176.00	0.12	0.72	3.61	3.27
		Total Annual Load (kg)	13.10	2.60	24.40	15.10	7950.00	7.87	8.28	5.38	46.60
		% Non-storm Load	76.80	50.90	2.20	17.80	2.20	1.50	8.70	67.00	7.00
	Piru Creek	Annual Storm Load (kg)	8.72	0.65	164.00	101.00	146000.00	34.10	106.00	9.72	296.00
		Annual Non-storm Load (kg)	60.10	2.24	6.91	21.90	4610.00	2.18	15.90	19.70	9.67
		Total Annual Load (kg)	68.80	2.89	171.00	123.00	151000.00	36.30	121.00	29.40	306.00
		% Non-storm Load	87.30	77.50	4.00	17.80	3.10	6.00	13.10	67.00	3.20
	Sespe Creek	Annual Storm Load (kg)	3.58	2.01	54.00	48.20	72500.00	15.30	53.50	6.91	143.00
		Annual Non-storm Load (kg)	3.68	2.08	0.60	7.54	865.00	0.20	5.78	11.50	2.91
		Total Annual Load (kg)	7.26	4.09	54.50	55.80	73300.00	15.50	59.30	18.40	146.00
		% Non-storm Load	50.70	50.90	1.10	13.50	1.20	1.30	9.70	62.50	2.00
Intermittent	Tenaja Creek	Annual Storm Load (kg)	0.87	0.40	3.35	2.77	3950.00	1.71	1.44	0.60	14.80
		Annual Non-storm Load (kg)	0.80	0.04	0.18	0.07	116.00	0.07	0.36	0.41	0.54
		Total Annual Load (kg)	1.66	0.44	3.53	2.84	4070.00	1.78	1.80	1.01	15.40
		% Non-storm Load	47.90	9.80	5.00	2.50	2.80	3.90	19.80	40.90	3.50
	Santiago Creek	Annual Storm Load (kg)	1.44	0.71	1.62	2.50	792.00	0.73	1.74	6.77	9.53
		Annual Non-storm Load (kg)	1.24	0.19	0.56	1.06	334.00	0.06	2.03	2.47	1.89
		Total Annual Load (kg)	2.68	0.90	2.18	3.56	1120.00	0.79	3.77	9.23	11.40
		% Non-storm Load	46.40	21.00	25.80	29.80	29.70	8.00	53.90	26.70	16.60

Table 26. Annual load estimation of nutrients and solids and the contribution of the non-storm flow loads in the annual loads.

Stream Type	Site Name	Contribution Type	Ammonia	Total Nitrogen	Dissolved Organic Carbon	Total Organic Carbon	Orthophosphate	Total Phosphorus	Total Dissolved Solids	Total Suspended Solids
Perennial	Arroyo Seco	Annual Storm Load (mt)	0.09	7.66	23.18	22.45	0.27	0.03	1379.00	368.00
		Annual Non-storm Load (mt)	0.03	2.03	13.14	14.83	0.08	0.20	1257.00	1.00
		Total Annual Load (mt)	0.12	9.69	36.32	37.28	0.35	0.22	2636.91	369.00
		% Non-storm Load	22.90	20.90	36.20	39.80	22.30	87.70	47.70	0.40
	Piru Creek	Annual Storm Load (mt)	0.48	43.25	106.86	124.00	1.03	-	-	100452
		Annual Non-storm Load (mt)	0.32	16.12	91.57	298.00	0.96	-	-	76.00
		Total Annual Load (mt)	0.80	59.37	198.43	421.19	1.99	-	-	100529
		% Non-storm Load	40.40	27.20	46.10	70.70	48.40	-	-	0.10
	Sespe Creek	Annual Storm Load (mt)	0.95	33.21	55.24	66.61	0.55	-	4174.00	519565
		Annual Non-storm Load (mt)	0.07	4.34	27.80	54.94	0.38	-	6907.00	3.00
		Total Annual lLoad (mt)	1.01	37.55	83.04	121.54	0.93	-	11081.69	519568
		% Non-storm Load	6.50	11.60	33.50	45.20	41.00	-	62.30	0.00
Intermittent	Tenaja Creek	Annual Storm Load (mt)	0.07	1.86	7.43	7.16	0.13	0.22	416.00	219.00
		Annual Non-storm Load (mt)	0.00	0.14	3.01	2.55	0.00	0.10	230.00	1.00
		Total Annual Load (mt)	0.07	1.99	10.44	9.71	0.13	0.32	646.00	221.00
		% Non-storm Load	4.20	6.90	28.90	26.30	1.70	31.70	35.70	0.60
	Santiago Creek	Annual Storm Load (mt)	0.11	6.60	21.41	21.02	0.09	0.37	2189.00	91.00
		Annual Non-storm Load (mt)	0.01	1.03	7.94	9.24	0.09	0.11	1114.00	2.00
		Total Annual Load (mt)	0.12	7.63	29.34	30.26	0.18	0.49	3302.00	94.00
		% Non-storm Load	10.20	13.50	27.00	30.50	51.80	23.60	33.70	2.60

