UNIVERSITY OF CALIFORNIA

Los Angeles

Quantification of Metals, Nutrients, and Solids from Natural Catchments During Wet- and Dry-weather in Southern California

A dissertation submitted in partial satisfaction of the requirements for the degree

Doctor of Environmental Science and Engineering

by

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2006

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2006

To

Mom and Dad,

Hyuk-Jin, Seung-Jin, Kyung-A, Sol, Kang,

The other Dad in Phoenix,

And

Efrem, my best friend who makes me laugh all the time

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ACKNOWLEDGMENTS

The author of this study would like to thank Drs. Ambrose, Ingersoll, Stenstrom, and Trimble for guiding and challenging my endeavors. I would like thank everyone at SCCWRP who were always willing to help me and answered my questions with great care. I also thank Jay Shrake, Sean Porter, Richard Rusnik, and the rest of the MacTec Engineering field crews for their assistance and dedication in collecting storm water samples and Liesl Tiefenthaler and Dawn Petschauer for assistance in collecting the dry-weather samples. I would like to thank Myrna Gordon's help on logistics that was especially complicated in my situation. I am indebted to Dr. Eric Stein's support. He gave me this great opportunity to work on the project. He also showed me how to be an independent scientist and provided me all necessary academic, financial, and even emotional supports for me to accomplish this work.

I would like to thank my incredible family. I owe my love of knowledge and adventure to my parents, Mi-Sook Moon and Chang-Duk Yoon. I owe tremendous debts to my brothers, Seung-Jin and Hyuk-Jin who took great care of my parents while I was away.

Finally, I would like to acknowledge the role of the interagency technical advisory committee, who provided valuable suggestions and guidance in the study design. The U.S. Environmental Protection Agency Region IX, the Los Angeles Regional Water Quality Control Board, and the Southern California Coastal Water Research Project (SCCWRP) provided funding for this study.

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Yoon, Kyonga, Marish, E., Ambrose, R., and Harmon, T. (May, 2003), Phytoremediation for soil contaminated with petroleum hydrocarbons with native California species, Poster Presentation at Southern California SETAC, Santa Barbara, CA

Yoon, Kyonga and Kim, W. (2000) Development and reproduction of *Eucylops serrulatus* (Copepoda: Cyclopoida) in laboratory culture, Korean Journal of Limnology 33(1) March: 1-8

ABSTRACT OF THE DISSERTATON

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Ever-increasing urban development in southern California coastal watersheds has resulted in significant impacts on their water quality. However, we currently have no basis for differentiating water quality problems from natural variability. Observing high levels of constituents that occur naturally in water does not automatically indicate the water is polluted, since the constituents might have high natural background levels. This study investigated natural background water quality in streams from natural coastal watersheds of southern California and environmental factors to control the natural background water quality for dry weather and wet weather. Twenty-one sites were selected for inclusion in the study. They are located across six counties and 11 watersheds. Data were collected from each of the selected sampling sites during both dry weather and wet weather. Water samples were collected and analyzed for pH, TDS, TSS, hardness, TOC and DOC, nitrate, nitrite, ammonium, TKN, TP, OP, and total recoverable metals (As, Cd, Cr, Cu, Fe, Pb, Ni, Ni, Se, and Zn). The results of this study yielded important conclusions: 1) Concentrations in natural catchments are typically between one to two orders of magnitude lower than in developed watersheds, 2) Wet-weather fluxes of nitrate+nitrite, TKN, and TSS in natural catchments are not significantly different from those in developed catchments, 3) Differences between natural and developed catchments are greater in dry weather than in wet weather, 4) Dry-weather loading can be a substantial portion of total annual load in natural catchments, 5) Concentration and load peak later in a storm in natural catchments than in developed catchments, and concentrations and loads spread out widely over the course of a storm, 6) Metal concentrations in natural catchments are below existing water quality standards in both dry and wet weather, with the exception of copper in wet weather, 7) Concentrations of both wet- and dry-weather TP and dry-TN in natural catchments are similar to or lower than the EPA proposed nutrient criteria with wet-weather TN concentration is three-fold higher than the criteria, 8) Catchments underlain by sedimentary rock generally produce higher constituent concentrations than those underlain by igneous rock, 9) This study produced regionally applicable flux estimates for natural catchments during both storm and non-storm conditions.

CHAPTER 1 – INTRODUCTION

1. Statement of problem

In industrialized countries, concern over the quality of surface waters has resulted in a considerable amount of public funds being invested in water quality management during the last several decades (Berryman et al. 1988). Southern California, where over 25 percent of the nation's coastal population lives (Culliton et al. 1990), is no exception. Four coastal counties alone have about 17 million people, a number that is expected to grow by another three million by 2010 (Schiff et al. 2000). The increased influx of people has been accompanied by increased urban development and the increased development has placed more pressure on waters in southern California coastal watersheds (Davis et al. 2001; Schueler 1994; USEPA 1995). Prior to the 1800's, southern California contained rivers with wide, unobstructed floodplains that were fed by numerous tributaries and flowed freely to the sea (Office of Technology Assessment 1984; Rairdan 1998). As a result of increased development, however, southern California coastal watersheds have been seriously altered and the overall health of the watersheds has declined. The water quality in many southern California coastal watersheds is impaired for their beneficial uses. More than 650 waters in California are listed as impaired by USEPA under Section 303(d) of the Clean Water Act, including approximately 280 in the Los Angeles, Santa Ana, and San Diego regions (State Water Resources Control Board 2003).

The major causes of these impairments include elevated levels of bacteria, nutrients (and associated algal blooms and low dissolved oxygen), metals, and other toxics. In most cases, these impairments will result in the development of Total Maximum Daily Loads (TMDLs), 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 natural contributions from natural catchments. Most impaired waterbodies in southern California consist of both developed and natural catchments. For instance, in the Malibu Creek watershed, California, natural area accounts for about 85 percent of the watershed as a whole (Los Angeles County 2005). These natural catchments in the coastal watersheds can be a source of metals, nutrients, and solids in waters. Unlike other man-made chemicals, metals, which are sources of impairment in many watersheds, occur naturally in the environment (Horowitz and Elrick 1987; Trefry and Metz 1985; Turekian and Wedepohl 1961). One well-known example is selenium, which may occur at high level in water due to natural weathering of bedrock (Seiler et al. 1999). In a study of geochemistry of selenium, mobilization by the weathering of pyretic shale in San Joaquin Valley, California, drainage from soils transported selenium to Kesterson National Refuge catchments in amounts elevated enough to cause a threat to wildlife (Presser and Swain 1990). In Southern California, the metavolcanics that make up the Transverse ranges are known to release certain metals as they weather (Schiff and Tiefenthaler 2000). Bedrock is also a source for certain nutrients as well as metals. The Monterey formation that is common in Southern California has been reported to be a source of phosphate loadings (Dickert 1966), which may contribute to algal growth in streams or estuaries. Vegetation or land cover in natural landscape can be also the natural source of certain elements (Detenbeck et al. 1993; Gergel et al. 1999; Johnes et al. 1996; Johnson et al. 1997b; Larsen 1988; Richards et al. 1996). 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 the 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 and silt and particulate organic carbon that are influenced by the land cover in the natural landscape (Gergel et al. 1999; Johnson et al. 1997b; Richards et al. 1996). Previous studies on the impact of land cover type on nutrient loadings have focused primarily on developed catchments to monitor human impact on loadings (Johnson et al. 1997b). The impact of land covers of the natural catchments on loadings has been investigated only in a few studies (Naslas et al. 1994).

There have been prior studies on natural background water quality (Clark et al. 2000; Reginato and Piechota 2004; Smith et al. 2003), however, few studies have attempted to quantify background (or reference) levels of water quality in southern California, and little to no information is available on this issue. To compensate for the lack of adequate information on natural sources of metals and nutrients, many TMDLs are written with load allocations based on data from other parts of the country or, worse yet, with 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. For instance, selenium can be found naturally at high level determined by the geology of surrounding catchments. If the target level of selenium is established without consideration of the high background level and is set even lower than the background level, it may be impossible to reduce the level of selenium in water to the target level by controlling discharges from both non-point sources[1] and point sources[2] and also be the waste of limited resources.

To fully evaluate the extent of anthropogenic activities, it is important to

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[1] Pollutants from non-point sources are not required to have a National Pollutant Discharge Elimination System Permit (NPDES). NPDES permits are required for cities, industries, storm water runoff from cities over 100,000 population, storm water runoff from certain industries and animal feedlots with more than 1000 animal units. Everything left over is a non-point pollutant source such as soil erosion from farmland fields as well as construction sites, fertilizer runoff from both rural and urban areas, pesticide runoff from both rural and urban areas, and animal waste management.

[2] Pollutants that are coming from a concentrated originating point like a pipe from a factory or a large registered feedlot with a specific point of discharge.

describe water quality in streams draining natural environments and to understand factors that control it. The overall goal of this study is to evaluate the properties of stream reaches in natural catchments throughout southern California and their contribution to overall water quality.

2. Background

The water quality of natural streams varies both spatially and temporally, and is affected by factors such as climate, atmospheric deposition, soils, and chemical weathering of soils and bedrock (Likens et al. 1977). Climate is an important natural factor affecting water quality as a result of changes in precipitation, runoff, and evaporation. Water quality also can be affected by the chemistry of precipitation. Atmospheric deposition introduces sulfur, nitrogen, base cations, and acidity to relatively natural areas in the Northeastern United States (Likens et al. 1996). In some Midwestern and Northeastern streams, atmospheric deposition of nitrogen can account for nearly all downstream nitrogen loads (Puckett 1995; Smith et al. 1987). Direct atmospheric deposition has also been shown to contribute 4 to 8 percent of the total metals loading to storm water runoff in San Francisco Bay Region, CA (Tsai et al. 2001). Sabin and others (2005) have shown that atmospheric deposition potentially accounted for as much as 57-100 percent of the total metal loads in stormwater in a small impervious urban watershed in Los Angeles, CA. Atmospheric deposition may also influence the weathering rate and buffering capacity of underlying soils and bedrock (Clow and Mast 1999; Lawrence and Huntington 1999; Murdoch et al. 1998). Soils can affect water quality as a source of suspended sediment and soluble materials (Apodaca et al. 1996).

Geologic formations affect water quality because rocks are the source of many chemical constituents in the water. The interaction of water and the atmosphere with rocks and minerals result in the process of weathering. Rainwater can add sodium, chloride, and sulfate to a solution, leading to the chemical breakdown of minerals and bedrock. Depending on the individual mineral and the climate regime, the reaction of those minerals with water will vary. The amount of solute dissolved in a liquid is dependent on the temperature and pressure of the water (Hounslow 1995). Although some dissolved constituents in surface water are added through rainfall, most dissolved substances are introduced through the chemical breakdown of rocks (Dunne and Leopold 1978). The weathering of bedrock results in clays and organic polymers, soluble cations, bicarbonate, and silica. The resulting minerals depend on temperature, precipitation, biologic activity, and drainage. The fluid leachate is then transported in surface water and groundwater (Dunne and Leopold 1978; Hounslow 1995). A mineral's resistance to weathering and degree of solubility dictate the type and amount of dissolved constituents found within surface water and groundwater. For example, limestone is more easily weathered by water than quartzite. Thus, in limestone regions, one would expect to find higher concentrations of calcium bicarbonate. Weathering of other minerals, depending on the chemical make-up of the rock, yield sodium, calcium, fluorine, and even lead to groundwater and surface water (Dunne and Leopold 1978). High pH's are also associated with high concentrations of dissolved solids.

Several studies have demonstrated the impact of geologic formations on water quality. Ledin and others (1989) found that chromium, copper, zinc, cadmium, and lead in Swedish ground water were primarily from igneous crystalline bedrock. They also showed that levels of metals in the ground water were related to concentration levels in bedrock, as well as to pH, suggesting that background concentrations resulted from biogenic weathering of these metals. Numerous studies of elevated selenium levels in the southern Coast Range of California have documented the correlation between geology and water quality (Lakin and Byers 1941; Ohlendorf et al. 1988; Ohlendorf et al. 1986; Presser et al. 1994; Tidball et al. 1991; Tracy et al. 1990). In the San Diego Creek watershed, Hibbs and Lee (2000) concluded that high selenium concentration in surface runoff was due to contributions from ground water. Selenium in groundwater was derived from weathering of high selenium Cretaceous marine strata in the watershed (Hibbs and Lee 2000). A USGS study (Seiler et al. 1999) identified areas of potential selenium contamination of water in the Western United States based mainly on geology and climate of the areas.

Land cover type, which is the type of vegetation in natural areas, can also have a significant impact on water quality (Detenbeck et al. 1993; Gergel et al. 1999; Johnes et al. 1996; Johnson et al. 1997a; Larsen 1988; Richards et al. 1996). One of the primary ways land cover influences surface water quality is through sediment runoff (erosion). Sediment impairment is the most common cause of impairment nationally and management of this pollutant can cost an estimated $16 billion annually in North America (Pons 2003). Trimble (1997a) found that stream channel erosion was the major contributor to long-term sediment yield from an urbanizing watershed in California. Natural land cover and soil type are major factors that determine streambank and in-channel erosion, which can account for 85 percent of total watershed sediment yields (Simon et al. 2000; Trimble 1997b; Wynn et al. 2006)). Furthermore, a substantial portion of the total mass of metals in surface water is associated with sediments, including clay and silt, and particulate organic carbon that are influenced by land cover type (Gergel et al. 1999; Johnson et al. 1997a; Richards et al. 1996).

The decomposition of plant litter can also be a source of metals in surface water. Hale and Johnson (2002) investigated the contribution of foliage and fine roots as sources of copper, nickel, lead, and zinc. They found that fine roots were the dominant source of copper, nickel, and lead, and that zinc was introduced in equal proportions by both fine roots and foliage.

3. Present conditions

3.1. Studies on natural background water quality

Although there have been prior studies on natural background water quality (Clark et al. 2000; Reginato and Piechota 2004; Smith et al. 2003), their utility for southern California is limited for the following reasons. First, the studies have mainly focused on natural sources in developed watersheds, which were not free from anthropogenic influences; thus, the results could not be used as reference water quality in natural watersheds. Second, the previous studies have investigated mainly dry-weather conditions instead of quantifying both wet weather and dry weather conditions at a consistent set of sites. Third, only specific constituent classes (most commonly copper, zinc, and total suspended solids) have been examined in most of the studies. Few studies have conducted a comprehensive evaluation of a suite of constituent classes at a single set of sites. Fourth, the prior studies have primarily concentrated on static measures and have not investigated spatial and temporal variations such as within storm patterns that may have influenced natural loadings. Last, the majority of studies have been carried out in areas with different climate or physiographic conditions than southern California.

Data on contributions of pollutants from natural lands during both wet- and dry-weather are limited. In addition, few or no historic data on water quality of the pre-development era are available. Only a limited number of studies have been conducted to investigate background water quality, and these studies have occurred in limited areas for a limited set of constituents. Clark and others (2000) assessed nutrient concentration and yields in natural stream basins of the United States. They found that concentrations and yields of total nitrogen were highest in the southeastern part of the nation and in part of the upper Midwest. In the northeast, nitrate was generally the predominant form of nitrogen, and in the southeast and part of the upper Midwest, organic nitrogen was the dominant form. California was included in the study; however, only two reference sites were assigned in California, neither of which was located in southern California. This type of the nation-wide study may provide a general idea on background water quality, however, it is insufficient to account for potential variation in water quality of southern California's unique geologic and topographic setting. To compensate for having a limited reference data set, several researchers have developed surrogate predictors to assess background water quality. For instance, annual runoff has been used as a surrogate for background nutrient yields (Gilliom 1981; Lewis et al. 1999; Smith et al. 2003). According to these studies, annual mean runoff was correlated with mean annual yields of total fixed nitrogen and total phosphorus. Although mean annual runoff might be strongly correlated with nutrient yields, the prediction was based on limited concentration data from a limited number of reference sites that were mainly located in the northeast part of the country. Reginato and Piechota (2004) investigated background levels of nutrients in the Las Vegas Valley, where 85 percent of the region was undeveloped. Their data included only a limited number of nutrients and total suspended solids and no metals. The background water quality for nutrients from this study is valuable information; however, its application to southern California should be approached with caution because of different climatic features that control loading. In the Las Vegas region, the majority of loading occurs during summer monsoons. In contrast, southern California experiences almost no summer storm loading; rather the majority of storm runoff occurs during several brief, intense winter storms.

3.2. Review of existing data from ambient-water monitoring programs

A number of ambient water quality monitoring programs and studies have been carried out across southern California to investigate the impact of development on water quality. Most of these studies included water quality data from natural areas for reference conditions. An important first step of this study was to compile these reference data and identify key data gaps in the existing databases. In addition, these data can provide guidance for screening potential study. The following monitoring programs were reviewed and summarized.

- State of California's Surface Water Ambient Monitoring Program (SWAMP)
- USEPA's Environmental Monitoring and Assessment Program (EMAP)
- UCLA study
- Heal the Bay's Stream Team Program Monitoring Program
- USGS's Hydrologic Benchmark Network
- USGS's National Water Quality Assessment (NAWQA) Program

- Santa Barbara Coastal Long Term Ecological Research Project (SBC-LTER)
- Water quality monitoring and bioassessment programs from USFS and local and state government agencies including Los Angeles, Orange, Ventura, San Diego, and San Bernardino counties and associated cities

Existing monitoring programs with data that were relevant to investigation of natural stream conditions in southern California were the SWAMP sampling conducted by the Los Angeles RWQCB, the EMAP sponsored by EPA Region 9, and the UCLA study, 'Environmental Monitoring and Bioassessment of Coastal Watersheds in Ventura and Los Angeles' sponsored by Los Angeles RWQCB. The other programs/studies did not contain usable data because they lacked sufficient water chemistry data, the survey sites were not located in natural areas, or the sites were not located in southern California.

The SWAMP program is designed to assess the conditions of surface waters throughout the state of California. The SWAMP water chemistry data obtained for this analysis were from the Santa Clara River watershed, and were collected from 2001 through 2003. EMAP is designed to monitor and assess national status and trends of ecological resources. The data used for this analysis were from the EMAP Western Pilot Study. The EMAP water quality data were collected from one-time samplings, carried out from 2000 through 2001. The UCLA study was carried out by UCLA during Fall 2001 and involved collection of water chemistry, physical, and biological data. These three data sets contained concentrations for total suspended solids (TSS), dissolved organic carbon (DOC), total phosphorous (TP), ammonium (NH_4), sulfate (SO_4), nitrate (NO_3), total nitrogen (TN), selenium (Se), and zinc (Zn). Four survey sites from SWAMP, five reference sites from the UCLA study, and forty-five sites from EMAP were located in natural areas and contained suitable water chemistry data that were relevant to the goals of our study.