Table 27. Total annual fluxes of metals (kg/year km^2), nutrients (kg/year km^2), and solids (mt/year km^2) in natural streams in natural areas in comparison with fluxes of another urban stream (Ballona Creek) and other natural streams (numerous perennial streams across the nation). No data available ('-'). Stream type: intermittent (I) and perennial (P).

Stream Type	Site Name	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Zinc
P	Arroyo Seco	0.31	0.06	0.58	0.36	189.50	0.19	0.20	0.13	1.11
P	Piru Creek	0.22	0.01	0.54	0.39	474.10	0.11	0.38	0.09	0.96
P	Sespe Creek	0.06	0.03	0.43	0.44	573.30	0.12	0.46	0.14	1.14
I	Santiago Creek [a]	0.16	0.05	0.13	0.21	65.70	0.05	0.22	0.54	0.67
I	Tenaja Creek [a]	0.03	0.01	0.07	0.05	77.10	0.03	0.03	0.02	0.29
	Developed Stream	-	-	1.20[b]	4.00[b]	-	1.40[b]	1.10[b]	-	16.70 [c]

Stream Type	Site Name	Ammonia	Total Nitrogen	Dissolved Organic Carbon	Total Organic Carbon	Orthophosphate	Total Phosphorus	Total Dissolved Solids	Total Suspended Solids
P	Arroyo Seco	3	230	860	890	8	5	62.78	8.79
P	Piru Creek	3	190	620	1320	6	-	-	315.14
P	Sespe Creek	8	290	650	950	7	-	86.58	4059.12
I	Santiago Creek [a]	7	450	1710	1770	11	28	192.67	5.47
I	Tenaja Creek [a]	1	40	200	180	2	6	12.24	4.18
	Developed Stream	-	-	-	-	-	-	-	15.30[b]
	Natural Streams [d]	8.10	86	-	-	2.80	8.50	-	-

[a] Total fluxes are only for the eight months of the study from December 2005 through August 2006.
[b] McPherson *et al.* 2005
[c] Tiefenthaler *et al.* in review
[d] Clark *et al.* 2000