The existing water quality data that were reviewed contain several critical limitations for our goals and objectives. First, the data were collected from one-time sampling. The result from one-time sampling should not be extrapolated for an entire weather or a year. Second, samplings were conducted as part of separate studies and samples were collected in the same weather nor in the same year. Third, sampling was conducted mostly in dry weather. Fourth, the methods to collect water samples were not consistent among the different studies. For example, a grab sampling method was used to collect the SWAMP data, yet a composite sampling method was used for the EMAP data. The detailed results of the review on the existing water quality data are included in Appendix I. For these reasons, the existing data are neither sufficient nor consistent enough to estimate ranges of expected loadings from natural waterbodies in southern California.

The present study was designed to build on previous work and to overcome the limitations of existing data, by sampling a series of sites over both wet- and dry-weather and comparing the resultant runoff data to catchment characteristics, such as geology and land cover. The results of the study allow a more precise estimation of background water quality in southern California.

4. Structure of the study

The study was accomplished in four phases: review of previous water quality data collected from natural sites, characterization of the ranges of existing natural conditions in southern California, selection of representative sampling sites, and collection of wet- and dry-weather data. The main steps of the study design are summarized below.

4.1. 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 summary of the review of the existing data sources was presented in '3.2. Review of existing data from ambient-water monitoring programs.' Our *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. To test this hypothesis, preliminary analysis of the existing data on water quality in natural areas of southern California was conducted using data from EPA'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, which were only constituents collected in all three studies. 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. The detailed results of the preliminary investigation are included in Appendix I. 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. 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 to guide development of the study design for this project.

4.2. 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 (Detenbeck et al. 1993; Dunne and Leopold 1978; Gergel et al. 1999; Hibbs and Lee 2000; Hounslow 1995; Johnes et al. 1996; Johnson et al. 1997b; Lakin and Byers 1941; Larsen 1988; Ledin et al. 1989; Ohlendorf et al. 1988; Ohlendorf et al. 1986; Presser et al. 1994; Richards et al. 1996; Tidball et al. 1991; Tracy et al. 1990). 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 (NOAA Coastal Change Analysis Program (CCAP) 1999). The results of the analysis for this phase are provided in Appendix II.

4.3. Selection of sampling sites

The goal of Phase 3 was to select sampling sites that would represent the ranges of natural conditions throughout southern California. Using the characterization and the list of data gaps produced under Phases 1 and 2, a series of 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.

4.3.1. 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, our sampling design involved stratified sampling based on these two independent variables. The overall sampling matrix for the project is shown in Table 1.

Geologic forms consist of a certain lithologic type or combination of types; it may be igneous, sedimentary, or metamorphic and be consolidated or unconsolidated (American Geological Institute 1984). Due to resource constraints, we prioritized sites in areas that represented 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. These prioritized geology-land use combinations account for the majority of natural area in the coastal watersheds of southern California.

4.3.2. Criteria for site selection

Criteria were developed to provide objective guidelines for classifying catchments in various conditions and selecting 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, and after consulting various agencies that were 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[3] and would be representative of the range of natural conditions that exist in southern California.

The criteria include:

- Catchments draining to the sites should be natural and as close to pristine condition as possible. Contributing drainage area should be at least 95 percent undeveloped.
- Target watersheds should be 3rd order watersheds whose 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 whose 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 that the data from this study will be compared with.

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[3] 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 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 and land cover types and be in relatively homogenous setting. Sites screened with the general criteria were grouped in terms of the representative geology and land cover of southern California (Table 1). The goal was to select a minimum of 4 - 5 sites that represent each of the priority treatments in the sampling framework (i.e. locations with an "A" prioritization on Table 1).
- Sites should have either year-round or prolonged dry weather flow that allows them to be sampled during both wet- and dry-weather. A stream with the prolonged dry weather flow can be defined as a stream still flowing one to two months after the end of the last storm in the previous winter even though it dries up in the summer.
- Sites should not be within catchments that have burned during the previous three years. According to the study on the impact of wildfire in 1993 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 are still

impacted by wildfires are not representative of natural condition and should be excluded in the study.

- 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 areas 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

4.3.3. Selected sampling sites

Candidate sites were selected based on a review of existing data from the Surface Water Ambient Monitoring Program (SWAMP), Environmental Monitoring and Assessment Program (EMAP), 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 U.S. 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, 22 sites were selected for inclusion in the study. They are located across six counties and twelve different watersheds: Ventura River, Santa Clara River, Calleguas Creek, Arroyo Sequit, Malibu Creek, Los Angeles River, San Gabriel River, Santa Ana River, San Mateo Creek, San Juan Creek, San Luis Rey River. The sites are shown in Figure 1 and listed in the Table 2. More detail description of the sites are provided in Appendix III.

4.4. Wet- and dry-weather sampling

The goal of Phase 4 was to collect samples at the 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. Details of the sampling and analysis are contained in the subsequent chapters of this dissertation.

5. Organization of the dissertation

This dissertation consists of five chapters. This chapter, Chapter 1, is the introduction for the whole dissertation. Chapter 2 quantifies natural contributions during dry weather in Southern California coastal catchments and examines impact of natural landscape characteristics on dry-weather water quality using multivariate analyses. Chapter 3 presents a quantification of natural contributions during wet weather and examines the impact of natural landscape characteristics on stormwater-runoff water quality using multivariate analyses. Chapter 4 expands the results of the Chapter 2 and the Chapter 3 by estimating annual fluxes and loadings of metals, nutrients, and solids and examining the contribution of the dry-weather loading to the annual loadings. Chapter 5 presents the conclusions and implications of the study for managing water quality and catchments and recommends the further studies based on the findings of the study.

Specific questions that are addressed in Chapters 2, 3, and 4 are:

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

4. What are estimates of annual loadings and fluxes of metals, nutrients, and solids from natural catchments?

TABLE 1. SAMPLING FRAMEWORK. LETTERS INDICATE PRIORITY-SAMPLING LOCATIONS.

Land cover	Dominant Geology		
	Sedimentary rocks	Metamorphic rocks	Igneous rocks
Forest	A	C	A
Shrub	A	C	A
Grassland	B	C	B

*Letters indicate sampling priorities. A = highest priority, C = lowest priority.

TABLE 2. STUDY SITES. TABLE INCLUDES WATERSHED, LOCATION, SETTING, AND WHETHER SITES WERE SAMPLED FOR WET WEATHER, DRY WEATHER OR BOTH.

Site Name	Watershed	Sampling weather	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

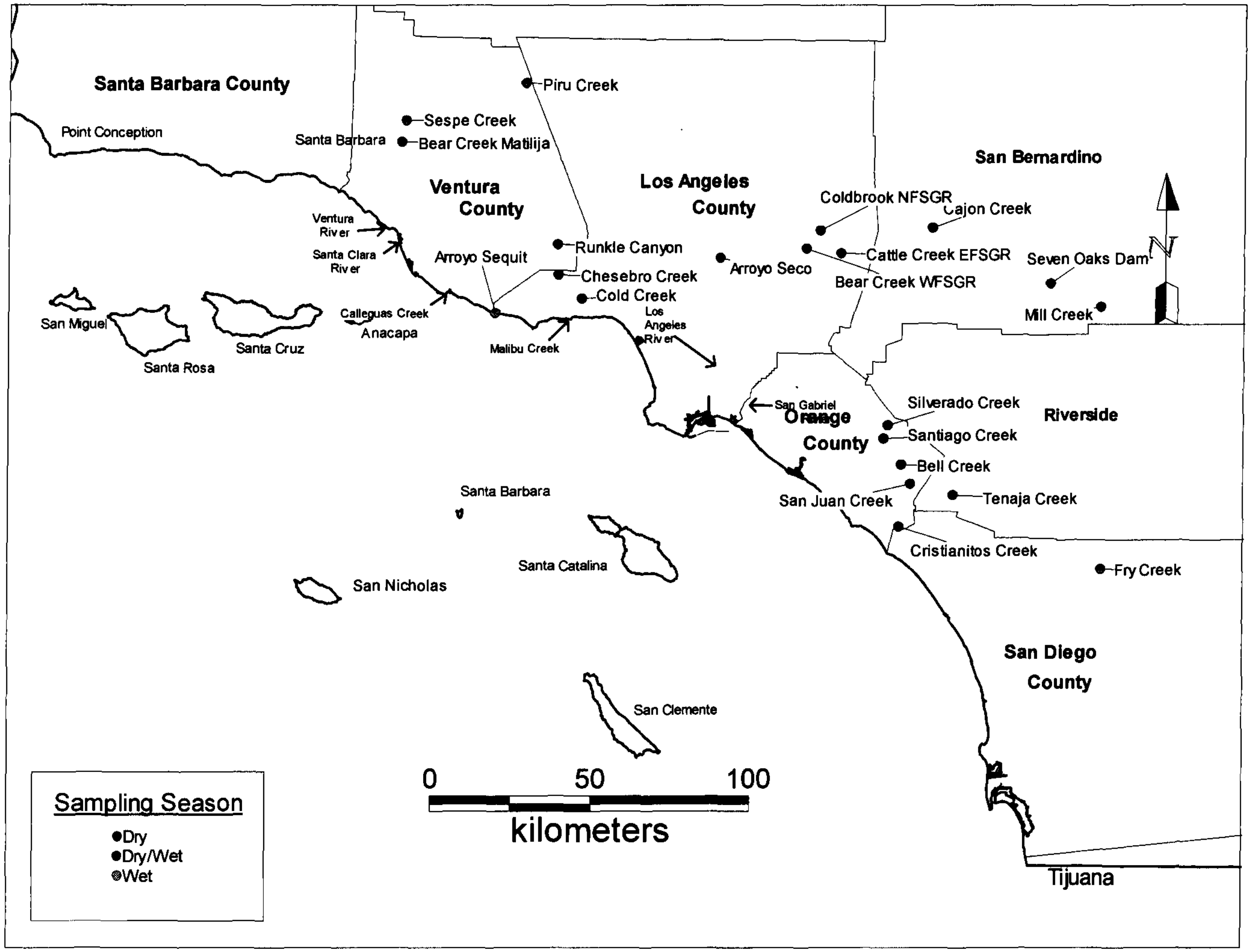

FIGURE 1. MAP OF STUDY SITES. RED DOTS INDICATE SAMPLING SITES FOR DRY WEATHER ONLY; BLUE DOTS FOR BOTH DRY AND WET WEATHER; GREEN DOTS FOR WET WEATHER ONLY

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CHAPTER 2 – QUANTIFICATION OF METALS, NUTRIENTS, AND SOLIDS FROM NATURAL CATCHMENTS DURING DRY WEATHER IN SOUTHERN CALIFORNIA

Abstract

Southern California's coastal watersheds are some of the most highly urbanized areas in the United States, which produces stress in coastal ecosystems and can lead to poor water quality. Previous studies have focused mainly on the effects of storm water. However, non-storm (dry weather) flows could also contribute substantial amounts of metals, nutrients, and solids. To evaluate the effects of anthropogenic activities, it is essential to assess the contribution of both developed areas and the natural streams draining relatively undeveloped portions of a watershed because both ultimately affect water quality in downstream receiving waters. This is particularly true during dry-weather conditions, where differences in runoff between developed and undeveloped landscapes may be extreme. This study assessed dry-weather concentrations and loads of metals, nutrients, and solids from nineteen representative natural streams in nine watersheds in southern California. Dry-weather concentrations, loads, and fluxes from natural catchments exhibited a broad range of variability; however, levels were significantly lower than both those from developed catchments and existing water quality standards. Dry-weather levels of metals, nutrients, and solids were typically one to two orders of magnitude lower in the natural streams than developed streams. Redundancy analysis showed that geology type was the dominant factor that influenced variability in water quality data.

1. Introduction

Coastal watersheds in southern California are some of the most highly urbanized areas in the United States. Approximately 17 million people live in these areas, a number that is expected to grow by another 3 million by 2010 (Schiff et al. 2000). Continuing urbanization of these areas results in increased pressure on coastal ecosystems and can lead to deteriorated water quality (Ahn et al. 2005; Roesner and Bledsoe 2003; Santa Monica Bay Restoration Project 1994; USEPA 1993). Considerable portions of the coastal watersheds in southern California are currently impaired for their beneficial uses according to the 303(d) list of the state of California (State Water Resources Control Board 2003).

Over the last decade, efforts to manage water quality have concentrated mainly on storm water, which is currently perceived to be the largest source of pollutant loading (Ackerman and Schiff 2003; Driscoll et al. 1990; Lau et al. 1994; Noble et al. 2000; Schiff 2000; Wong et al. 1997). However, dry-weather pollutant loadings may also constitute a significant impact to water quality both in terms of concentration and load (McPherson et al. 2005; McPherson et al. 2002; 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 (Stein and Ackerman in press). In southern California, which is characterized by a dry Mediterranean climate with low annual precipitation, the majority of rainfall occurs in the winter and the average number of rainfall days is only 37 days/year (Ackerman and Weisberg 2003; Nezlin and Stein 2005). Thus, dry-weather flow can constitute a significant portion of the total annual flow, particularly during dry years. Although concentrations of pollutants in dry-weather flow might be relatively low (Duke et al. 1999; Mizell and French 1995), dry weather flow can be a chronic source of pollution and may impose threats to aquatic life because of its consistent contribution (Ackerman et al. 2003; Bay and Greenstein 1996; Stein and Ackerman In press; Stein and Tiefenthaler 2005). Thus, it is important to investigate natural background water quality in the dry-weather flow as well as storm water.

Unlike man-made compounds, metals, nutrients, and solids in surface water can originate from natural sources as well as anthropogenic sources (Dickert 1966; Horowitz and Elrick 1987; Seiler et al. 1999; Trefry and Metz 1985; Turekian and Wedepohl 1961). Most previous water quality assessments have focused primarily on an evaluation of the anthropogenic contribution of constituents, with little or no attention given to the contribution from natural sources. To exacerbate this data gap, the majority of costal watersheds contain considerable portions of open areas, and much of the upper watershed areas are primarily undeveloped (NOAA Coastal Change Analysis Program (CCAP), 2003). To evaluate the relative extent of anthropogenic activities, it is essential to assess the contribution of the natural streams draining relatively natural environments because both natural processes and anthropogenic activities will ultimately affect water quality in downstream receiving waters.

Several ambient water quality monitoring programs and studies have been carried out across southern California to investigate the impact of development on water quality. Most of these studies included water chemistry data from relatively natural areas for reference conditions. However, the existing data were collected from a limited number of sites that did not account for the complexity of environmental settings in the coastal watersheds of southern California. Southern California's coastal watersheds occur in diverse geologic and topographic settings, have a variety of soil types, and contain several natural vegetation communities (USGS 2006). These environmental factors are known to influence natural loadings (Goodwin 1996; Presser and Swain 1990; Richards et al. 1996) and existing data are insufficient to characterize natural background concentrations across the region. In addition, the existing reference data were from relatively natural areas, but were not free of human influences from agricultural runoff and rural residences (e.g., septic systems). Consequently, these reference sites may not be representative of natural background conditions of southern California's coastal watersheds. Thus, it is necessary to assess dry-weather concentration and loads from natural watersheds and to investigate the effect of environmental settings on water quality, which can be extrapolated to other parts of southern California.

The goal of this study is to evaluate the dry-weather natural background levels of metals, nutrients, and solids in stream reaches that are representative of existing natural conditions in southern California. Specific questions that will be addressed are:

1. What are the ranges of concentrations, loads, and fluxes of various water quality constituents associated with natural areas during the dry weather?
2. How do catchment characteristics influence dry-weather concentrations and loads from natural landscapes?
3. How do the ranges of constituent concentrations and loads associated with natural areas compare to those associated with developed areas?

2. Materials and methods

2.1. Study design

Numerous environmental factors can influence water quality in undeveloped areas, including climate, vegetation, geologic formations, and land use (Likens et al. 1977). Previous studies found that geology and land cover were the primary factors influencing surface water quality (Detenbeck et al. 1993; Gergel et al. 1999; Johnes et al. 1996; Johnson et al. 1997a; Lakin and Byers 1941; Larsen 1988; Ohlendorf et al. 1988; Ohlendorf et al. 1986; Presser et al. 1994; Richards et al. 1996; Tidball et al. 1991; Tracy et al. 1990). Review of existing data from ambient water quality monitoring programs in southern

California also suggested that surficial geology and dominant land cover likely influenced water quality loading from minimally developed watersheds (see Chapter 1 Introduction 3.2. Review of existing data from ambient-water monitoring programs). Consequently, our sampling design involved stratified sampling based on these two independent variables. Sites in areas that represented the largest proportion of undeveloped areas in the study region were prioritized: sedimentary rocks-shrub group, igneous rocks-shrub group, sedimentary rocks-forest group, and igneous rocks-forest group. The prioritized geology-land cover combinations account for the majority of undeveloped area in the coastal watersheds of southern California (California Division of Mines and Geology (1962) and land cover maps (NOAA Coastal Change Analysis Program (CCAP) 1999)).

To ensure that sampling would capture natural conditions without influence from any land-based anthropogenic input, and would be representative of the range of natural conditions that existed in southern California, the following criteria were applied to select study sites:

1) contributing drainage area should be at least 95% undeveloped,
2) relatively homogenous setting,
3) either year-round or prolonged dry weather flow to allow sampling during both wet and dry seasons,

4) sites should not be within watersheds that have burned during the previous three years. According to the study on the impact of wildfire in 1993 in Santa Monica Mountains (Gamradt and Kats 1997), erosion following the 1993 wildfire produced major changes in stream morphology and composition.

2.2. Study areas

Nineteen sites in nine watersheds were selected across coastal areas in southern California based on the site selection criteria listed above (Figure 1 and Table 1). The sites were selected to encompass the range of catchment sizes that occur in southern California. 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 digitized geology maps (Jennings and Strand 1969; Rogers 1965; 1967; Strand 1962) and land cover maps (NOAA Coastal Change Analysis Program (CCAP) 2003). The rest of the catchment characteristics were assessed using ArcView GIS7.0 (ESRI, Redlands, CA). Percent canopy cover was estimated as percent vegetation cover over a stream based on field measurements using a spherical forest densitometer (Wildco, Buffalo, NY).