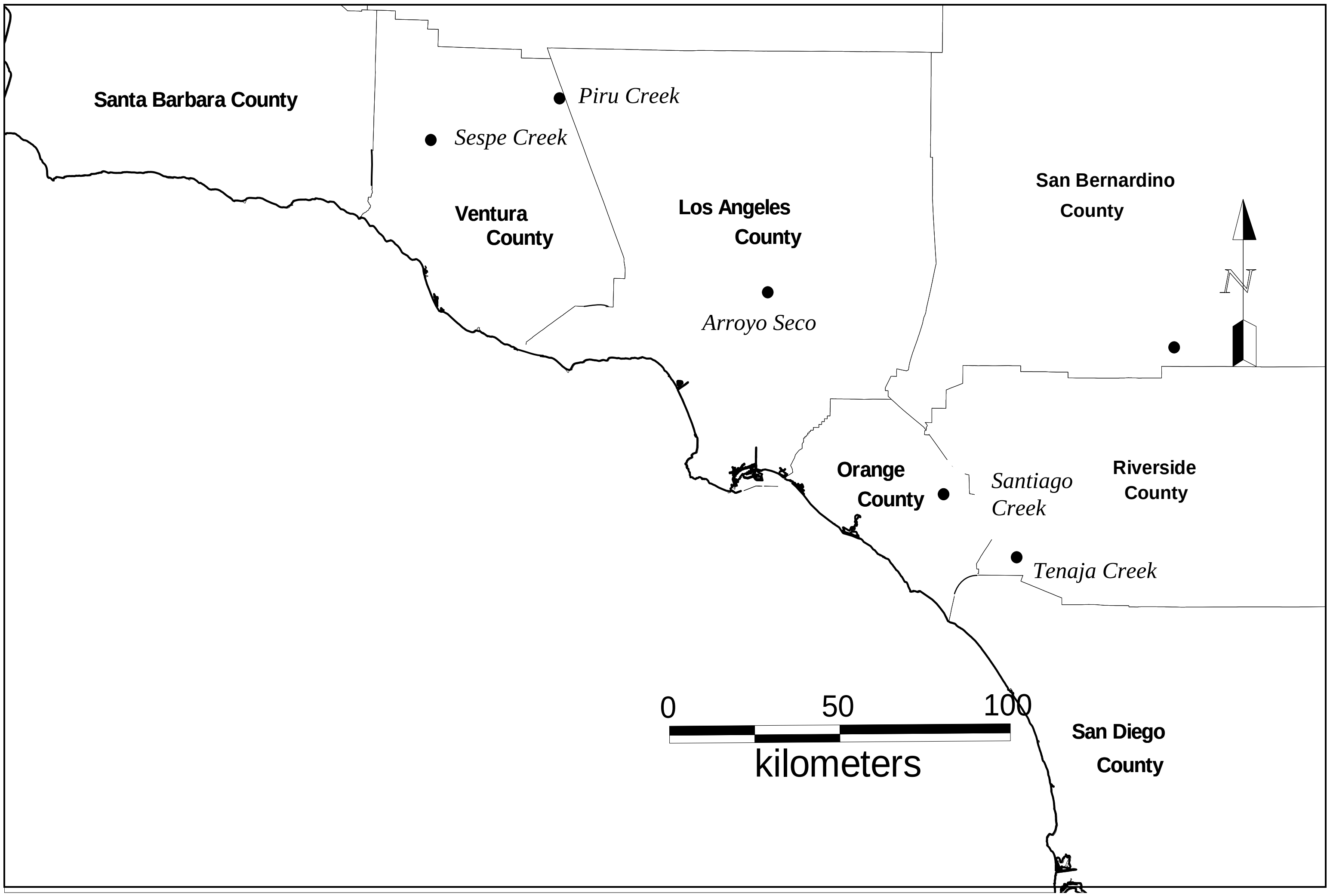

Figure 20. Map of study sites for the estimation of annual loads.

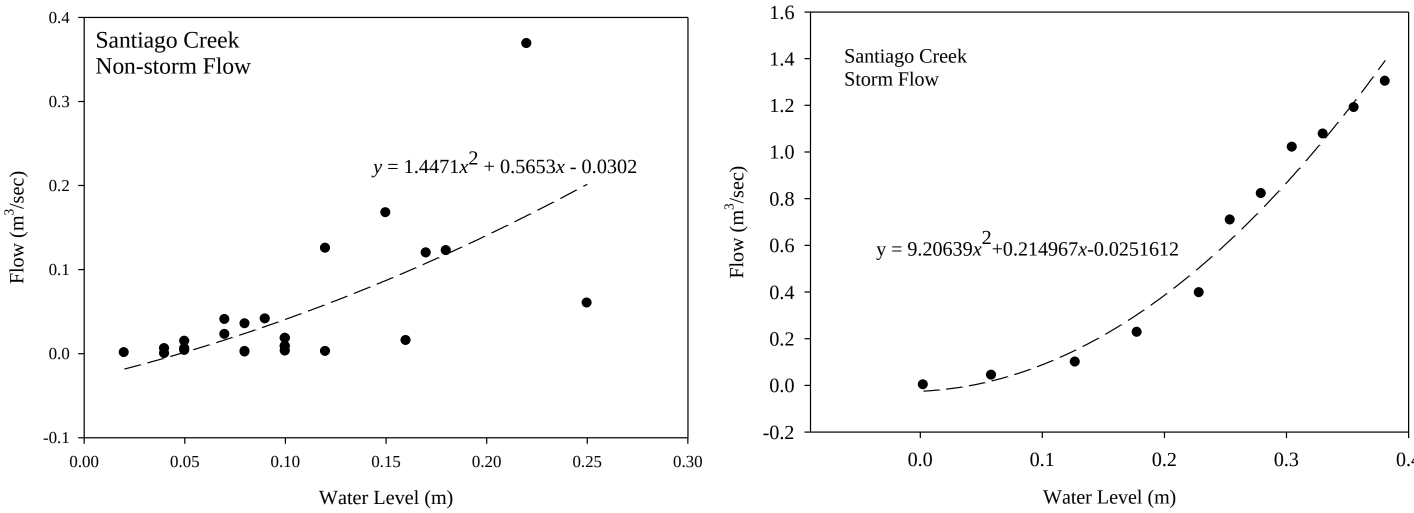

Figure 21a. Rating curves at Santiago Creek for non-storm and storm flows. r^2 Values are 0.43 and 0.97 for non-storm and storm flows, respectively.