2.3. Sampling

Three dry-season sampling events were conducted: spring 2005, fall 2005, and spring 2006. Dry season sampling was initiated following at least 30 consecutive days with no measurable rain to minimize effects of residual stormwater return flow. Water samples were collected as composite grab samples, with equivalent volumes collected from three different points across the stream (approximately 10, 50, and 90% distance across). A replicate water sample was collected in the same way 10 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 DO were measured in the field using Orion 125 and Orion 810 field probes (Thermo Electron Corporation, Waltham). 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, Maryland). The flow meter measures 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 averaged to estimate overall flow at each site.

2.4. Laboratory analysis

Water samples were analyzed for pH, DO, hardness, conductivity, total-recoverable metals, nutrients, and solids following protocols approved by the US Environmental Protection Agency (1983) and Standard Methods 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. 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 storm water through a tarred 1.2 mm (micron) Whatman GF/C filter. The filters plus solids were dried at 60° C for 24 h, cooled, and weighed. Nitrate and nitrite were analyzed using the 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 2 shows the list of analytes and a minimum detection limit and applicable units for each analyte.

2.5. Data analysis

Three 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 natural background water quality. Loads were calculated by multiplying flow by concentration for each site:

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

where F_i was a mean flow at sampling site i and C_i was a concentration at site i. A mass loading was expressed as load/day. 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 are presented as geometric means and upper and lower ends of 95% confidence intervals[4]. If the data were normally distributed, results are presented 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

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[4] 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.

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). 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). 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 or sedimentary rock), land cover types (forest or shrub), latitude of site, catchment area (km^2), elevation of site (m), slope of catchment, mean flow (m^3/sec), and percent canopy cover. Dummy values were assigned for the categorical variables (geology and land cover types). For example, a sampling site within a catchment was assigned the value of one if it was dominated by igneous rock and a value of zero if it was dominated by 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 variables when adding a variable to the regression model). The variable with the largest extra fit was then included, and the process was repeated until none of the excluded variables could significantly improve the fit. The statistical significance of the effect of including a variable was determined by means of a Monte Carlo permutation test. The number of permutations to be carried out was limited to 199 because the power of the test increases with the number of permutations, but only slightly so beyond 199 permutations (Lepš and Šmilauer 2003).

The results of the multivariate analysis were visualized using biplots that represent optimally the joint effect of the environmental variables on water quality variables in a single plane (ter Braak 1990).

In addition, the entire water quality data set was grouped based on the most influential environmental variables. Analysis of variance, ANOVA (Sokal and Rohlf 1995), was carried out in order to examine the significance of differences among the groups with a significance level of $p<0.05$. If data failed in either normality test or equal variance test, Kruskal-Wallis one-way ANOVA on ranks (Kruskall 1952; Kruskall and Wallis 1952) was performed to examine difference between the groups. The Kruskal-Wallis test is most commonly used when there is one attribute variable and one measurement variable, and the measurement variable does not meet the assumptions of ANOVA: normality and homoscedasticity[5]. It is the non-parametric analogue of a single-classification ANOVA.

Lastly, concentrations and fluxes in natural catchments were compared with previous data collected from developed catchments to determine if significant differences existed between the two groups. Data for developed catchments were obtained from Southern California Coastal Water Research Program (SCCWRP)'s dry weather studies of metals, nutrients, and total suspended solids in Ballona Creek, Coyote Creek, Los Angeles River, San Gabriel River, San Jose Creek, and Walnut Creek in the greater Los Angeles area, California (Ackerman and Schiff 2003; Stein and Ackerman In press; Stein and Tiefenthaler 2005). Differences between natural and developed catchments were investigated using Analysis of Variance, ANOVA, (Sokal and Rohlf 1995) with a significance of $p<0.05$[6]. Means for concentration and flux per each sampling site were estimated. Eight metals (arsenic, cadmium, copper, iron, lead, nickel, selenium, and zinc), three nutrients (ammonia, nitrate+nitrite, and total

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[5] This assumption means that the variance around the regression line is the same for all values of the predictor variable (X).

[6] If data failed in either normality test or equal variance test, Kruskal-Wallis one-way ANOVA on ranks (Kruskall 1952; Kruskall and Wallis 1952) was performed.

phosphorus), and total suspended solids were examined. Mean concentration and flux data were log-transformed and compared between the natural catchments and the developed catchments using ANOVA. To determine how variability observed in natural catchments was related to variability observed in developed catchments, coefficients of variance (CVs)[7] of the two data sets were compared. The CV accounts for differences in sample size and in the magnitude of means and provides a relative measure of variability. Results were back-transformed for presentation in summary tables to allow easier comparison with other studies. In all cases non-detects were assigned values of ½ minimum detection limits.

3. Results

3.1. 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 an overall 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 %.

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[7] CV = (s / X) x 100; Where, s = standard deviation, and X = mean (average)

Flow at natural sites varied at multiple time scales. Flow in intermittent streams decreased consistently after the last storm of the season to zero after a period of months. Review of monthly average flow data from USGS (USGS National Water Information System: Web Interface, http://waterdata.usgs.gov/ca/nwis) showed that based flow in perennial streams (Arroyo Seco, Sespe Creek, and Piru Creek) varied over one order magnitude, with the highest flows occurring in May and the lowest in September.

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

Nutrients were neither normally nor log-normally distributed except total organic carbon (TOC) and total phosphorus (TP). Metals were mostly 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 (Table 3). For example, the geometric mean of total dissolved solids was 274.4 mg/L and its 95% CI ranged from 183.0mg/L to 411.5 mg/L. Non-detects often occurred due to relatively low levels of constituents at the natural catchments. The percent of NDs for a given constituent ranged from 1.8% for total suspended solids to 59.6% for total phosphorus (Table 4).

No significant difference among sampling events in Spring 2005, Fall 2005, and Spring 2006 was observed for most of constituents. The exceptions were for concentrations of dissolved organic carbon (DOC), total organic carbon (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 in Spring 2005 and Spring 2006. However, there were no consistent or systematic differences where one sampling event had higher concentrations for all four significantly different constituents. Mean flows of sampling sites were significantly lower in Fall 2005 than Spring 2005 and Spring 2006.

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

Geologic type (sedimentary and igneous rocks) 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 5). 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 6).

The predominant source of variability among the data was geology. The first axis of the RDA model explained 66.4% of variance in the data set and was primarily determined by the two geology variables (Tables 6 and 7). Among the variables retained in the RDA model, slope contributed least to variation along the first axis and most along the second axis (Table 7). 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.

Correlation between water quality and environmental variables are explained in the biplot (Figure 2). Copper, selenium, zinc, nickel, iron, total dissolved solids, total organic carbon, and total Kjeldahl nitrogen were positively correlated with sedimentary rock. Nitrate+nitrite was negatively correlated with sedimentary rock and positively so with igneous rock. Other constituents exhibited no strong correlation with any of environmental variables.

Concentrations of several constituents exhibited significant difference between the different geology groups. Results of the ANOVA indicate that copper, iron, nickel, selenium, orthophosphate, and total dissolved solids concentrations were significantly higher in natural catchments underlain by sedimentary rock than those underlain by igneous rock ($p<0.05$). Other constituents did not exhibit any significant difference between the geologic groups. The ANOVA results are provided in the Appendix IV-1 (1.Effect of geology type).

3.4. Comparison with developed catchments

Concentrations differed significantly between the natural and developed sites for all constituents according to the ANOVA results ($p<0.005$). Metal concentrations at the natural catchments were one to two orders of magnitude lower than concentrations observed in the developed catchments (Figure 3). For example, the geometric means for copper were 0.56 μg/L in the natural catchments and 132.40 μg/L in the developed catchments. Concentrations of ammonia, total phosphorous, nitrate+nitrite, and total suspended solids in the natural catchments were two to three orders magnitude lower than concentrations in the developed catchments (Figure 4). For instance, the geometric mean concentration of ammonia was 0.061 mg/L in the natural areas, while it was 6.05 mg/L in the developed areas. Fluxes also differed significantly between the natural and developed sites for all constituents according to the ANOVA results ($p<0.005$). For example, the geometric mean flux of ammonia was 896g/ km^2 day in the developed areas, while it was 3g/km^2 day in the natural areas. The difference between the natural and developed sites was, however, smaller for the fluxes than for the concentrations. The ranges of concentrations of the natural and developed sites were not overlapped for Cu, Fe, Pb, Zn, ammonia, nitrate+nitrite, and TP (Figures 3 and 4), while, those of fluxes were partially overlapped (Figures 5 and 6). Detail ANOVA results are provided in the Appendix IV-1 (2. Natural catchments vs. developed catchments)

In all cases, the variability observed in the natural areas was generally substantially higher than that observed in developed areas (Table 8). 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.

4. Discussion

Dry-weather concentrations of metals, nutrients, and solids from natural catchments in the southern California Costal region were lower than those from developed catchments by about two orders of magnitude in most cases. Dry-weather concentrations documented in this study were even lower than reference water quality from prior studies. Concentrations for metals and nutrients except dissolved organic carbon (DOC) were one to three orders of magnitude lower than concentrations for reference sites in existing ambient monitoring programs that are USEPA's Environmental Monitoring and Assessment Program (EMAP) and the State of California's Surface Water Ambient Monitoring Program (SWAMP) (Table 9). This difference likely results from the fact that EMAP and SWAMP 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 (NOAA Coastal Change Analysis Program (CCAP), 2003). In contrast, in this study sites were rigorously selected to exclude potential effects of non-natural land uses or covers.

Dry-weather concentrations from natural landscapes were consistently lower than established water quality management targets. Mean concentrations of metals were compared with chronic standards of the California Toxics Rule (CTR) for inland surface waters (freshwater aquatic life protection standards; Table 10a)[8] by plotting a concentration of metal for each sample with the CTR criterion for hardness-independent metals (arsenic and selenium) and both a concentration and a hardness value for each sample with the criterion for hardness-dependent metals (cadmium, chromium, copper, nickel, lead, and zinc). Concentrations of metals were below the standards for all metals investigated. The CTR was developed as a guideline to protect aquatic life and have been referred to establish ambient water quality objectives. However, it should be cautious of using the CTR for the ambient water quality objectives. According to

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[8] The formula for calculating the acute objectives for hardness dependent metals (cadmium, chromium, copper, lead, nickel, and zinc) in the CTR takes the form of the following equation: $\text{CMC} = \text{WER} * \text{CCF} * e^{[(mC)(\ln(\text{hardness})+bc]}$

where: WER = Water Effects Ratio (assumed to be 1), CCF = Chronic conversion factor (to convert from the total to the dissolved fraction), m_c = slope factor for chronic criteria, and b_c = y intercept for chronic criteria. The CTR allows for the adjustment of criteria through the use of a water-effect ratio (WER) to assure that the metals criteria are appropriate for the site-specific chemical conditions under which they are applied. A WER represents the correlation between metals that are measured and metals that are biologically available and toxic. A WER is a measure of the toxicity of a material in site water divided by the toxicity of the same material in laboratory dilution water. No site-specific WER has been developed for any of the waterbodies in southern California. Therefore, a WER default value of 1.0 was assumed. The coefficients needed for the calculation of objectives are provided in the CTR for most metals.

this study, the natural background levels of metals in dry weather were significantly lower than the CTR standards. This implies that more rigid standards than the CTR may be required as the objectives in order not to jeopardize the continued existence of a number of endangered and threatened species in southern California. The findings of this study can provide valuable information for developing appropriate objectives to protect aquatic lives in southern California.

There are currently no established nutrient standards against which to compare data collected from the natural catchments. However, in December 2000, USEPA proposed standards for TKN, nitrate+nitrite, total nitrogen, and total phosphorus for Ecoregion III, 6, which include southern California (USEPA 2000). Although these proposed standards have not been approved, they provide a reasonable basis of comparison to levels of potential environmental concern. The geometric means of all nutrients were below or similar to the proposed EPA regional nutrient criteria (Table 10.b). The EPA criteria were developed for the entire year and do not separate dry weather condition from wet weather condition. The criteria are based on medians of 25th percentiles of concentrations from four seasons that include wet weather. This study showed the levels of nutrients are considerably different between dry and wet weather for a number of constituents (Chapter 2 Table 3 and Chapter 3 Table 3). The finding of this study may provide valuable information for development of dry-weather specific nutrient guidelines in southern California.

The background concentrations may be affected by treatment of non-detects (NDs). Samples that are ND can be assigned a value ranging from zero to the minimum detection limit (MDL). In this study, zero was not considered because zero values do not allow calculation of geometric statistics. To be conservative, in this study, we assigned a value of half the MDL to ND samples. Use of the MDL instead of ½ MDL for ND samples would have resulted in less than a 2% increase in median concentration for most constituents. The exceptions were ammonia, nitrate+nitrite, orthophosphate, and total suspended solids, which would have increased by 12, 18, 30, and 8%, respectively.

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; NADP 2006). Smith et al. (2003) showed that estimates of annual loading of total nitrogen and total phosphate could be 16-30% lower when corrected for atmospheric deposition rates. In addition, mountainous areas within the South Coast air basin, which includes our study area, receive the highest nitrogen deposition rates in the country (Fenn et al. 2003; Fenn and Kiefer 1999). Over large areas of California, dry deposition[9] of nitrogen was of greater magnitude than wet deposition[10] due to the arid climate (Bytnerowicz and Fenn 1996). In addition, 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). Thus, the dry-weather concentrations of nutrients that are derived solely from natural sources may be even lower than values presented in this study.

The concentrations of metals, nutrients, and solids from natural catchments were highly variable. This may result from numerous factors, such as temporal and spatial variability. Environmental settings such as geology and land cover have been shown to affect water quality in natural catchments (Detenbeck et al. 1993; Dunne and Leopold 1978; Gergel et al. 1999; Hibbs and Lee 2000; Hounslow 1995; Johnes et al. 1996; Johnson et al. 1997a; Lakin and Byers 1941; Larsen 1988; Ledin et al. 1989; Ohlendorf et al. 1986; Presser et al. 1994; Richards et al. 1996; Tidball et al. 1991; Tracy et al. 1990). In our study, geology was the primary factor to determine dry-weather water quality in natural catchments. Levels of TDS and other constituents were generally higher in streams draining sedimentary than igneous catchments. This difference can be explained by the higher erodibility of sedimentary rock, which results in the

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

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

release of more 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, lead, nickel, and zinc (Garnaud et al. 1999; McPherson et al. 2005; Stenstrom et al. 1997). 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 during dry weather than wet weather conditions, most likely due to a lower amount of overland (surface) runoff (Chapter 4).

Although other studies have documented the importance of land cover on water quality (Nolan and Hitt 2003; Willett et al. 2004), land cover did not have a significant effect on dry-weather water quality in this study. Binkley et al. (2004) reported phosphorus levels in hardwood-forested streams that were more than two orders of magnitude higher than the concentrations we found in this study. In our study, landcover types, which included forest type, however, did not show any significant influence on levels of any constituents including any phosphorus-related constituents according to the RDA results. 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 (Sharp 1994; Sharp and Glazner 1993; USGS 2006). These soils may not be substantially different than those found in scrub-shrub areas; hence, we would not expect differences in nutrient loading.

TABLE 1. DRY-WEATHER STUDY SITES. TABLE INCLUDES CATCHMENT, LOCATION, AND GEOLOGIC AND LAND-COVER SETTING; WFSGR, EFSGR, NFSGR, WEST FORK, EAST FORK, NORTH FORK OF SAN GABRIEL RIVER, RESPECTIVELY.

Site Name	Watershed	Catchment size (km^2)	Geology	Land cover
Arroyo Seco	LA River	43.5	Igneous	Forest
Bear Creek, a tributary to WFSGR	San Gabriel	72.9	Igneous	Forest
Cattle Creek, a tributary to EFSGR	San Gabriel	48.9	Igneous	Shrub
Coldbrook, a tributary to NFSGR	San Gabriel	15.0	Igneous	Forest
Chesebro Creek	Malibu Creek	7.5	Sedimentary	Forest
Cold Creek	Malibu Creek	1.5	Sedimentary	Shrub
Cristianitos Creek	San Mateo	48.9	Sedimentary	Shrub
San Juan Creek	San Juan	101.8	Sedimentary	Shrub
Santiago Creek	Santa Ana	17.1	Sedimentary	Shrub
Bell Creek	San Juan	18.2	Sedimentary	Shrub
Silverado Creek	Santa Ana	16.9	Sedimentary	Shrub
Santa Ana River at Seven Oaks Dam	Santa Ana	9.8	Igneous	Shrub
Cajon Creek	Santa Ana	82.1	Igneous	Shrub
Mill Creek	Santa Ana	15.8	Igneous	Shrub
Fry Creek	San Luis Rey	0.1	Igneous	Forest
Piru Creek	Santa Clara River	477.7	Sedimentary	Shrub
Sespe Creek	Santa Clara River	128.5	Sedimentary	Shrub
Bear Creek, a tributary to NF Matilija	Ventura River	9.7	Sedimentary	Forest
Tenaja Creek	San Mateo	52.8	Igneous	Shrub

TABLE 2. CONSTITUENTS ANALYZED

Analyte	MDL	Units
pH	0.1 pH unit	pH unit
Conductance	0.1 micromhos	micromhos
DO	0.01 mg/L	mg/L
Temperature	0.01 °C	°C
Hardness	1.0 mg/L	mg/L
NH_3	0.01mg/L	mg/L
TKN	0.14mg/L	mg/L
Nitrate+Nitrite	0.02mg/L	mg/L
TP/OP	0.016mg/L	mg/L
TSS	0.5mg/L	mg/L
TDS	0.1mg/L	mg/L
TOC	0.5mg/L	mg/L
DOC	0.5mg/L	mg/L
Arsenic	0.1μg/L	μg/L
Cadmium	0.1μg/L	μg/L
Chromium	0.1μg/L	μg/L
Copper	0.1μg/L	μg/L
Iron	1.0μg/L	μg/L
Lead	0.05μg/L	μg/L
Nickel	0.1μg/L	μg/L
Selenium	0.1μg/L	μg/L
Zinc	0.1μg/L	μg/L

NH_3 = Ammonia; TDS= total dissolved solids; TSS=total suspended solids; TOC= total organic carbon; DOC= dissolved organic carbon; TKN=total Kjeldahl nitrogen; TP=total phosphorus; OP= orthophosphate.

TABLE 3. DRY-WEATHER GEOMETRIC MEANS, UPPER AND LOWER LIMITS OF 95% CONFIDENCE INTERVAL (CI) FOR CONCENTRATIONS, MASS LOAD, AND FLUX (MASS LOAD PER UNIT AREA)

Metals	Concentration (µg/L)			Mass load (g/day)			Flux (g/km^2 day)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Arsenic	0.6646	0.9407	0.4696	7.9033	13.7158	4.5540	0.3277	0.5099	0.2106
Cadmium	0.1123	0.1450	0.0869	1.3354	2.1962	0.8119	0.0554	0.0950	0.0322
Chromium	0.1707	0.2169	0.1343	2.0297	3.2187	1.2799	0.0842	0.1398	0.0507
Copper	0.5583	0.7242	0.4305	6.6395	10.5887	4.1632	0.2753	0.4289	0.1767
Iron	83.90	109.83	64.0992	997.79	1628.97	611.18	41.37	69.19	24.73
Lead	0.0460	0.0611	0.0346	0.5467	0.8861	0.3373	0.0227	0.0378	0.0136
Nickel	0.2992	0.4054	0.2208	3.5575	6.0339	2.0975	0.1475	0.2445	0.0890
Selenium	0.5842	0.8413	0.4057	6.9470	11.8360	4.0775	0.2880	0.4917	0.1687
Zinc	0.5632	0.8224	0.3857	6.6971	10.5161	4.2650	0.2777	0.4959	0.1555

Nutrients	Concentration (mg/L)			Mass load (kg/day)			Flux (kg/km^{2}day)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Ammonia	0.0061	0.0067	0.0055	0.0722	0.1137	0.0458	0.0030	0.0048	0.0019
Nitrate+Nitrite	0.0505	0.0756	0.0337	0.5793	1.0826	0.3100	0.0246	0.0453	0.0133
TKN	0.2768	0.3095	0.2475	3.2912	5.0712	2.1360	0.1365	0.2158	0.0863
Dissolved organic carbon	2.6804	3.3928	2.1176	31.8737	49.8638	20.3742	1.3215	2.1721	0.8040
Total organic carbon	2.8490	3.3734	2.4061	33.8791	51.1778	22.4276	1.4046	2.1776	0.9060
Orthophosphate	0.0163	0.0242	0.0110	0.2046	0.3253	0.1287	0.0078	0.0135	0.0045
Total Phosphorus	0.0478	0.0610	0.0374	0.5682	0.8881	0.3636	0.0236	0.0382	0.0145

Solids	Concentration (mg/L)			Mass load (kg/day)			Flux (kg/km^{2}day)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Total Dissolved Solids	274.43	411.49	183.0197	3132.46	5804.84	1690.37	137.86	250.53	75.87
Total Suspended Solids	0.8512	1.2680	0.5714	10.1218	17.7986	5.7561	0.4196	0.7818	0.2253

TABLE 4. DRY-WEATHER PERCENT NON-DETECTS (%ND); CONSTITUENTS THAT ARE NOT SHOWN HERE DO NOT HAVE NDS.

	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

TABLE 5. RESULT OF STEPWISE SELECTION OF ENVIRONMENTAL VARIABLES USING REDUNDANCY ANALYSIS (RDA) IN DRY WEATHER: 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.

Environmental variables	Extra fit	Cumulative fit	Significance (p value)
Igneous rock	0.0731	0.0731	0.005
Sedimentary rock	0.0731	0.1462	0.005
Slope	0.0403	0.1865	0.04
Mean Flow	0.0385	0.225	>0.05
Elevation	0.0343	0.2593	>0.05
Catchment Size	0.0323	0.2916	>0.05
Canopy Cover	0.0319	0.3235	>0.05
Latitude	0.0249	0.3484	>0.05
Forest	0.0234	0.3718	>0.05
Shrub	0.0234	0.3952	>0.05

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

		Axes			
		1	2	3	4
Eigenvalues		0.075	0.038	0.224	0.116
Water quality-environment correlations		0.65	0.658	0	0
Cumulative percentage variance of	Water quality data	7.5	11.3	33.8	45.4
	Water quality-environment relation	66.4	100	0	0

TABLE 7. 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	-0.6319	-0.1535
Igneous rock	0.6319	0.1535
Slope	0.1608	0.6376

TABLE 8. COMPARISON OF COEFFICIENTS OF VARIANCE (CVS) BETWEEN NATURAL SITES AND DEVELOPED SITES FOR METALS, NUTRIENTS, AND SOLIDS IN THE DRY-WEATHER CONDITION; NA= DATA WERE NOT AVAILABLE

	Natural			Developed		
	Sample Size	Concentration CV	Flux CV	Sample Size	Concentration CV	Flux CV
Arsenic	51	534	1529	4	81	950
Cadmium	51	2262	12941	4	977	13855
Chromium	51	1404	7551	8	41.3	200
Copper	51	462	1828	11	4.4	72
Iron	51	3.2	15.8	8	0.14	1.2
Lead	51	6116	28488	10	15.1	239
Nickel	50	1011	4279	8	5.0	29
Selenium	51	647	2438	8	52	379
Zinc	51	706	2980	11	1.7	23
Ammonia	51	23680	185377	10	321	715
Nitrate+Nitrite	51	8516	37095	8	97	549
Total Kjeldahl Nitrogen	50	543	3896	0	NA	NA
Dissolved Organic Carbon	51	88	463	0	NA	NA
Total Organic Carbon	51	65	352	0	NA	NA
Orthophosphate	51	25231	91310	0	NA	NA
Total Phosphorus	49	5088	24661	8	348	3409
Total Dissolved Solids	51	1.6	6.3	0	NA	NA
Total Suspended Solids	50	502	2299	8	10.8	53

TABLE 9. COMPARISON OF DRY-WEATHER GEOMETRIC MEANS OF CONCENTRATION OF THE NATURAL CATCHMENTS WITH GEOMETRIC MEANS FROM REFERENCE SITES OF THE EMAP AND SWAMP*

	EMAP and SWAMP Reference sites	Natural catchments
Selenium (µg/L)	13.76	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)	301.21	0.32
Total suspended solids (mg/L)	495.83	0.85

*USEPA's Environmental Monitoring and Assessment Program (EMAP) and the State of California's Surface Water Ambient Monitoring Program (SWAMP)

TABLE 10A. 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 THE HARDNESS OF 100 MG/L. 4-DAY CRITERIA ARE USED FOR THE COMPARISON OF THE DRY WEATHER WATER QUALITY.

	Continuous concentration (µg/L) 4-day average	Note
As	150.00	Hardness independent
Cd	2.46	Hardness dependent
Cr	180.00	
Cu	9.33	
Ni	52.16	
Pb	2.50	
Se	5.00	Hardness independent
Zn	119.82	Hardness dependent

TABLE 10B. COMPARISON OF EPA PROPOSED NUTRIENT CRITERIA FOR RIVERS AND STREAMS FOR ECOREGION III, 6 (CENTRAL AND SOUTHERN CALIFORNIA) WITH DRY-WEATHER GEOMETRIC MEANS AND UPPER 95% LIMITS OF THE NATURAL CATCHMENTS

	Ecoregion III, 6	Natural catchments in dry weather
		Geometric mean
Total Kjeldahl Nitrogen (mg/L)	0.363	0.2768
Nitrate+Nitrite (mg/L)	0.155	0.0505
Total Nitrogen (mg/L)	0.518	0.3273
Total Phosphorus (mg/L)	0.030	0.0478

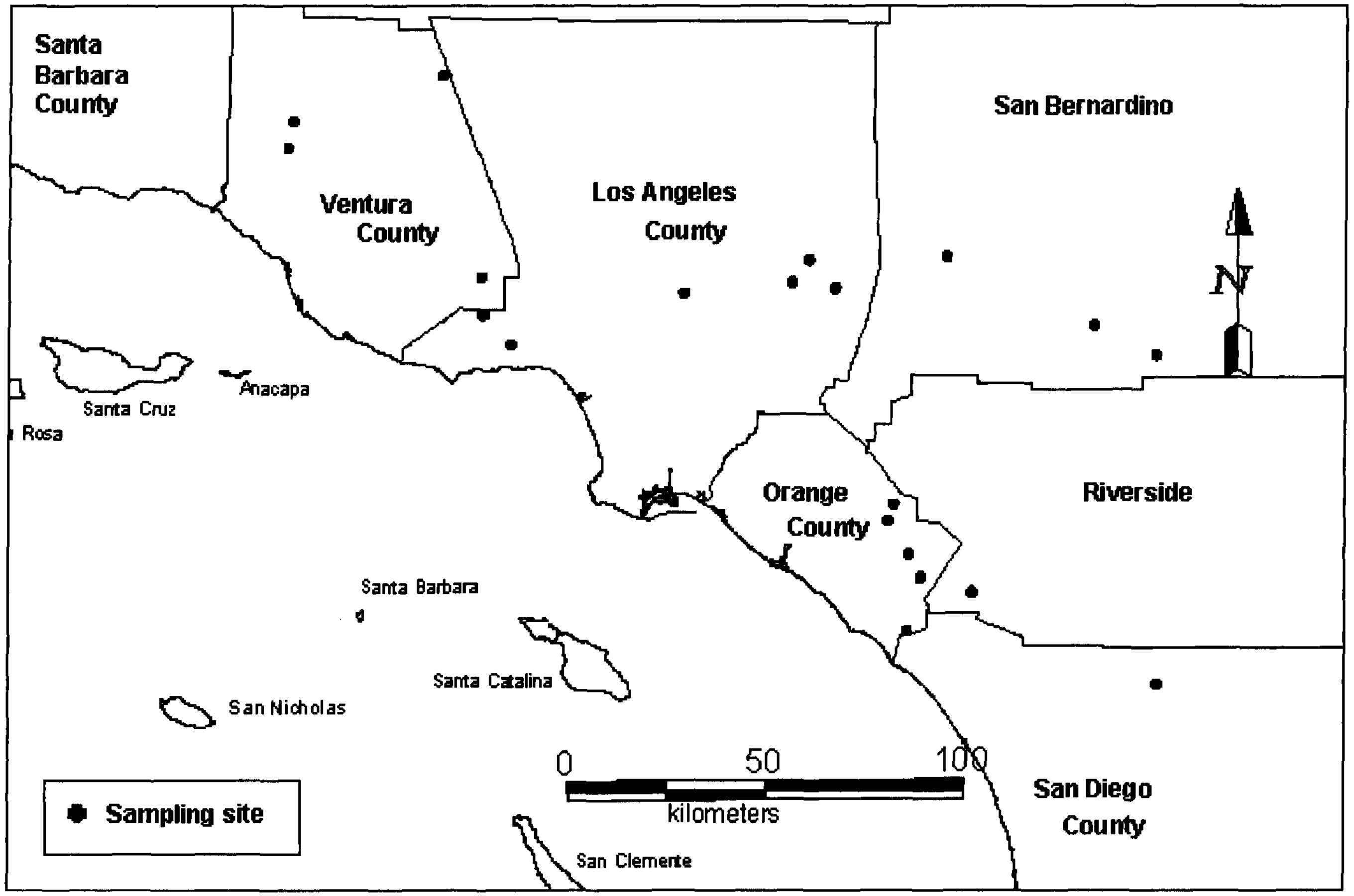

FIGURE 1. MAP OF THE DRY-WEATHER STUDY SITES

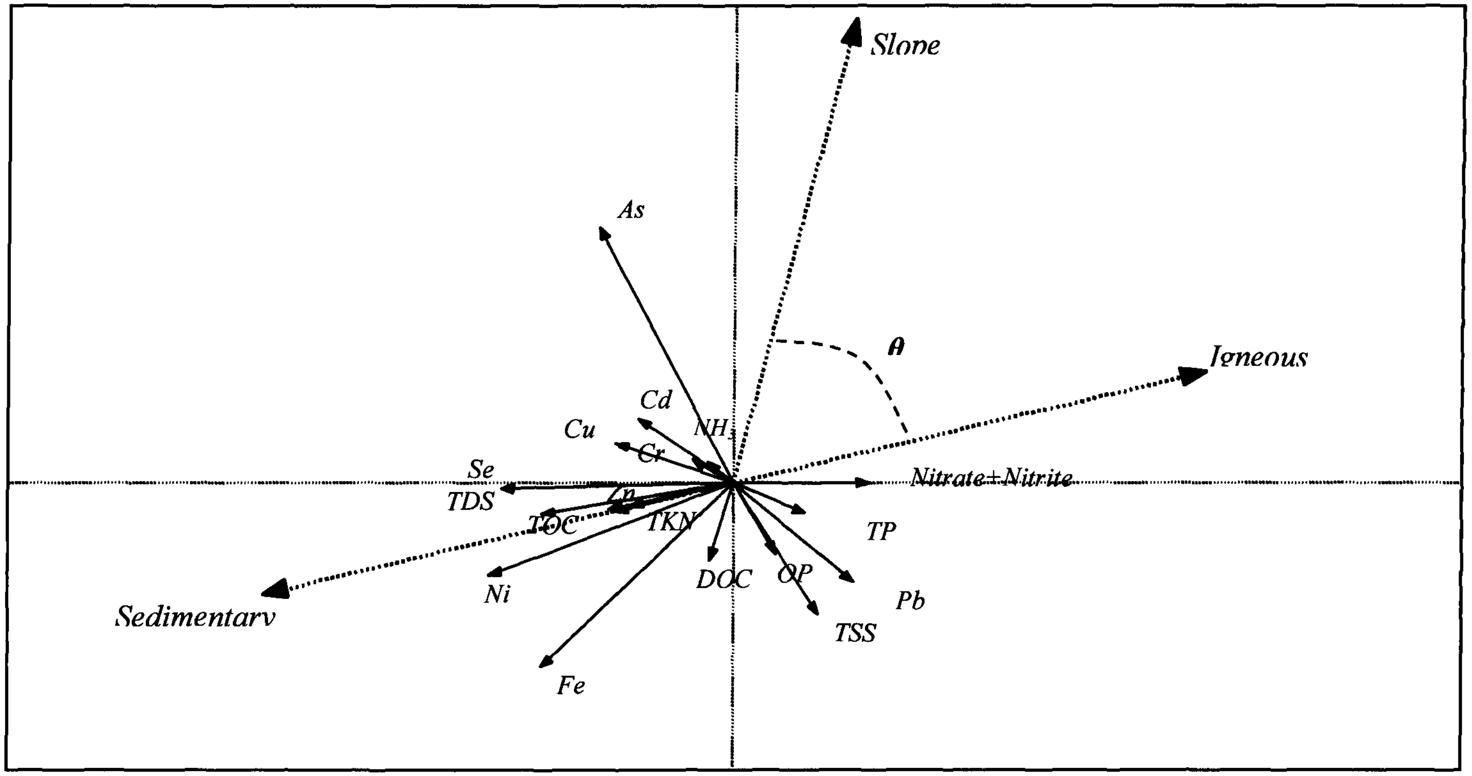

Figure 2. Correlation biplots showing the relations between dry-weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigen values: 0.151 and 0.0280 for the first (horizontal) and second (vertical). cos Θ ≈ correlation coefficient between two variables (arrows). Longer arrow indicates which factor is more important in generating variability (Ter Braak, 1995). TDS= total dissolved solids; TSS=total suspended solids; TOC= total organic carbon; DOC= dissolved organic carbon; TKN=total Kjeldahl nitrogen; TP=total phosphorus; OP= orthophosphate; NOx = Nitrate+Nitrite

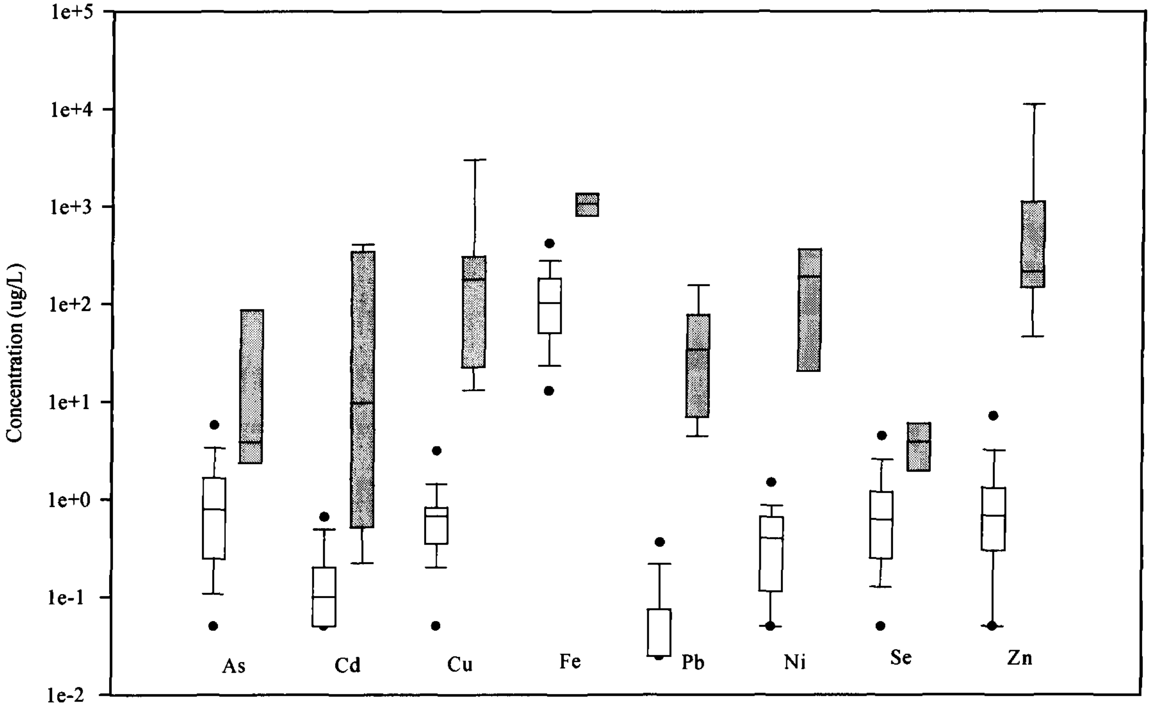

FIGURE 3. COMPARISON OF DRY-WEATHER CONCENTRATIONS OF METALS BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL SITES, WHILE GRAY BOXES REPRESENT DEVELOPED SITES. SOLID LINE IS A MEDIAN OF ALL VALUES IN THE CATEGORY. A BOX INDICATES 25TH AND 75TH PERCENTILES AND ERROR BARS INDICATE 10TH AND 90TH PERCENTILES. SOLID DOTS ARE FOR 5TH AND 95TH PERCENTILES. ALL CONCENTRATIONS ARE EXPRESSED IN μG/L. Y-AXIS IS IN LOG SCALE.