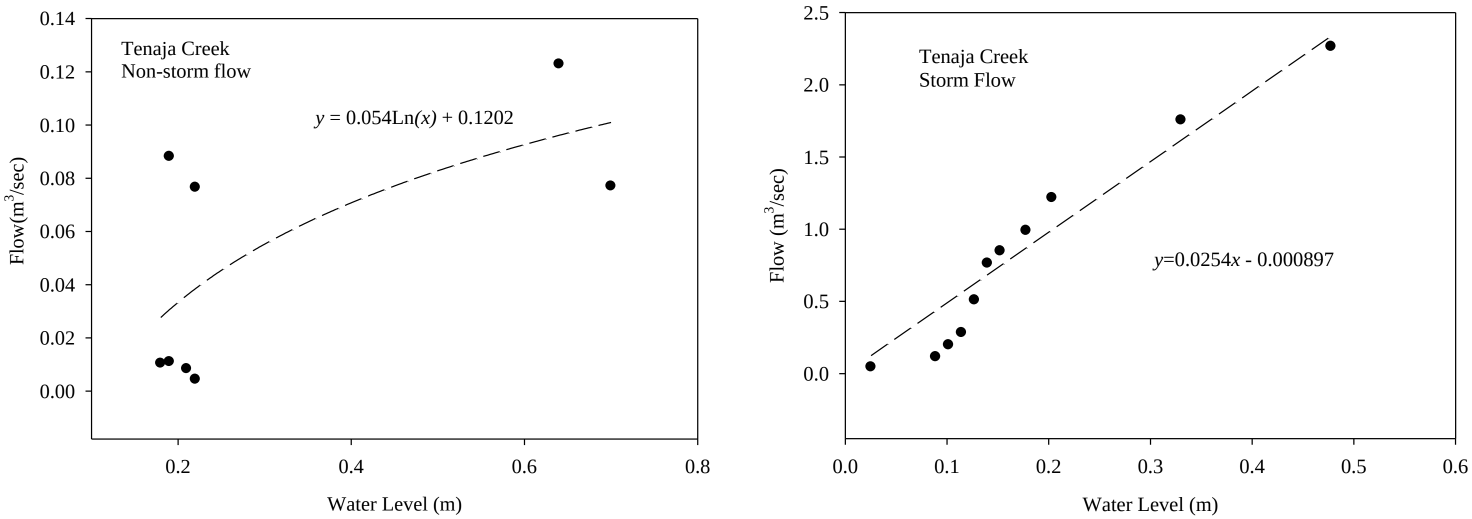

Figure 21b. Rating curves at Tenaja Creek for non-storm flow and storm flows. r^2 Values are 0.43 and 0.97 for non-storm and storm flows, respectively.