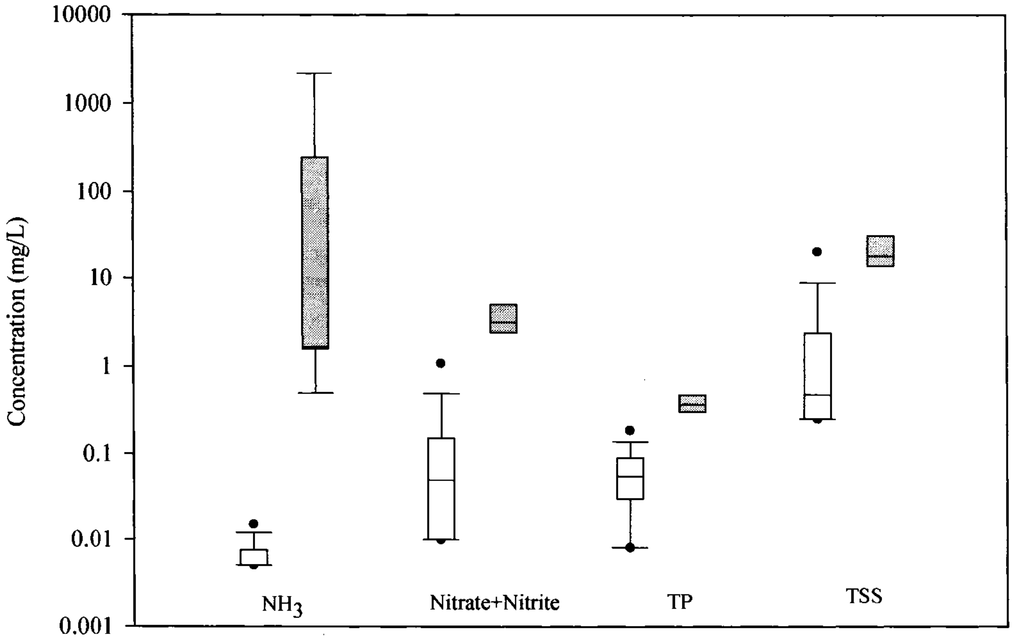

FIGURE 4. COMPARISON OF DRY-WEATHER CONCENTRATIONS OF AMMONIA (NH_3), NITRATE+NITRITE, TOTAL PHOSPHORUS (TP), AND TOTAL SUSPENDED SOLIDS (TSS) BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL SITES, WHILE GRAY BOXES REPRESENT DEVELOPED SITES. ALL CONCENTRATIONS ARE EXPRESSED IN MG/L. Y-AXIS IS IN LOG SCALE.

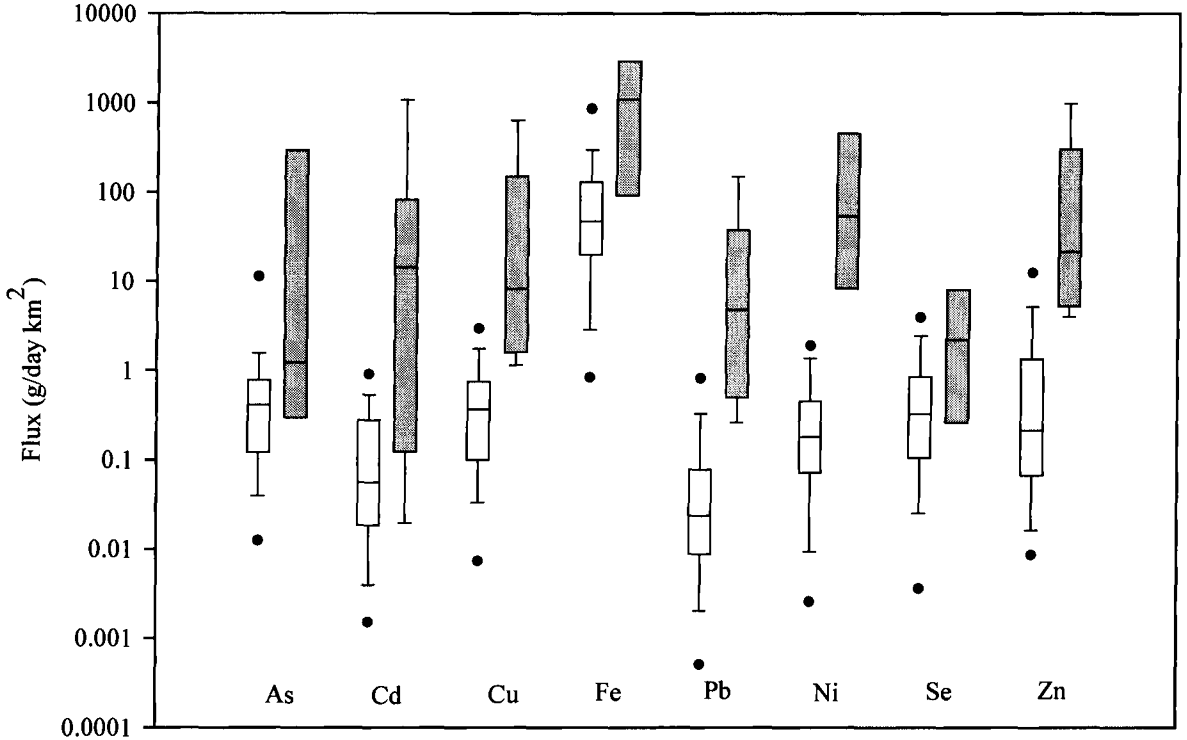

FIGURE 5. COMPARISON OF DRY-WEATHER FLUXES OF METALS BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL SITES, WHILE GRAY BOXES REPRESENT DEVELOPED SITES. ALL FLUXES ARE EXPRESSED IN G/DAY KM^2. Y-AXIS IS IN LOG SCALE.

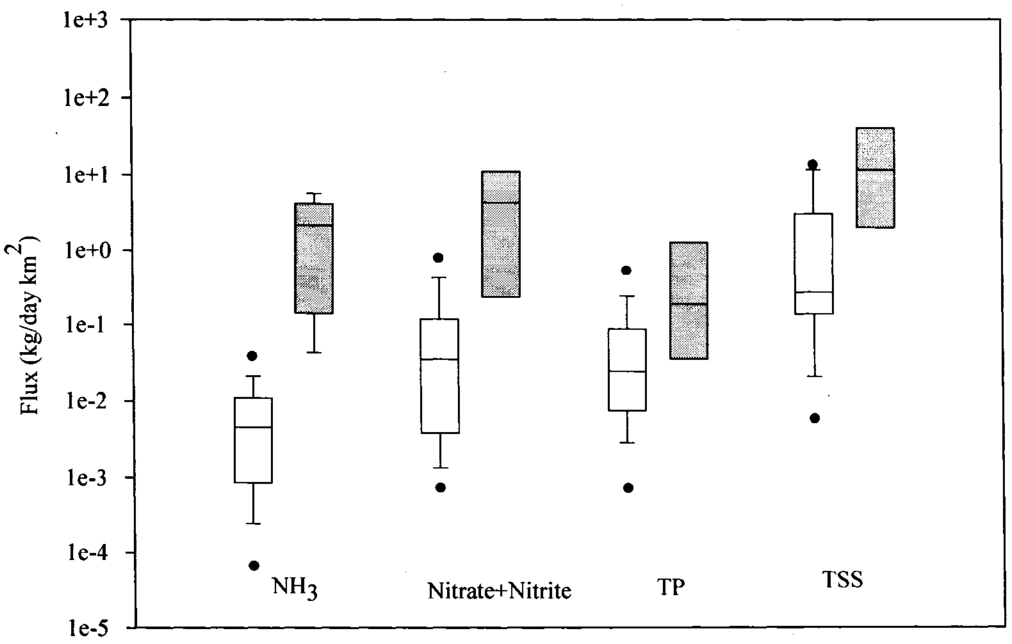

FIGURE 6. COMPARISON OF DRY-WEATHER FLUXES OF AMMONIA (NH_3), NITRATE+NITRITE, TOTAL PHOSPHORUS (TP), AND TOTAL SUSPENDED SOLIDS (TSS) BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL SITES, WHILE GRAY BOXES REPRESENT DEVELOPED SITES. ALL FLUXES ARE EXPRESSED IN KG/DAY KM^2. Y-AXIS IS IN LOG SCALE.

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CHAPTER 3- QUANTATIFICATION OF METALS, NUTRIENTS, AND SOLIDS FROM NATURAL CATCHMENTS DURING WET WEATHER IN SOUTHERN CALIFORNIA

Abstract

Storm water runoff has been recognized as a major contributor to coastal water pollution in southern California; consequently, much attention and many resources have been devoted to evaluation and management of this pollutant source. One of the challenges associated with storm water management is accounting for the natural contributions from undeveloped areas (natural loadings) to overall water quality. Unlike some man-made compounds, metals, nutrients, and solids can originate from natural sources as well as anthropogenic sources. To manage fully pollutants of concern, it is necessary to understand contributions from natural sources. Pollutant inputs can conveniently be classified into wet-weather and dry-weather periods. This study evaluated the wet-weather natural background concentrations and loadings for metals, nutrients, and solids in 18 streams in 11 watersheds that were representative of existing natural conditions in southern California. The influence of watershed characteristics on water quality was also investigated. Levels of metals, nutrients, and solids in storm water runoff from natural catchments varied largely among the catchments. However, constituent concentrations, except TSS, from the natural catchments were typically one to two orders of magnitude lower than those from developed catchments. Wet weather fluxes of nutrients and TSS in natural catchments are not significantly different from those in developed catchments.

Redundancy analysis showed that geology types and elevation were the most influential factors on variability in water quality of the natural catchments. Catchments underlain by sedimentary rock had higher concentrations of metals, nutrients, and total suspended solids. In most of cases, concentrations of metals were below the California Toxic Rules standards. Total nitrogen was higher than the nutrient standards for Ecoregion III, 6 proposed by USEPA. The findings of this study may provide valuable information for developing realistic water quality standards and accurate assessments of natural contributions to loadings of metals, nutrients, and solids.

1. Introduction

Storm water runoff has been recognized as a major source of pollution to many of US's waterways (Characklis and Wiesner 1997; Davis et al. 2001). In southern California, pollutants associated with storm water 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 many resources have been devoted to the evaluation and management of storm water (Ackerman and Schiff 2003; Ahn et al. 2005; USEPA 1995; Wong et al. 1997). One of the challenges associated with storm water management is accounting for the natural contribution from undeveloped areas (natural loadings) to overall water quality. Unlike man-made compounds such as Polychlorinated Biphenyls (PCBs), constituents such as metals, nutrients, and suspended solids can originate from natural as well as anthropogenic sources (Dickert 1966; Horowitz and Elrick 1987; Seiler et al. 1999; Trefry and Metz 1985; Turekian and Wedepohl 1961). Therefore, high levels of these constituents may not directly imply a water quality problem, and it might be difficult to distinguish anthropogenic causes from natural variability in the system. This challenge is exacerbated by the fact that even the most developed coastal watersheds in southern California can contain substantial amounts of undeveloped area. For example, the highly urbanized Los Angles River watershed consists of approximately 40% natural open space, whereas the undeveloped portion of the Malibu Creek watershed accounts for about 85% of that watershed (County of Los Angeles 2004). To manage effectively pollutants of concern, it is necessary to understand relative contributions from natural as well as anthropogenic sources. Without such information, it is difficult for environmental managers to determine what proportions of storm water pollutant loadings are contributed by human sources, and hence what portion might be controlled. Similarly, it is difficult for environmental regulators to set reasonable standards or management targets that incorporate realistic background concentrations or loads.

Existing ambient monitoring programs typically include a few reference streams in relatively undeveloped areas, but mainly focus on dry weather water quality and devote little, if any, resources to characterizing reference conditions for storm water runoff. The lack of attention to natural storm water loading is partly due to difficulties in monitoring storm water runoff in undeveloped areas. Most undeveloped catchments are located in remote and/or mountainous regions, where it is difficult and dangerous to access and sample during storms. In general, the majority of washoff occurs following storms and in developed areas storm water has higher concentrations and loads than non-storm flow (Duke et al. 1999; Stein and Ackerman In press). It is important to understand the role of natural areas to overall storm water loading. To compensate for the lack of data on natural storm water loadings, water quality standards were often written using load allocations based on data from other parts of the country or with anecdotal data from previous time periods (USEPA 2000). As a result, these standards may be ineffective or overly stringent.

Concentrations from natural areas can vary significantly depending on environmental setting, such as underlying geology and land cover (Bisson et al. 1987; Hughes et al. 1994; Keller and Swanson 1979; Leopold et al. 1964; Richards 1982). Underlying geologic formations in undeveloped areas can be a source of many chemical constituents in the water. For example, geologic composition can substantially affect levels of metals, which are a pollutant of concern in many watersheds (Horowitz and Elrick 1987; Trefry and Metz 1985; Turekian and Wedepohl 1961). In southern California, the Monterey formation has been reported to be a source of phosphate loadings (Dickert 1966), which may contribute to algal growth in streams or estuaries. Land cover (or the composition of vegetative cover natural areas) can also have a significant impact on water quality (Detenbeck et al. 1993; Gergel et al. 1999; Johnes et al. 1996; Johnson et al. 1997a; Larsen 1988; Richards et al. 1996; Richards 1982). 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). Coastal watersheds in southern California (like many other areas of the world) exist in a diverse array of environmental settings in terms of soil types, geology, vegetation, elevation, and climate. All these factors may affect water quality concentrations in natural areas; therefore, it is crucial to account for the effect of these watershed characteristics when assessing the contribution of natural sources in storm water loadings.

The goal of this study is to evaluate the natural background concentrations and loading of metals, nutrients, and solids in storm water in series of catchments representing the range of existing natural conditions in southern California. Specific questions addressed are:

4. What are the ranges of concentrations, loads, and fluxes of various water quality constituents associated with storm water runoff from natural areas?
5. How does water quality vary among different types of natural streams and what factors influence this variability?
6. How do the ranges of constituent concentrations and fluxes associated with natural areas compare with those associated with southern California's developed areas?

2. Materials and Methods

2.1. Study areas

We sampled eighteen natural stream reaches in eleven watersheds across coastal areas in southern California (Figure 1 and Table 1). To ensure that sampling sites represented natural conditions without influence from any land-based anthropogenic input, we established the following selection criteria. 1) All sampling sites were along streams with at least 95% undeveloped contributing drainage area. 2) No known grazing, agriculture or septic systems were in the drainage area. 3) Contributing drainage areas were homogenous in terms of underlying geology and land cover. 4) To balance the need for homogenous catchments and sufficient catchment area to generate extended non-storm flow, we targeted third-order drainage basins. 5) No fires had occurred in the drainage area within for at least three years prior to sampling. 6) Sites were accessible and safe to sample. Sampling sites were selected to represent the dominant geology and land cover types present in southern California's coastal watersheds. Prior to sampling, each catchment was characterized for its environmental settings in terms of: 1) land cover type (forest/shrub), 2) geology type (sediment/igneous), 3) catchment size, 4) average slope, 5) elevation, 6) latitude, 7) percent canopy cover. Geology and land cover types were determined by plotting catchment boundaries over digitalized geology maps (Jennings and Strand 1969; Rogers 1965; 1967; Strand 1962) and land cover map (NOAA Coastal Change Analysis Program (CCAP), 2003). The rest of catchment characteristics were assessed using ArcView GIS (ESRI, Redlands, CA). Percent canopy cover was measured using a spherical densitometer (Wildco, Buffalo, NY) in the field during each sampling event.

2.2. Storm water 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. A site was decided as eligible for sampling if it had not received measurable rainfall for three consecutive days and flow was no more than 20% above baseflow in order to avoid influence of groundwater discharge due to the previous rainfall. When rain was forecast, field crews were deployed and sampling was initiated when flows were greater than base flows by approximately 10-20%. Streams were sampled using manual sampling 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 at 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 in the data logger software.

2.2.1. Manual sampling (pollutograph)

Manual sampling was used at streams where safety and access permitted. Between 10 and 12 discrete grab samples were collected per storm at approximately 30 to 60 min 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 that were fixed at the bottom of the channel, pointed in the upstream direction in an area of undisturbed flow. After collection, the samples were stored on ice in pre-cleaned glass bottles with Teflon-lined caps until shipped to the laboratory for analysis. Streams were sampled until flow measurements indicated that the peak flow had subsided and the hydrograph was descending in order to capture concentrations around the highest flow. Flow was at least 50% of the peak flow at the cessation of sampling. For prolonged events, water quality sampling was terminated after 24 hours. Even after the end of sampling, flow measurements often continued to monitor the prolonged descending tail of the hydrograph for days.

2.2.2. *Automatic sampling*

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

2.3. Laboratory analysis for water quality constituents

Both automatic and manual samples were stored and shipped in ice and analyzed within designated holding time for each constituent. Analysis for pH, DO, hardness, conductivity, total-recoverable metals, nutrients, and solids followed protocols approved by the US Environmental Protection Agency (1983) and Standard Methods by the American Public Health Association (Greenberg et al. 2000). Metals were prepared by digestion and analyzed by inductively coupled plasma-mass spectrometry (ICP-MS). The ICP-MS provided concentrations of arsenic, cadmium, copper, chromium, iron, lead, nickel, selenium, and zinc. Total dissolved solids (TDS) were analyzed using the gravimetric technique described by Banse and others (1963) using a flow injection analyzer (Lachat Instruments model Quik Chem 8000). Total suspended solids were analyzed by filtering a 10 to 100 mL aliquot of storm water through a tarred 1.2 mm (micron) Whatman GF/C filter. The filters plus solids were dried at 60° C for 24 h, cooled, and weighed. Nitrate and nitrite were analyzed using the 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 (Shimadzu North America, Columbia, MD). Orthophosphate was analyzed using a titration method. Total phosphorus was persulfate-digested. Table 2 shows the list of analytes and a minimum detection limit for each analyte. All standard laboratory quality insurance measures (e.g. blanks, duplicates, matrix spikes) were conducted to ensure reliability of results.

2.4. Data analysis

Three 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, 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. Last, concentrations and loads in natural catchments were compared with previous data collected from developed catchments to determine if significant differences existed between natural and developed areas.

2.4.1. Ranges and variability of concentrations, loads, and fluxes

Event flow-weighted mean concentrations (FWMC), mass loadings, and flux rates were calculated for each site. Using only those samples for a single storm, the event FWMC was calculated according to Equation 1:

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

where: FWMC = Flow-weighted mean concentration for a particular storm

C_i = Individual runoff sample concentration of i^{th} sample

F_i = Instantaneous flow at the time of i^{th} sample

n = Number of samples per event

Event mass loadings were calculated as the product of the FWMC and the storm volume during the sampling period. Flux estimates facilitated loading comparisons among catchments of varying sizes. Flux was calculated as the ratio of the mass loading per storm and contributing catchment area.

All data were analyzed to determine if they were normally distributed. For those constituents that were not normally distributed, results are presented as geometric means and upper and lower 95% confidence intervals[11]. If the data were normally distributed, results are presented as arithmetic means ± the 95% confidence interval.

2.4.2. Temporal variability: variability within a storm event and a season, and between years

Temporal variability of levels of constituents within a storm event, within a season, and between years was examined. Within a storm event, flows and concentrations were evaluated by examining the time-concentration series relative to the hydrograph using a plot we term a pollutograph. A first flush in concentration from individual storm events, which was defined as when the peak in concentration preceded the peak in flow, is often observed in small urban watersheds (Buffleben et al. 2002; Characklis and Wiesner 1997; Sansalone and Buchberger 1997; Stein et al. 2006). This was quantified using cumulative discharge plots whereby cumulative mass emission was plotted against cumulative discharge volume during a single storm event (Bertrand-Krajewski et al. 1998). When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined when ≥75% of the mass was discharged in the first 25% of runoff volume. A moderate first flush was defined

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[11] 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.

when ≥30% and ≤75% of the mass was discharged in the first 25% of runoff volume. No first flush was assumed when ≤30% of the mass was discharged in the first 25% of runoff volume.

Changes in proportions of metals between particulate phase and dissolved phase over the course of storm were examined and compared with concentrations of total suspended solids, total dissolved solids, and flow. A Pearson correlation analysis was conducted to test correlation of the ratios with flow.

Seasonal patterns of concentrations, loads, and fluxes were analyzed relative to cumulative annual rainfall. Cumulative rainfall was calculated as the sum of rainfall from the first day of a wet season, Oct 1 of the year, up to the sampling day. Rainfall data were from the closest rainfall gaging station for each site. If there were more than one station nearby, the average of the closest stations was used. For this analysis, all study sites were analyzed as a group to examine differences between early- and late-season storms across sites.

For an assessment of variation between years, levels of constituents for different years (water year 2005 and year 2006) were compared using ANOVA(Sokal and Rohlf 1995). Coefficients of variance (CVs) were also compared in order to test change in variability of constituent levels between the years.

2.4.3. Multivariate analysis: Redundancy Analysis

Relationships between catchment characteristics and constituent concentration were investigated using redundancy analysis (RDA). RDA is a canonical extension of principal component analysis (PCA) and a form of direct gradient analysis that describes variation between two multivariate data sets (Rao 1964; ter Braak and Verdonschot 1995). 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). RDAs were performed using the program CANOCO 4.54 (ter Braak and Smilauer 1997). Water quality variables used in the RDA were flow-weighted mean concentrations (FWMC) of water quality constituents. Environmental variables used were geologic setting (igneous or sedimentary), land cover (forest or shrub), latitude, catchment area (km^2), elevation of sampling location (m), slope of drainage area, total rainfall of storm event (cm), baseline flow (m^3/sec), mean flow (m^3/sec), peak flow of storm event (m^3/sec), total volume of storm water runoff (m^3), and percent canopy cover (%). All variables were log transformed prior to analysis to improve normality. Each set of variables was centered and standardized so that the coefficients with different units of measurement would be comparable. Thus, water quality data were transformed by scaling them all at the same range. The environmental variables were standardized to zero mean and unit variance. Interaction terms were not considered.

The importance of the environmental variables was determined by stepwise selection. In each step the extra fit was determined for each variable, i.e. the increase in regression sum of squares over all species when adding a variable to the regression model. The variable with the largest extra fit was then included, and the process was repeated until no variables remained that could significantly improve the fit. The statistical significance of the effect of including a variable was determined by means of a Monte Carlo permutation test. The number of permutations to be carried out was limited to 199 because the power of the test increases with the number of permutations, but only slightly so beyond 199 permutations (ter Braak 1995). The results of the multivariate analysis were visualized by means of a biplot, which represents 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 $p<0.05$. Constituents that passed both normality and equivariance tests were analyzed using ANOVA. The rest of constituents that failed in either the normality test or equivariance test were examined using Kruskal-Wallis one-way ANOVA on ranks (Kruskall 1952; Kruskall and Wallis 1952).

2.4.4. Comparison with developed catchments

Storm water data from developed catchments in the greater Los Angeles area were obtained courtesy of the Southern California Coastal Water Research Project (SCCWRP) and the Watershed Protection District of the County of Ventura. 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 data and flux data were log-transformed and then compared. If data failed in either normality or an equal variance tests, Kruskal-Wallis ANOVA on ranks was performed to examine difference between the groups. To determine how the variability observed in natural catchments related to that observed in developed catchments, coefficients of variation (CVs)[12] of the two data sets were compared. The CV accounts for differences 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.

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[12] $CV = (s / X) \times 100$; where, s = standard deviation, and X = mean (average)

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 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.

3. Results

3.1. Rainfall and Flow

Event total rainfalls over the study period ranged from 0.81 to 17.20 cm. The mean total rainfall per storm event among the study catchments varied between the two years of sampling. During 2004, mean rainfall was 7.3cm/storm event, while in 2005 it was 4.6cm/storm event. The higher rainfall translated to average mean flows during 2004 being approximately four times larger than in 2005. Mean storm flow was 1.39±2.31 (m^3/sec) and flow varied from 1.51 x 10^{-2} to 9.76 (m^3/sec). Peak flows ranged from 6.88 x 10^{-2} to 53.72 (m^3/sec) with the mean of 4.82±11.42 (m^3/sec). The means of peak flow were 1.3±1.6 (m^3/sec) in 2004-05 and 8.1± 15.3(m^3/sec) in 2005-06.

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

Concentrations observed in natural streams during the storms were relatively low. The concentrations were, however, higher than those in the dry weather. Geometric means were one-digit values (μg/L) for metals except iron and one-digit or below one-digit values for nutrients (mg/L). Geometric means of solids were two- to three-digit values (mg/L). Concentrations, loads and fluxes for each constituent are summarized as geometric means and upper and lower ends of 95% confidence interval in Table 3. In all cases, concentrations and loads observed from the natural catchments exhibited a great deal of variability, as indicated by large 95% confidence intervals; concentrations, loads, and fluxes generally varied over one order of magnitude.

3.3. Temporal variability; variability within a storm and a season and between years

No first flush was observed in storm water runoff in any natural catchments, as indicated by the cumulative mass loading plots of all constituents for each storm event. 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 2). Similarly, peak concentrations for metals, nutrients, and solids occurred after the peak flow, unlike the pattern typically observed in developed catchments where peak concentrations occur on the rising limb of the hydrograph. An example of the pollutograph for Piru Creek shows that the peak concentration of copper occurred after a peak flow (Figure 3).

Ratios of particulate over dissolved concentrations of metals changed over the course of storms. In all cases particulate metals increased with the increase of flow and the increase of the concentration of total suspended solids (TSS) and decreased at the descending limb of hydrograph. Figure 4 shows an example of this pattern from a storm event at Bear Creek. The concentration of TSS sharply increased with the increase of rainfall and flow, while the concentration of TDS dropped primarily due to the dilution effect of increased flow. Once the flow dropped, the concentration of TSS also dropped and the concentration of TDS returned to the pre-storm levels in approximately two days (Figure 4A). The temporal pattern of TSS concentrations was synchronized with the increase in particulate metals and was inversely related to TDS concentrations (i.e. as TDS concentrations rose at the end of the storm, the particulate fraction of metals decreased and dissolved fraction increased). Arsenic (As) and selenium (Se) existed primarily in a dissolved phase and all samples were below 1:1 reference line (Figure 4.B). The ratios of particulate over dissolved metals for As and Se, however, increased by approximately two orders of magnitude. Copper (Cu), lead (Pb), and zinc (Zn) existed mainly in the dissolved phase prior to the storm. At the peak of the storm, particulate metals increased by three orders of magnitude and the majority of metals in stormrunoff were particulate forms. The ratios returned back to the pre-storm levels in two days after the peak. The ratios of all metals except cadmium and the concentration of TSS were correlated with flow ($p< 0.05$). All correlated metals except copper and selenium have correlation coefficients (r^2 values) that were larger than 0.4.

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

Levels of constituents varied between different years. The range of variability in the data was larger during the wetter 2004 than during the drier 2005. Variability among different storm events in 2004 was significantly larger than variability in 2005 for the majority of constituents (Table 1 in Appendix V). For example, the % CV of total suspended solids in 2004 was approximately three times larger than that in 2005: 1154 and 393, respectively. Geometric means for all constituents except dissolved organic carbon, total organic carbon, and total phosphorus were higher in 2004 than those in 2005 (Table 2 in Appendix V).

3.4. 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, redundancy analysis (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 4). Because sedimentary geologic setting, igneous geologic setting, and elevation were the variables that considerably contributed to the fitness of the RDA model (P values were smaller than 0.025, 0.025, and 0.1 for sedimentary type, igneous type, and elevation, respectively), subsequent RDA analysis was conducted with only these three environmental variables, thereby maximizing the ability of the model to resolve differences among environmental classes.

The RDA model with three environmental variables explains 66.6 % of variance in water quality data (Table 5). 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 variables that explain geologic setting. This axis had a canonical coefficient of ±0.5167 and explained 84.5% of total model variance relating water quality variables to environmental variables

(Tables 5 and 6). The second axis of the RDA model was determined by elevation and had a canonical coefficient of 0.3777 and explained 15.5% of total model variance (Table 6).

Most metals, total suspended solids, and a few nutrients were correlated with geology variables. Correlation between the water quality variables and the environmental variables are explained in the biplot (Figure 5). Most metals except arsenic and total suspended solids were positively correlated with sedimentary rock. Dissolved organic carbon and total organic carbon were negatively correlated with sedimentary rock and positively correlated with igneous rock. Total Kjeldahl nitrogen was strongly positive-correlated with elevation. Arsenic, orthophosphate and total dissolved solids were negatively correlated with elevation. Other constituents exhibited no strong correlation with any of environmental variables. The regression analysis reconfirmed the correlations between the water quality constituent variables and the environmental variables suggested by the RDA results.

Concentrations of several constituents exhibited significant difference between the different geology groups. Result of the ANOVA indicate that Cu, Ni, Se, and NH_3 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 significant difference between the geologic groups. The ANOVA results are provided in the Appendix IV-2 (1. Effect of geology type).

3.5. 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 developed catchments (Figure 6). Ratios of both mean flow and total runoff volume to catchment size also increased less sharply in response to the increase of rainfall in natural catchments than in developed catchments.

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 according to the ANOVA results. In addition, fluxes for arsenic, copper, iron, lead, nickel, zinc, and ammonium were significantly different ($p<0.05$) between the natural catchments and the developed catchments. Comparisons were conducted for a total of nine metals (arsenic, cadmium, chromium, copper, iron, lead, nickel, selenium, and zinc), four nutrients (ammonium, total Kjeldahl nitrogen, total phosphorus, and nitrate+nitrite), and total suspended solids, which were only available constituents from the developed data. Among them, cadmium, selenium, ammonium, total Kjeldahl nitrogen, and total suspended solids (TSS) passed both normality and equivariance tests and were analyzed using one-way ANOVA. The rest of constituents that failed in 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 (Figure 7). Concentrations of ammonium and total Kjeldahl nitrogen in the natural catchments were about one order of magnitude lower than those in the developed catchments and those of nitrate+nitrite were less than one order of magnitude lower, while total suspended solids concentrations show no significant difference (Figure 8). Comparison of fluxes (i.e. mass loading per unit area) between the natural and the developed catchments showed that fluxes for arsenic, copper, iron, lead, nickel, zinc, ammonium, and total phosphorus were also lower in natural catchments (Figure 9 and 10). The results of ANOVA are provided in Appendix IV-2 (2. Natural catchments vs. developed catchments).

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 coefficient of variation, CV (Table 7). For example, in the developed catchments, the geometric mean of FWMCs for iron was 9,729 μg/L and the geometric standard deviation was 18. Meanwhile, the geometric mean for iron was 962 μg/L and the geometric standard deviation was 11 in the natural catchments.

4. Discussion

4.1. Levels of constituents observed in natural catchments

In most cases, wet-weather concentrations in natural catchments were about one order of magnitude lower than those from the developed catchments, with the exception of total suspended solids (TSS). Both flow-weighted concentration and flux of TSS in the natural catchments were not different from those in the developed catchments. This indicates that natural areas may be a substantial source of sediment to downstream areas. Previous studies on developed catchments reported that a number of pollutants, especially metals, found in developed catchments existed primarily in particulate phase (Characklis and Wiesner 1997; Stenstrom et al. 1997). However, the high TSS in the natural catchments does not automatically imply the high particle-bound pollutants, as shown in this study. Therefore the nature of particles in the storm runoff from natural catchments needs to be identified. It is important to identify how particle size of sediment from natural sources differs from that from anthropogenic sources because the particle size will affect transport and depositional patterns of sediment and particle-bound pollutant.

Metal concentrations were compared with the California Toxics Rules (CTR) for inland surface waters (freshwater aquatic life protection standards) for acute toxicity standards (Table 8a) by plotting the concentrations of metals for each sample with the criteria for hardness-independent metals and the concentrations and hardness for each sample with the criteria for hardness-dependent metals. Concentrations of metals were consistently below the CTR standards for all metals except for a few isolated exceedances for copper. When compared to the CTR criteria, total recoverable copper concentrations exceeded the standard in 15 individual samples out of a total of 133 samples analyzed (11%) (Figure 11). However, when dissolved concentrations of copper[13] were compared with the CTR standard, only one out of 133 values exceeded CTR standard (Figure 12). The CTR criteria are based on dissolved concentrations of metals, however the CTR also provides the simple conversion matrix for the application of total concentrations if dissolved concentrations are not available. However, the total concentrations vary over the course of the storm, so difficult to infer toxicity from an instantaneous sample. It is also difficult to identify how much of the total fraction is dissolved and how much of the dissolved fraction is bioavaliable since various factors affect the partitioning between particulate and dissolved forms, such as the suspended solid types and concentrations, pH, total metal concentrations, and dissolved organic carbon (DOC) concentration and character (Paulson and Amy 1993). Most of all, our observation that ratio of particulate to dissolved metals changed over the course of the storm, leads to the conclusion that direct measure of dissolved metals is necessary to estimate metal toxicity in storm water.

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

There are no established nutrient standards against which to compare data collected from the natural catchments. However, in December 2000, USEPA proposed standards of 0.363 mg/L, 0.155 mg/L, 0.518 mg/L, and 0.030mg/L for total Kjeldahl nitrogen (TKN), nitrate+nitrite, total nitrogen (TN), and total phosphorus (TP), respectively for Ecoregion III, 6, which includes southern California (USEPA 2000). The standards are shown in Table 8b. The geometric means of flow-weighted concentrations of TKN and TP in the natural catchments were below/similar to the proposed standards, but the geometric means of nitrate+nitrite and TN were above these proposed levels. Higher levels of nitrate+nitrite, which led to higher TN (TN = TKN+ Nitrate+Nitrite), at the natural catchments than the USEPA proposed nutrient standards may suggest the wet-weather natural background levels for the nutrients may be even higher than the proposed standards. This may be because the EPA proposed standards are not specified for the wet weather only but they are averaged conditions for the entire year including dry weather. The EPA proposed standards were developed based on all existing nutrient data. First, 25th percentiles of four seasons were selected and then the median values of the 25th percentiles was calculated as the standard reference condition. Thus, using the EPA standard for wet weather may result in the underestimation of the natural background nutrient levels. The high wet-weather TN found in this study is even close to the eutrophic condition defined by Dodds and others (Dodds et al. 1998). Dodds and others classified 100 temperate streams in the States and defined the levels nutrients of eutrophic condition as the upper third of distribution. This implies the natural streams in southern California can be substantial sources of nitrogen to downstream water bodies and may contribute algal growth. The finding of this study may provide more detail information on the wet-weather natural ranges of metals, nutrients, and solids and may assist to develop more realistic water quality standards for nutrients for the southern California region.

Several factors could have influenced the estimates of natural concentrations and fluxes provided by this study. The first one is the treatments of non-detects (NDs), which occur fairly frequently given the inherently low concentrations of constituents in natural catchments (Table 9). We do not expect that our assignment of a value of ½ the detection limit to NDs would 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 detection limits (Table 2). In our data, 53% of the total phosphorous samples were ND. If we assigned a value equal to the detection limit to these samples (instead of ½ the detection limit), the overall geometric mean concentration would only increase by 0.05%. This is mainly due to the large fluctuation of concentrations over the course of each storm event. Since several high concentrations during a storm event determine the FWMC, the value assigned to a few samples at lower concentrations does not substantially affect the mean. Concentrations of total phosphorus 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 is not likely to affect the flow-weighted mean concentrations.

A second factor that could have influenced our estimates is the role of aerial deposition, which was not corrected for in our estimates. If aerial deposition were considered, the natural background levels estimated by this study would be even lower. Atmospheric deposition can be a significant factor that affects loadings in natural areas. For instance, in Midwestern and Northeastern streams, atmospheric deposition of nitrogen can account for nearly all-downstream nitrogen loads (Puckett 1995; Smith et al. 1987). 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; NADP 2006). The study by Smith and others (2003) reported that loadings of total nitrogen and total phosphate could be 16-30% lower when they were corrected with atmospheric deposition rate. These suggest that the levels of nutrients in the natural catchments could be lower than vales presented in our study if they were corrected with atmospheric deposition rates. Sabin and others (2005) showed that atmospheric deposition potentially accounted for as much as 57-100 % of the total metal loads in stormwater in a small impervious urban catchment in Los Angeles, CA. Mountainous areas within the South Coast air basin, which include portions of four counties in the Los Angeles area, received the highest nitrogen deposition in the country (Fenn et al. 2003; Fenn and Kiefer 1999). The high level of nitrate+nitrite and TN compared to the EPA that were discussed before may be due to the high atmospheric deposition of nitrogen in the areas. Bytnerowicz and others (Bytnerowicz and Fenn 1996) presented that total inorganic nitrogen deposition in the most highly-exposed forests in the Los Angeles Air Basin might be as high as 2.5-4.5 mt/km^2 yr and nitrogen deposition in these highly-exposed areas has led to nitrogen saturation of chaparral and mixed conifer stands. In addition, Bytnerowicz and others showed that in nitrogen saturated forests high concentrations of NO_3- are found in stream water, soil solution, and in foliage and in locations close to photochemical smog source areas, concentrations of oxidized forms of nitrogen dominate. 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.