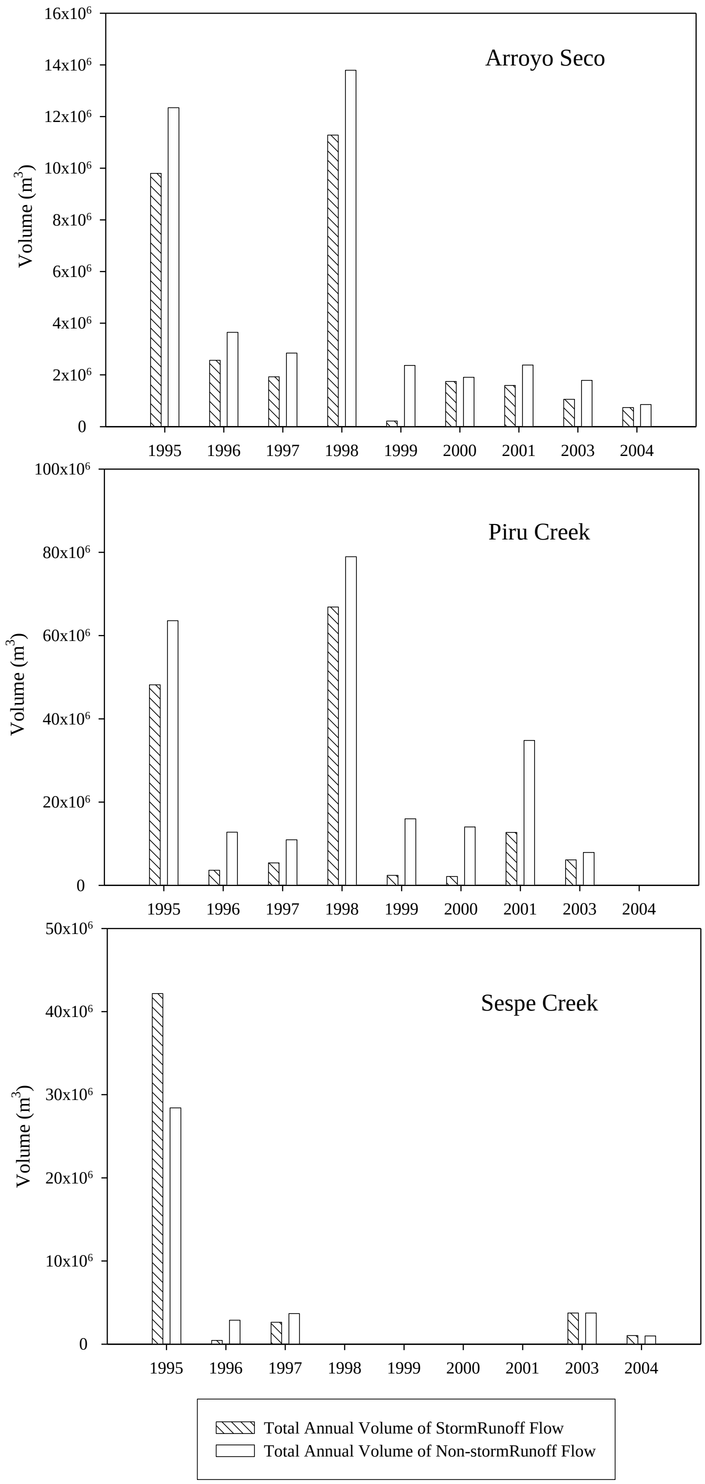

Figure 22. Comparison of annual storm flow and non-storm flow volumes. The flow data for the 2004 water year for Piru Creek and for the 1998 to2001 water years for Sespe Creek are not available. The flow data of the water year 2002 for Arroyo, Piru, and Sespe Creeks were not included in the analysis due to the insufficient quality of the data set.