4.2. Factors affecting water quality in natural catchments

Levels of constituents among natural catchments vary largely. The water quality of natural catchments varies both spatially and temporally and is affected by factors such as climate, land use types, vegetations, soils, and chemical weathering of soils and bedrock (Likens et al. 1996; Likens et al. 1977).

In this study, geology and elevation were the most influential factors on variability of water quality in natural catchments. Geology is the main factor that influences water quality in natural areas. A sedimentary rock is positively correlated with a variety of constituents in storm water runoff from natural areas. This is because sedimentary rocks can be more easily eroded and can release more suspended solids into the water than igneous rocks. Higher suspended solids can lead to higher suspended solids-related constituents in storm water such as chromium, copper, lead, nickel, and zinc, according to the RDA result of this study. Vegetation, soils, hydrology, and morphology are dependent upon geology, modified by the climatic conditions and are interdependent (Goodwin 1996). Geology should be a primary criterion for catchment stratification to estimate the background levels of water quality. Elevation was the second influential factor on variability of water quality. Levels of total Kjeldahl nitrogen (TKN) were positively correlated with elevation. There is no obvious direct link between TKN and elevation.

In our study, land cover did not exhibit significant impact on water quality. In previous studies, land use types including land cover types have been shown to have significant impact on water quality (Detenbeck et al. 1993; Gergel et al. 1999; Johnes et al. 1996; Johnson et al. 1997a; Larsen 1988; Richards et al.

1996). Previous studies have focused on the influence of natural vs. developed land cover on surface water quality or on the effect of different types of developed land use/land cover. The influence of different natural land cover on water quality loading has not been extensively examined prior to this study. Miller et al. (2005), however, addressed the importance of land cover on natural water quality. They reported that the forested system in mature forested Sierra catchments could be a significant source for nutrients. The concentrations of ammonia, nitrate, and phosphate were high in surface runoff from forested systems; as high as 87.2mg/L, 95.4mg/L, 24.4mg/L for ammonia, nitrate, and phosphate, respectively. These values are even greater (one order of magnitude) than maximum values for developed land uses that were observed in southern California coastal catchments (Ackerman and Schiff 2003). Miller et al.'s (2005) values were one to two orders of magnitude higher than the upper ends of 95% confidence interval values for nutrients presented in our study. Miller et al. (2005) suggested that nutrients that were driven from mature organic horizons (O-horizons[14]) 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 our natural

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[14] O-horizon: The top of the soil 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.

catchments 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[15] and the nutrient levels varied with up to two orders of magnitudes. This highlights the importance of identifying region-specific background water quality and potential significant impact of land cover on the water quality.

Other environmental factors such as catchment size, flow-related factors, rainfall, slope, and canopy cover did not exhibit significant impact on variability of water quality. This suggests that our findings may be extrapolated for natural background water quality to the southern California's coastal region. For instance, atmospheric deposition, and groundwater recharge. 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

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[15] 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).

significant difference of natural background concentrations among catchments with different size was observed in this study. This allows extrapolating the findings of this study 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 what is typically observed in developed catchments. No first flush was observed in natural catchments, even for small catchments where first flush tends to be most common. Pollutants deposited onto exposed areas can be dislodged and entrained by the rainfall-runoff process. In developed catchments, usually the storm water that initially runs off an area will be more polluted than the storm water that runs off later, after the rainfall has 'cleansed' the catchment. The storm water containing this high initial pollutant load is called the 'first flush'. The first flush can occur a few hours earlier than the peak flow during a storm (Hoffman et al. 1984; Smith et al. 2000; Stein et al. 2006). The existence of this first flush of pollutants provides an opportunity for controlling stormwater pollution from a broad range of land uses. First flush collection systems are employed to capture and isolate this most polluted runoff, with subsequent runoff being diverted directly to the stormwater system. Therefore, the information on the first flush helps to develop appropriate management tools specified for each watershed. The existence of first flush should not be assumed in all cases. Intensive monitoring of storm water 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). In natural catchments, sediment (and associated bound pollutants) generated from soil erosion, for example, will not give 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 (total suspended solids and total dissolved solids). This may partially explain why total suspended solids FWMC were comparable between natural and developed areas. As the RDA results showed, a number of constituents were correlated with TSS. Thus, there is also almost no limitation of supply of TSS-correlated constituents, especially metals, during storms. Unlike urban developed catchments where rainfall cleans accumulated pollutants off impervious surfaces, in natural catchments the rainfall-runoff process leads to continuous input of metals, nutrients, and solids throughout a storm, which is confirmed by e spread out shape of the pollutograph from natural areas.

Early-season storms did not have higher levels of constituents than late-season storms in the natural catchments. Numerous studies from developed watersheds reported seasonal flushing that pollutant levels in storm runoff were higher in early-season storms than in late-season storms (Buffleben et al. 2002; Hatje et al. 2001; Stein et al. 2006). Additionally, in the developed catchments, early-season storms wash off pollutants that were built up on the land surfaces so that late-season storms have less pollutant to carry in runoff. However, in the natural catchments storms wash off not only surface constituents but also those associated with eroded sediment. Because natural sites have a virtually limitless supply of sediments, the depletion of surface load observed in late season runoff from developed areas likely does not apply. Thus the strength of storms may be a more significant factor determining levels of constituents than seasonality of storms.

4.3. Implications of findings of this study

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, 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. 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. Significant unanswered questions include the contribution of aerial deposition to loading from natural watersheds and the particle size distribution, and associated pollutant binding, in storm water runoff from natural areas. This additional information will allow for further refinement of background concentrations for heuristic analysis or simulation models.

TABLE 1. WET-WEATHER STUDY SITES; EFSGR AND NFSGR ARE EAST FORK AND NORTH FORK OF SAN GABRIEL RIVER, RESPECTIVELY.

Site Name	Watershed	Catchment size (km^2)	Geology	Land cover
Arroyo Seco	LA River	43.5	Igneous	Forest
West Fork San Gabriel River	San Gabriel	112.3	Igneous	Forest
Cattle Creek, a tributary to EFSGR	San Gabriel	48.9	Igneous	Shrub
Coldbrook, a tributary to NFSGR	San Gabriel	15.0	Igneous	Forest
Chesebro Creek	Malibu Creek	7.5	Sedimentary	Forest
Cristianitos Creek	San Mateo	48.9	Sedimentary	Shrub
Santiago Creek	Santa Ana	17.1	Sedimentary	Shrub
Bell Creek	San Juan	18.2	Sedimentary	Shrub
Silverado Creek	Santa Ana	16.9	Sedimentary	Shrub
Santa Ana River at Seven Oaks Dam	Santa Ana	9.8	Igneous	Shrub
Mill Creek	Santa Ana	15.8	Igneous	Shrub
Fry Creek	San Luis Rey	0.64	Igneous	Forest
Piru Creek	Santa Clara River	477.7	Sedimentary	Shrub
Sespe Creek	Santa Clara River	128.5	Sedimentary	Shrub
Bear Creek North Fork Matilija	Ventura River	10	Sedimentary	Forest
Runkle Canyon	Calleguas	3.4	Sedimentary	Shrub
Tenaja Creek	San Mateo	52.8	Igneous	Shrub
Arroyo Sequit	Arroyo Sequit	27.4	Sedimentary	Shrub

TABLE 2. CONSTITUENTS ANALYZED

Analyte	MDL	Unit
pH	0.1 pH unit	pH unit
Conductance	0.1 micromhos	micromhos
Dissolved Oxygen	0.01 mg/L	mg/L
Temperature	0.01 °C	°C
Hardness	1.0 mg/L	mg/L
NH_3	0.01mg/L	/L
TKN	0.14mg/L	mg/L
Nitrate+Nitrite	0.02mg/L	mg/L
TP/OP	0.016mg/L	mg/L
TSS	0.5mg/L	mg/L
TDS	0.1mg/L	mg/L
TOC	0.5mg/L	mg/L
DOC	0.5mg/L	mg/L
Arsenic	0.1µg/L	µg/L
Cadmium	0.1µg/L	µg/L
Chromium	0.1µg/L	µg/L
Copper	0.1µg/L	µg/L
Iron	1.0µg/L	µg/L
Lead	0.05µg/L	µg/L
Nickel	0.1µg/L	µg/L
Selenium	0.1µg/L	µg/L
Zinc	0.1µg/L	µg/L

NH_3 = Ammonia; TDS= total dissolved solids; TSS=total suspended solids; TOC= total organic carbon; DOC= dissolved organic carbon; TKN=total Kjeldahl nitrogen; TP=total phosphorus; OP= orthophosphate.

TABLE 3. WET-WEATHER GEOMETRIC MEANS, UPPER AND LOWER LIMITS 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 STORMEVENT.

Metals	FWMC (μg/L)			Mass load (g)			Flux (g/km^2)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Arsenic	0.3883	0.7107	0.2121	17.3971	44.6294	6.7816	0.8711	1.9120	0.3968
Cadmium	0.1396	0.2377	0.0820	6.2564	15.4580	2.5322	0.3133	0.7252	0.1353
Chromium	1.3971	3.0945	0.6308	62.5936	188.8827	20.7428	3.1341	7.9793	1.2310
Copper	1.5366	3.1655	0.7459	68.8440	201.0659	23.5719	3.4470	8.6835	1.3683
Iron	962.01	2312.52	400.19	43100.49	139746.25	13293.04	2158.04	6160.27	755.99
Lead	0.5089	1.0600	0.2443	22.7980	64.8440	8.0154	1.1415	2.9365	0.4437
Nickel	1.0321	2.4613	0.4328	46.2426	152.0952	14.0595	2.3154	6.3572	0.8433
Selenium	0.3332	0.6038	0.1838	14.9263	41.2157	5.4056	0.7474	1.8525	0.3015
Zinc	5.3219	11.1580	2.5383	238.4352	680.9703	83.4858	11.9385	31.5163	4.5223

Nutrients	FWMC (mg/L)			Mass load (kg)			Flux (kg/km^2)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Ammonia	0.0427	0.0808	0.0225	1.9110	4.6798	0.7803	0.0957	0.2079	0.0440
Dissolved Organic Carbon	6.2605	9.5365	4.1098	338.6735	915.7560	125.2514	11.8321	30.3459	4.6134
Nitrate+Nitrite	0.3350	0.5814	0.1931	15.0110	36.2032	6.2240	0.7516	1.5366	0.3676
Orthophosphate	0.0383	0.0614	0.0239	1.9072	4.3463	0.8369	0.0956	0.1959	0.0467
Total Kjeldahl nitrogen	1.2139	1.5499	0.9508	70.7448	255.6595	19.5761	2.6282	7.1842	0.9615
Total Organic Carbon	6.2765	9.9064	3.9767	339.5424	935.8073	123.1974	11.8624	31.3118	4.4941
Total Phosphorus	0.0341	0.0630	0.0185	0.7558	1.6062	0.3557	0.0553	0.1274	0.0240

Solids	FWMC (mg/L)			Mass load (kg)			Flux (kg/km^2)		
	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI	Geometric mean	Upper CI	Lower CI
Total Dissolved Solids	251.8129	338.9060	187.1012	11250.6123	25318.5915	4999.3411	637.2509	1265.9114	320.7876
Total Suspended Solids	98.1192	280.8372	34.2810	5069.7023	20983.9001	1224.8382	257.2547	854.3920	77.4585

TABLE 4. RESULT OF STEPWISE SELECTION OF ENVIRONMENTAL VARIABLES USING REDUNDANCY ANALYSIS (RDA) IN WET WEATHER: 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 %AGE 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

Environmental Variable	Extra fit	Cumulative fit	Significance (p value)
Sedimentary rock	0.1196	0.1196	0.025
Igneous rock	0.1196	0.2392	0.025
Elevation	0.0942	0.3334	0.105
Peak Flow	0.0552	0.3886	0.3900
Mean Flow	0.0467	0.4353	0.2000
Catchment Size	0.0437	0.4790	0.8900
Canopy Cover	0.0435	0.5225	0.0800
Total Runoff Volume	0.0400	0.5625	0.3050
Latitude	0.0390	0.6015	0.19
Baseline Flow	0.0312	0.6327	0.9050
Total Rainfall	0.0274	0.6601	0.2200
Shrub	0.0232	0.6833	0.4450
Forest	0.0232	0.7065	0.4450
Slope	0.0173	0.7238	0.1650

TABLE 5. STATISTICAL SUMMARY OF RDA FOR WET-WEATHER CONCENTRATIONS OF METALS, NUTRIENTS, AND SOLIDS

		Axes			
		1	2	3	4
Eigenvalues		0.151	0.028	0.371	0.116
Water quality -environment correlations		0.599	0.556	0	0
Cumulative percentage variance of	Water quality data	15.1	17.9	55	66.6
	Water quality-environment relation	84.5	100	0	0

TABLE 6. 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	0.5167	-0.2815
Sedimentary	-0.5167	0.2815
Elevation	0.4397	0.3777

TABLE 7. COMPARISON OF COEFFICIENT OF VARIATION (CV) BETWEEN NATURAL AND DEVELOPED CATCHMENTS FOR METALS, NUTRIENTS, AND SOLIDS IN THE WET WEATHER CONDITION; NA = DATA WERE NOT AVAILABLE

	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	1.2	0.8	32	0.2	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	2.0	3.4
Ammonia	29	13566	8809	9	885	230
Dissolved Organic Carbon	19	41	69	0	NA	NA
Nitrate+Nitrite	29	1357	949	19	460	542
Orthophosphate	27	9095	7009	0	NA	NA
Total Kjeldahl Nitrogen	15	133	278	6	57	88
Total Organic Carbon	19	44	73	0	NA	NA
Total Phosphorus	21	12264	12753	13	3336	2174
Total Dissolved Solids	26	0.9	0.9	0	NA	NA
Total Suspended Solids	26	16	9	36	4	4

TABLE 8A. 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 THE HARDNESS OF 100 MG/L.

	Maximum concentration (μg/L) 1-hour average	Note
As	340.00	Hardness independent
Cd	4.3	Hardness dependent
Cr	550.00	
Cu	13.44	
Ni	469.17	
Pb	64.58	
Se	19.34	Hardness independent
Zn	119.82	Hardness dependent

TABLE 8B. COMPARISON OF EPA PROPOSED NUTRIENT CRITERIA FOR RIVERS AND STREAMS FOR ECOREGION III, 6 (CENTRAL AND SOUTHERN CALIFORNIA) WITH GEOMETRIC MEANS AND UPPER 96% LIMITS OF THE NATURAL CATCHMENTS: A UNIT IS MG/L.

	Ecoregion III, 6 (California)	Natural catchments in wet weather
		Geometric mean
Total Kjeldahl Nitrogen	0.363	0.335
Nitrate+Nitrite	0.155	1.214
Total Nitrogen	0.518	1.549
Total Phosphorus	0.030	0.0341

TABLE 9. WET-WEATHER PERCENT NON-DETECTS (%ND); CONSTITUENTS THAT ARE NOT SHOWN HERE DO NOT HAVE NDS.