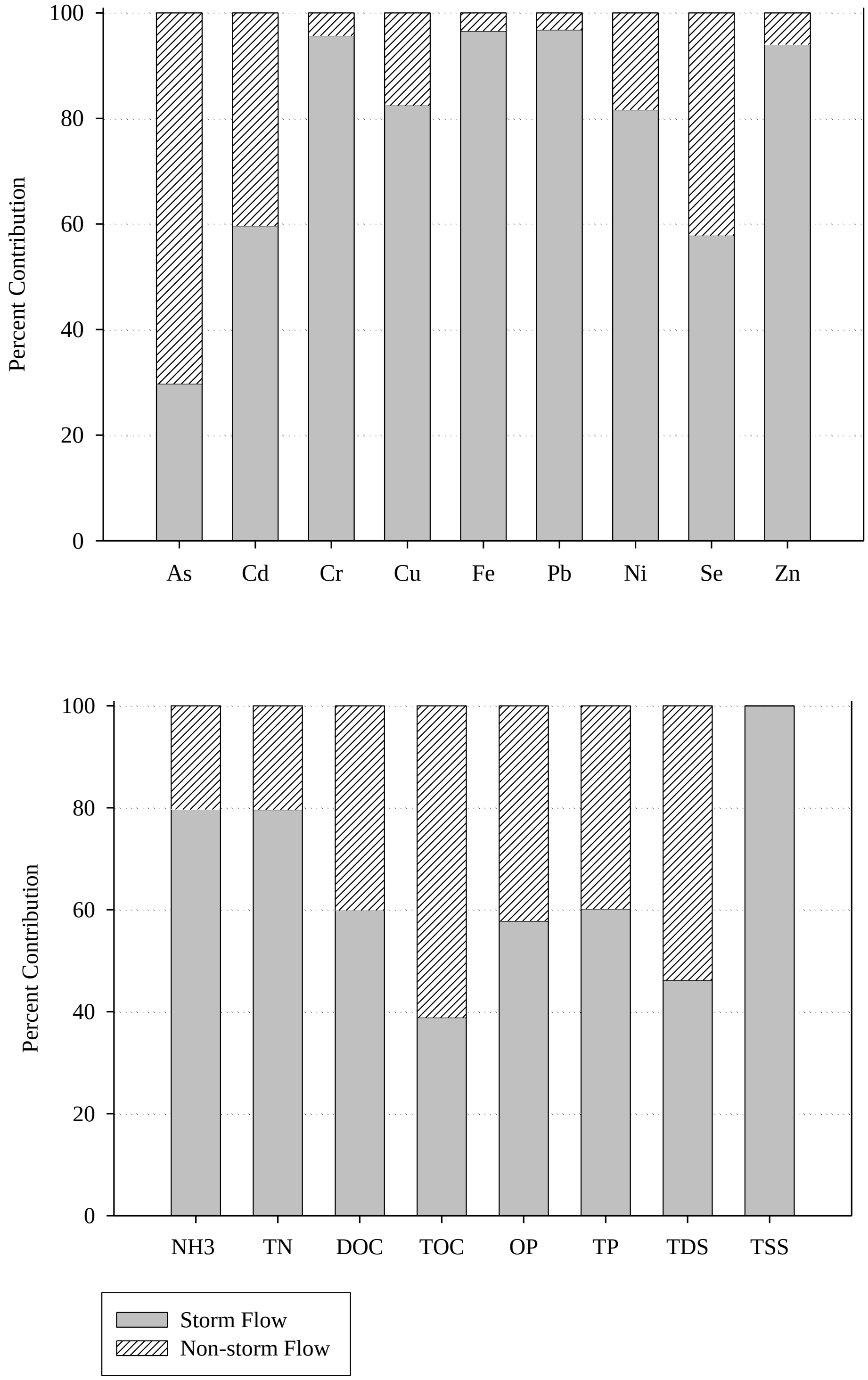

Figure 23. Percent contribution of storm flow and non-storm flow to total annual fluxes of metals, nutrients, and solids; ammonia (NH_3,); total nitrogen (TN); dissolved organic carbon (DOC); total organic carbon (TOC); orthophosphate (OP); total phosphorus (TP); total dissolved solids (TDS); and total suspended solids (TSS).

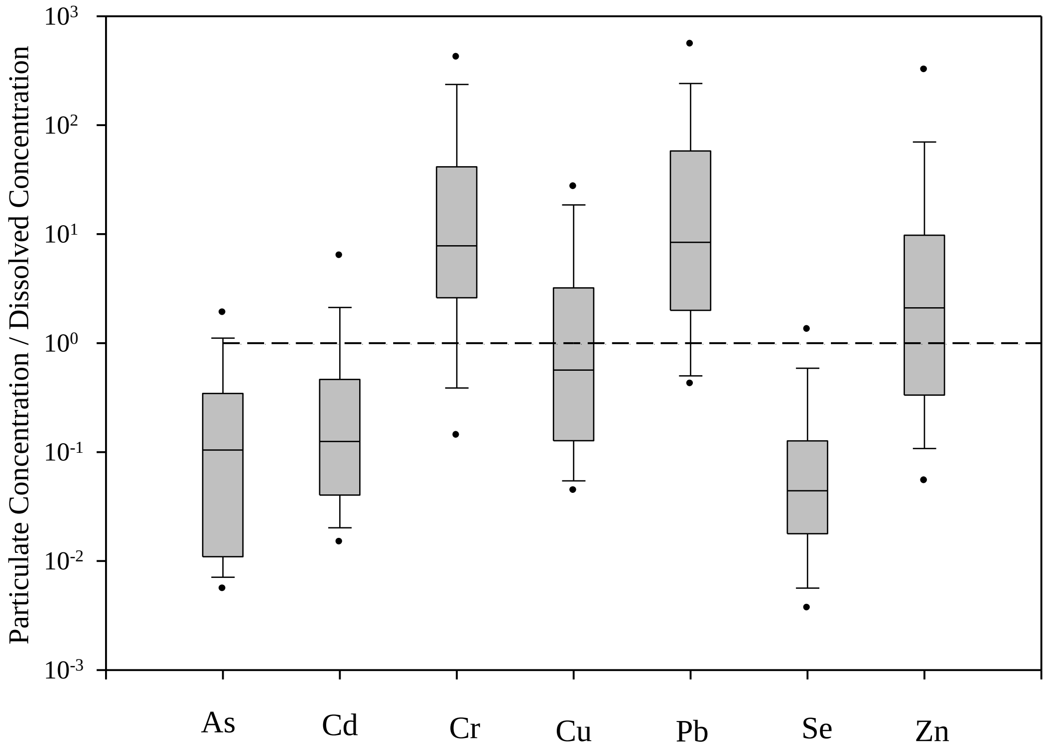

Figure 24. Ratios of particulate concentrations over dissolved concentrations for metals in storm flow. The dissolved and particulate concentrations were analyzed with samples of storm, which were collected in the winter of 2006. The dotted line references a 1:1 ratio; Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.

CONCLUSIONS

This study yielded the following conclusions about water quality in streams draining natural catchments.

1. Concentrations in natural areas are typically between one to two orders of magnitude lower than in developed watersheds. Dry and wet weather concentrations, loads, and fluxes from natural catchments ranged widely; however, the levels were significantly lower than both those from developed catchments and existing water quality standards.

2. Wet-weather TSS in the natural catchments was similar to those in the developed catchments. This implies that natural areas may be a substantial source of TSS to downstream areas. The level of TSS presented this study, however, should not be extended to interpretations or policy concerning overall sediment transport, sediment budget or adsorbed pollutants in the watersheds. In this study, the levels of TSS were measured in order to estimate suspended sediments in water column, which carries adsorbed metals and other water quality pollutants (Pitt *et al.* 1995). Using only TSS for sediment load, however, under-estimates the heavier soil particle fraction such as sand-size materials is especially critical in surface waters originating in areas where the dominant geology is sedimentary; USGS has declined to use it since 2000 because a documented persistent bias in the TSS results against sand-sized materials (Gray *et al.* 2000).

3. Both the storm and non-storm flux from the natural watersheds were significantly low compared with those from the developed watersheds. Therefore, control of natural sources would likely provide little overall load reduction for downstream receiving waters.

4. Differences between natural and developed areas during the dry season are much greater than during the wet season. Differences between natural and developed areas suggest that management of non-storm loading in developed watersheds has the potential to provide substantial water quality benefit.

5. Dry weather loading can be a substantial portion of total annual load in natural areas. Non-storm flow accounts for more than half of the annual discharge in the natural streams. Similarly, a considerable portion of annual load resulted from non-storm flow. In particular, annual loads of arsenic, cadmium, selenium, total organic carbon, orthophosphate, and total dissolved solids were largely contributed by non-storm flow. For chromium, iron, lead, nickel, zinc, ammonia, and total suspended solids the dominant portion of annual load was from storm flow.

6. Concentrations of metals were below the California Toxic Rules standards. Concentrations in natural areas were below CTR standards during both storm and non-storm conditions.

7. Wet-weather concentrations of E. coli, enterococcus, and total coliform and dry weather concentration for total coliform exceeded DHS freshwater standards in 40 to 50% of the samples. These results are based on relatively small sample size for bacteria analysis and are being investigated further by a subsequent study that involves more frequent sampling of bacteria from natural areas.

8. Concentrations of several nutrients were higher than the USEPA proposed nutrient guidelines for Ecoregion III, 6. It is important to note that the ultimate approach for nutrient criteria adopted in the State of California will likely differ from the approach used in the proposed EPA guidelines. Furthermore, the proposed guidelines were based on a combination of both wet and dry weather data. Nevertheless, this result indicates that background nutrient levels in southern California may be higher than in other portions of the country.

9. Concentration and load peak later in the storm in natural areas than in developed areas. Natural catchments do not appear to exhibit a first flush phenomenon during storms. Storm duration was longer in natural catchments than in developed catchments, and the pollutograph was more spread out (i.e., relatively high concentrations persisted for longer).

10. The ratio of particulate to dissolved metals varies over the course of the storm. Certain metals (e.g., As and Se) occur predominantly in the dissolved phase, while most others occur in the particulate phase. However, in all cases the ratio of particulate to dissolved metals peaks early in the storm in association with an increase in TSS. The ratios typically take several days to return to pre-storm levels.

11. Catchments underlain by sedimentary rock had higher concentrations of metals, nutrients, and total suspended solids, as compared to areas underlain by igneous rock. The RDA showed that geology types were dominant factors that influenced variability in water quality data.

13. Other environmental factors such as catchment size, flow-related factors, rainfall, slope, and canopy cover as well as land cover did not significantly impact the variability of water quality. This implies that the finding of our study may be extrapolated as natural background water quality to the southern California's coastal region.

APPLICATIONS AND NEXT STEPS

Natural background water quality estimates

Results of this study may be used by water quality managers and regulators to estimate background levels of metals, nutrients, and solids in surface water. Ranges of concentrations found in natural streams may be used to establish targets for basin planning or other water quality objectives. In terms of natural loading of metals, nutrients, bacteria, and solids, the flux estimates from this study could be used to estimate the contribution of natural areas to overall watershed load throughout the southern California region. Because the sampling sites are representative of the major geologic and natural land cover settings of the region, they can be used to estimate regional or watershed specific loading from natural areas. For example, in the Malibu Creek watershed, natural sources of selenium are a management concern. Based on the results of this study, the flux of selenium during the wet weather ranged from 0.3 (lower 95% CI) to 1.8 g/storm event $\cdot km^2$ (upper 95% CI). The area of Malibu Creek watershed is 285 km^2 and approximately its 85%, 241 km^2, is natural. Therefore, the event-based wet-weather load of selenium from the natural area in the Malibu Creek watershed can range from 2.4 to 36.2 g per storm event.

Annual dry weather loading from natural areas can be estimated by extrapolating the daily flux rates provided by this study over the number of non-storm days during the year. For example, in the Malibu Creek watershed, annual dry weather loading of selenium would be expected to range from 41 and 118g/$km^2 \cdot$day. Total annual loading from natural areas should account for contributions during both the wet and dry seasons.

Geology-specific loadings

Geology was shown to be the most dominant factor that influenced the natural background water quality in this study. Most of constituents were at higher levels in catchments underlain by sedimentary geologic material than in catchments underlain by igneous geologic material for both the dry weather and wet weather. Geology-specific background water quality may provide more precise estimation of natural loadings, which can account for the potential variation among watersheds due to different geology types. If geologic information is obtained for natural areas in a watershed of interest, average concentrations for each geology types can be used to estimate loadings from the natural areas with different geologic types. For instance, each Malibu Creek subwatershed consists of different portion of igneous and sedimentary rocks. The upper part of the watershed, which is north of freeway 101, is primarily sedimentary, but the middle and bottom parts of the watershed, which consists of Lake Sherwood subwatershed, Triunfo Canyon subwatershed, and Monte Nido, contain both geologic types. Thus, assigning the geology specific background concentrations may provide estimates that can reflect the mix of geologic conditions in the Malibu Creek watershed.

Further studies

More precise estimates of watershed loading for a storm could be obtained by using the storm event mean concentrations (EMCs) in static or dynamic watershed models that account for rainfall runoff rates and antecedent dry conditions. Such models can be used to simulate water quality loading under a range of rainfall conditions, based on expected constituent concentrations in land use washoff. Previously, concentrations assigned to washoff from natural areas were derived from either open space in developed areas or natural areas from other regions. The flow-weighted mean concentrations of this study provide relevant background water quality concentrations for the southern California region.

In this study, the geology types were divided into two groups: sedimentary rocks and igneous rocks. There is, however, possible variation within the groups, which may influence concentrations of constituents in water. To estimate more representative background water quality for a specific watershed of interest, more comprehensive classification of geology at a regional scale is necessary. Metamorphic type may have different influence on water quality due to its different physical characteristics even though the chemical composition of the metamorphic rocks may be similar to either sedimentary or igneous rocks.

This study quantified contributions from natural areas, but did not identify sources of natural loadings. Potential sources include; vegetation, soils, atmospheric deposition, and groundwater recharge. Measurement of constituent concentrations in subsurface flow and/or at groundwater discharge locations would help provide insight into these sources. Measurement of wet and dry deposition at natural areas would provide insight into the contribution of aerial deposition to natural loadings. Sabin *et al.* (2005) reported that dry deposition of trace metals to the land surface within developed watersheds was potentially a very large contributor to watershed loadings based on comparisons to load estimates from stormwater runoff. However, this has not been fully investigated for natural areas, where rates of interception by vegetation and infiltration are expected to be much higher.

Analysis of particle size distribution and associated binding of pollutants to various size particles would provide insight into the differences between natural and developed watersheds. Because many pollutants are bound to particulates in stormwater, understanding the proportional distribution among various particle size fractions would allow more precise modeling and isolation of the contribution of natural sources to downstream concentration and load. This would facilitate investigation of management strategies that target anthropogenic portions of pollutant load.

Wildfire is a potential constituent source that can significantly contribute to natural loadings. Fires occur regularly in southern California and are natural elements of native habitats. Post-fire water quality in natural areas can differ from the previous-fire water quality. In this study the impact of wildfire was not investigated (only natural sites with no history of wildfire over the past three years were included in the study). Thus, the results of this can be used for the comparison with post-fire water quality data in order to investigate the impact of wildfire on natural loadings. These studies would provide valuable information for development of freshwater water quality criteria by better characterizing appropriate background conditions.

Finally, the findings of this study indicate that a subset of natural sites be incorporated into ongoing monitoring programs in order to build a more extensive data set on background water quality under a range of conditions.

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APPENDICES

Appendix I: Review of pre-existing water quality monitoring data

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_I.pdf

Appendix II: Characterization of coastal watersheds in southern California by geology and land use types

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_II.pdf

Appendix III: Description of study sites

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_III.pdf

Appendix IV: Algal sampling protocol

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_IV.pdf

Appendix V: Description of developed sites for the comparison with natural sites

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_V.pdf

Appendix VI: Seasonal patterns in water quality data

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_VI.pdf

Appendix VII: Dry weather concentrations, loads, and fluxes for each study site

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_VII.pdf

Appendix VIII: Wet weather concentrations, loads, and fluxes for each study site

ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/500_NL_APPENDIX_VIII.pdf