	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

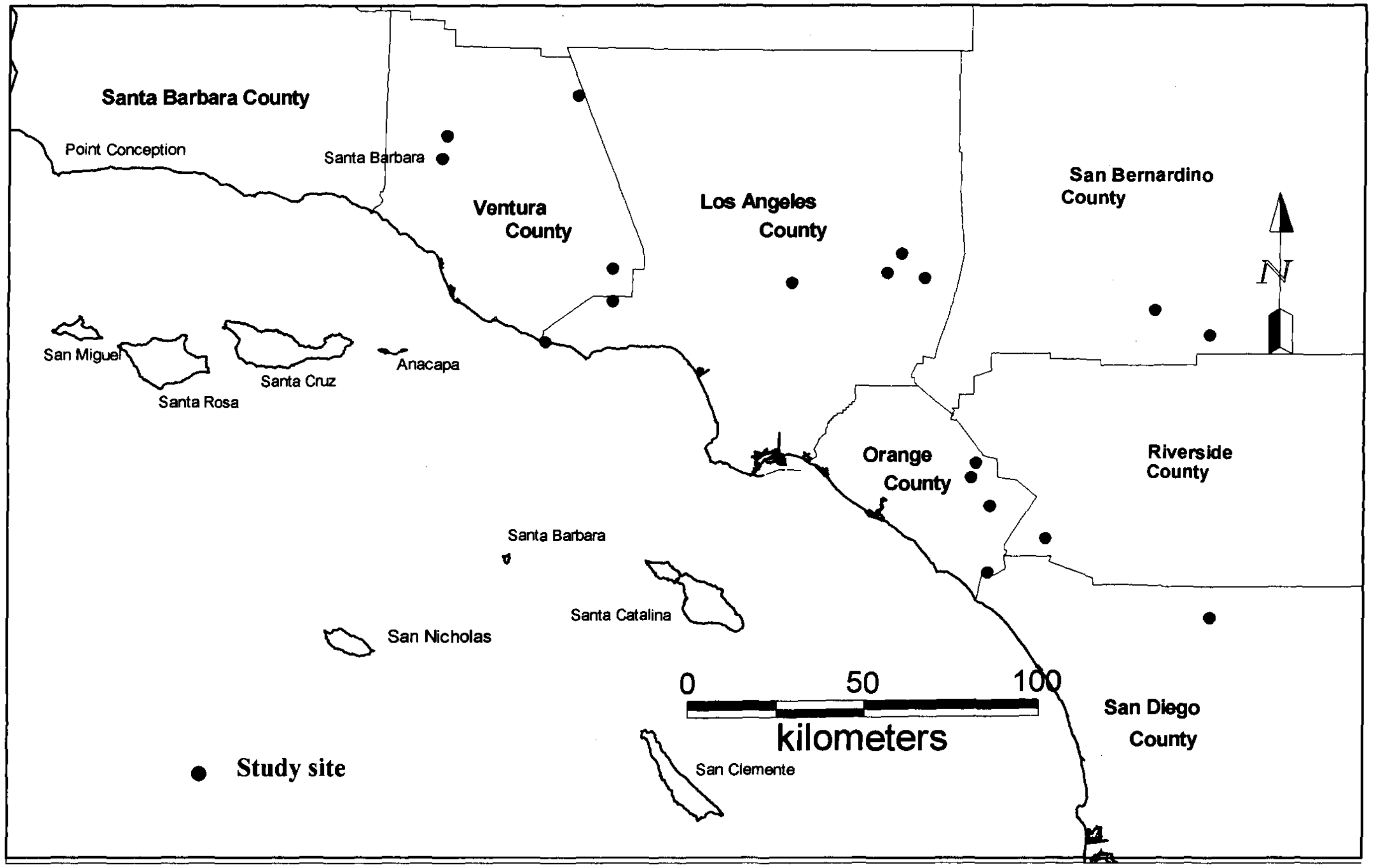

FIGURE 1. MAP OF WET-WEATHER STUDY SITES

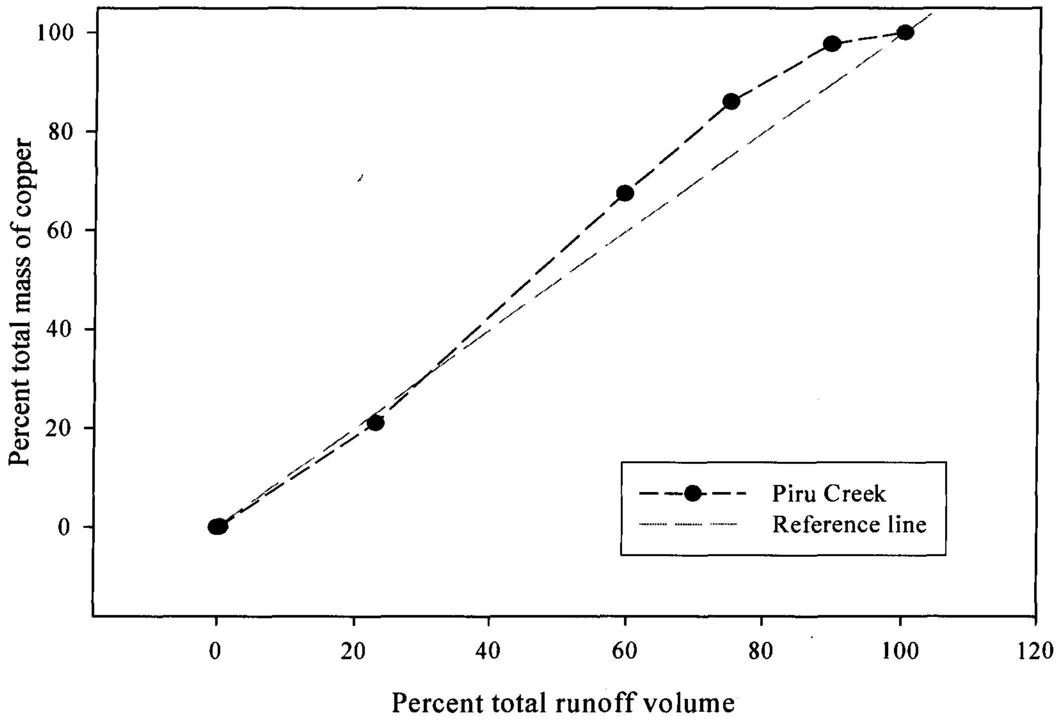

FIGURE 2. CUMULATIVE COPPER MASS LOADS FOR A STORM (FEB 27 –MARCH 1, 2006) AT PIRU CREEK. THE PLOT SHOWS % OF MASS WASHED OFF FOR A GIVEN PERCENT OF THE TOTAL RUNOFF. REFERENCE LINE INDICATES A 1:1 RELATIONSHIP BETWEEN VOLUME AND MASS LOADING. PORTIONS OF THE CURVE ABOVE THE LINE INDICATE PROPORTIONATELY HIGHER MASS LOADING PER UNIT VOLUME. PORTION BELOW THE LINE INDICATE THE REVERSE PATTERN.

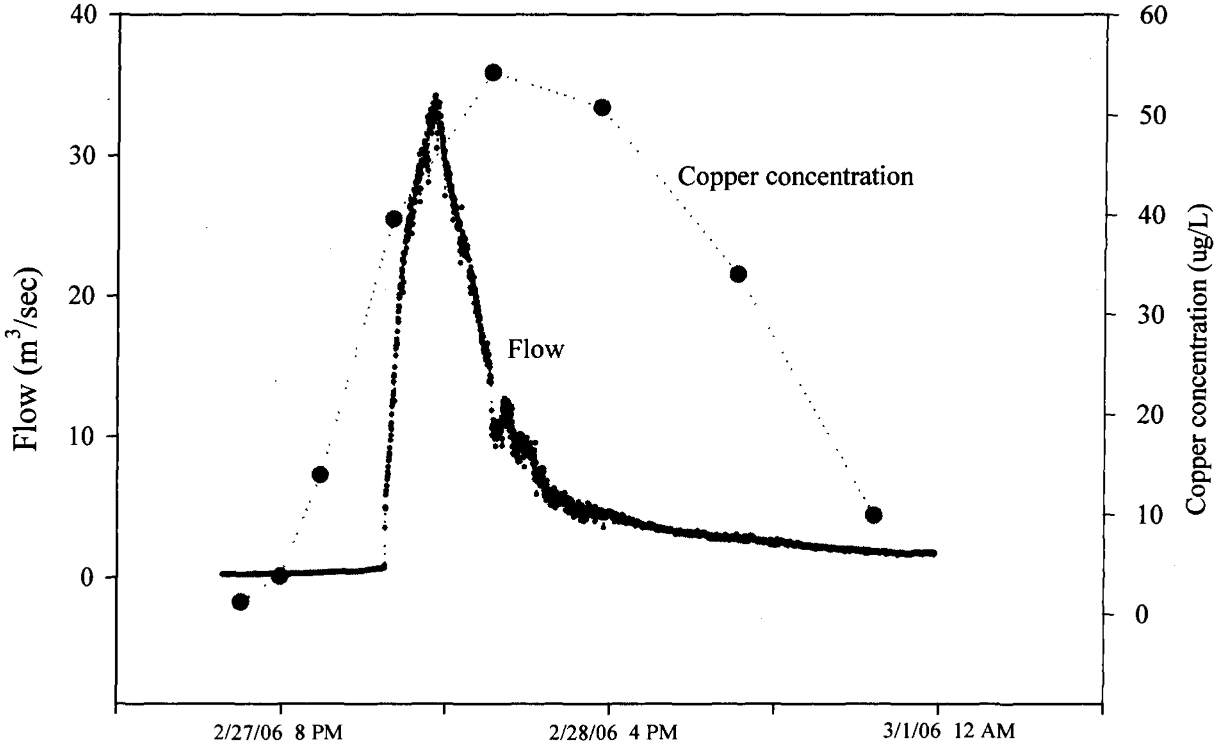

FIGURE 3. VARIATION IN TOTAL COPPER CONCENTRATIONS WITH TIME FOR STORM EVENT IN PIRU CREEK FROM FEB 27 THROUGH MARCH 1, 2006.

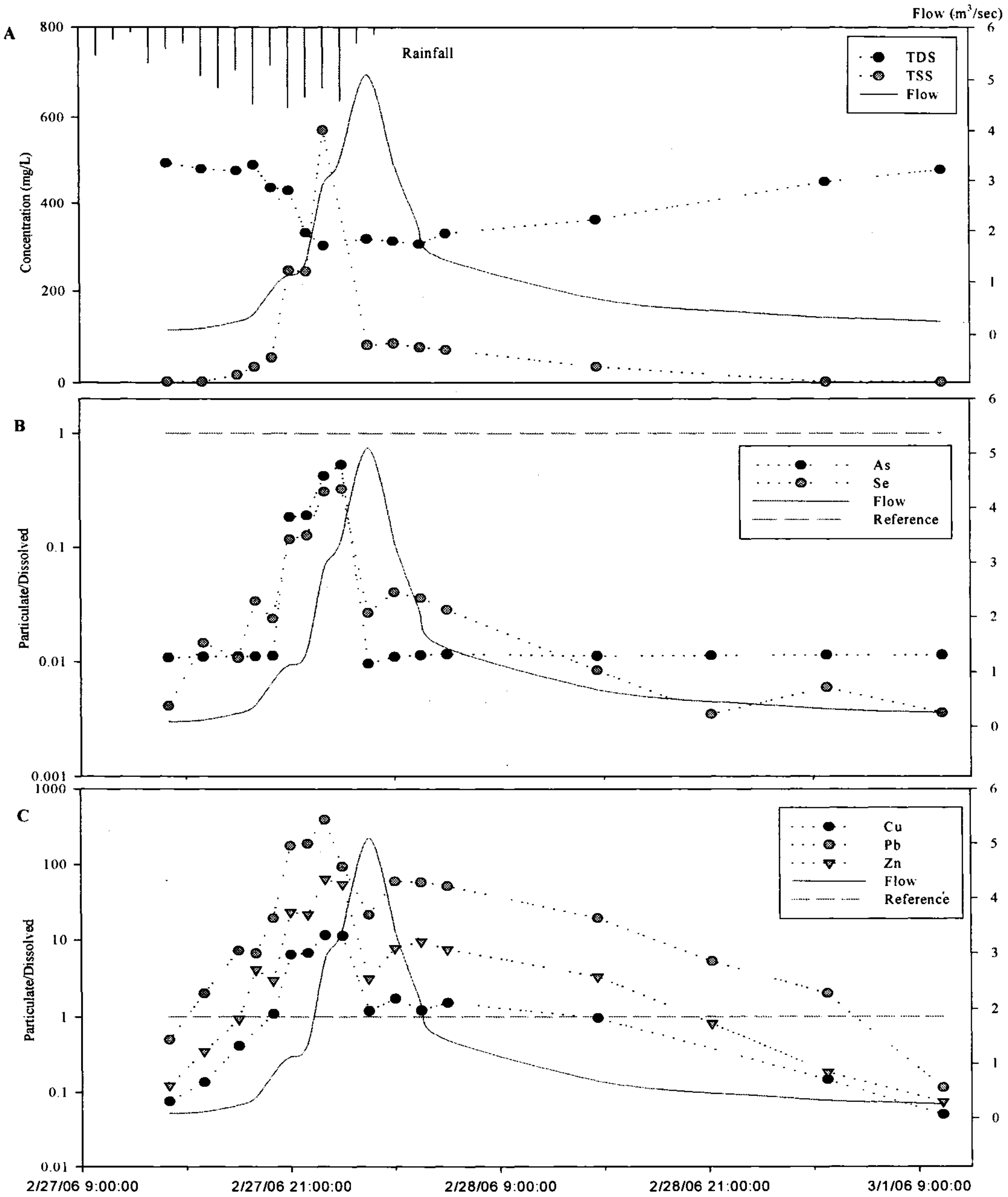

FIGURE 4. CHANGE IN THE RATIO OF PARTICULATE METALS OVER DISSOLVED METALS OVER THE COURSE OF A STORM EVENT AT BEAR CREEK, A TRIBUTARY TO NORTH FORK MATILIJA, CA. THE REFERENCE LINE INDICATES 1:1 RATIO BETWEEN PARTICULATE AND DISSOLVED CONCENTRATIONS. THE AXES OF THE RATIOS ARE IN LOG-SCALE. TOTAL RAINFALL WAS 14.6CM.

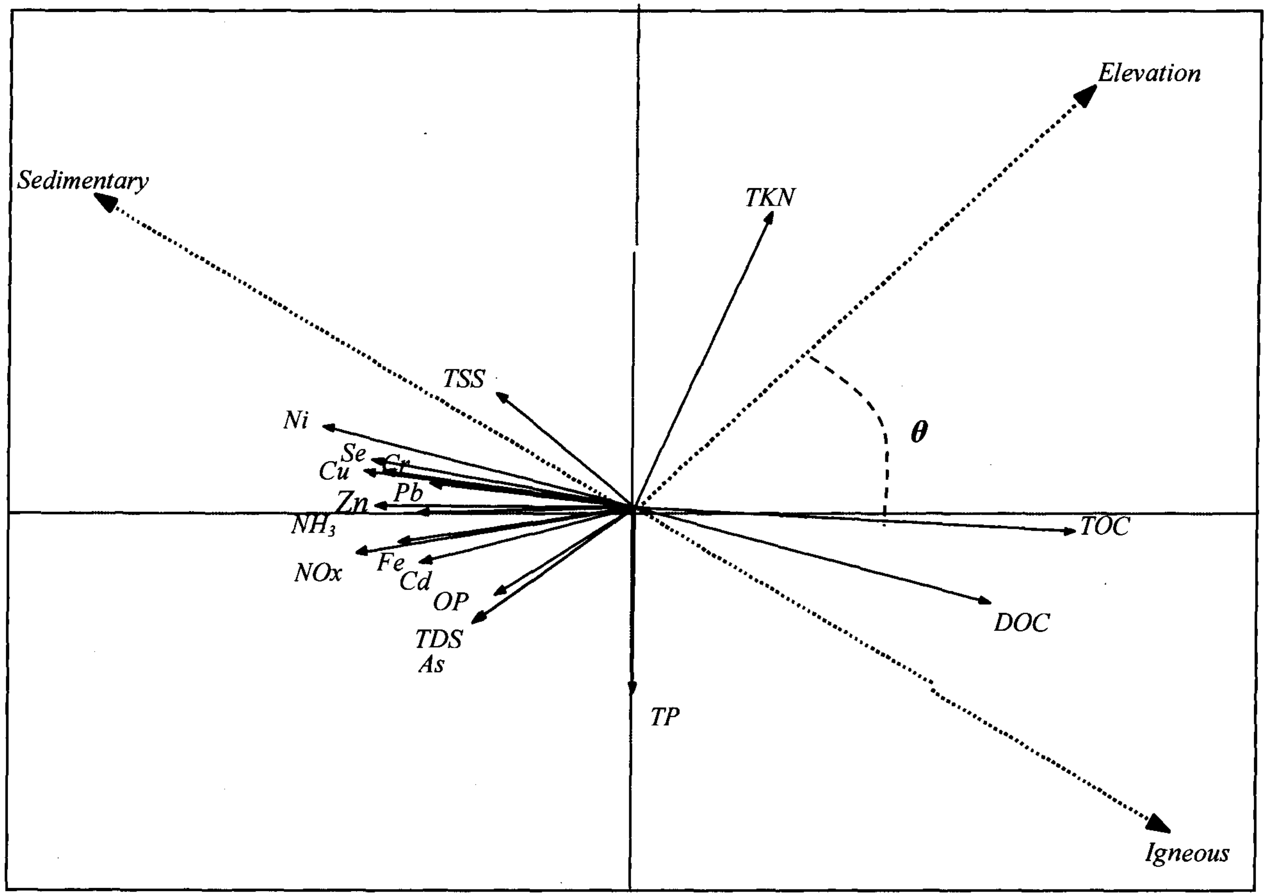

Figure 5. Correlation biplots showing the relations between wet-weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigen values: 0.151 and 0.0280 for the first (horizontal) and second (vertical) axes. *cos θ* ≈ correlation coefficient between two variables (arrows). Longer arrow indicates which factor is more important in generating variability (Ter Braak, 1995). TDS= total dissolved solids; TSS=total suspended solids; TOC= total organic carbon; DOC= dissolved organic carbon; TKN=total Kjeldahl nitrogen; TP=total phosphorus; OP= orthophosphate; NOx = Nitrate+Nitrite

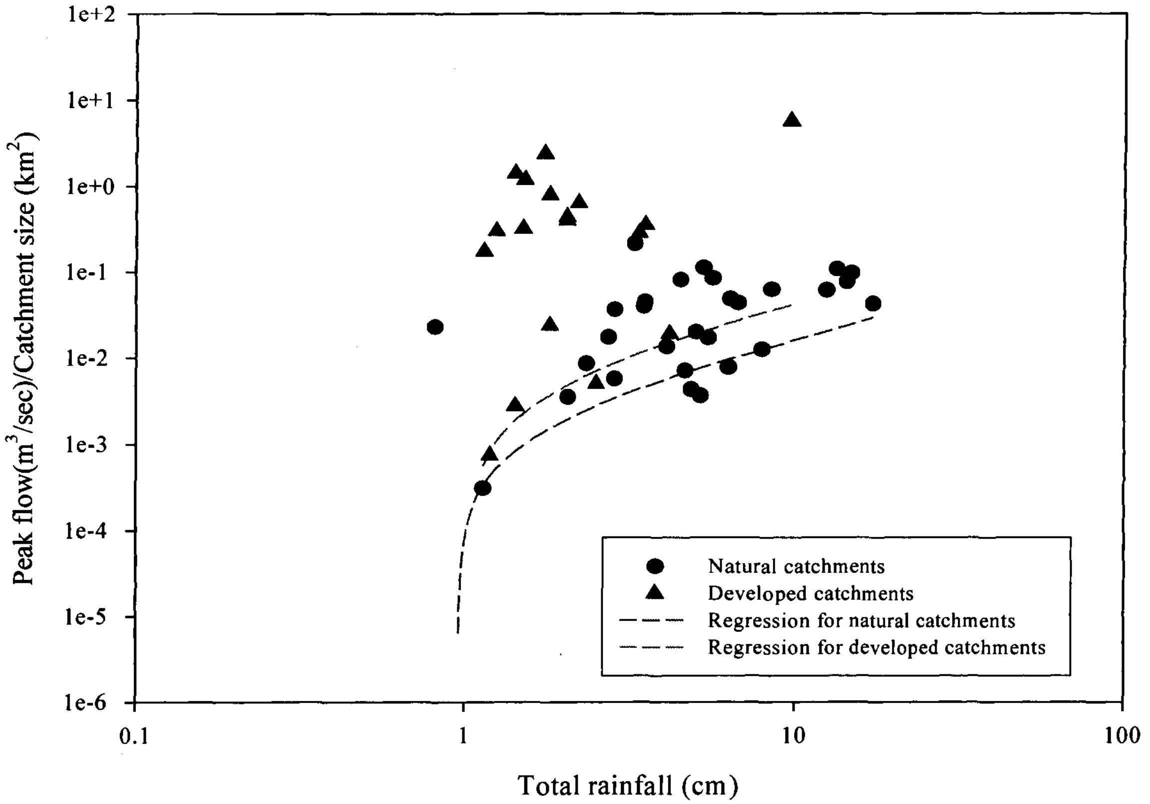

FIGURE 6. COMPARISON OF RATIO OF PEAK FLOW OVER CATCHMENT SIZE VS. RAINFALL BETWEEN NATURAL CATCHMENTS AND DEVELOPED CATCHMENTS; X- AND Y-AXES ARE IN LOG SCALE. R2 VALUES ARE 0.136 AND 0.43 FOR THE NATURAL CATCHMENTS AND THE DEVELOPED CATCHMENTS RESPECTIVELY. THE LINEAR REGRESSIONS ARE Y= 0.00467993X-0.00478469 AND Y=0.00176519X -0.0016883 FOR THE NATURAL CATCHMENTS AND THE DEVELOPED CATCHMENTS RESPECTIVELY.

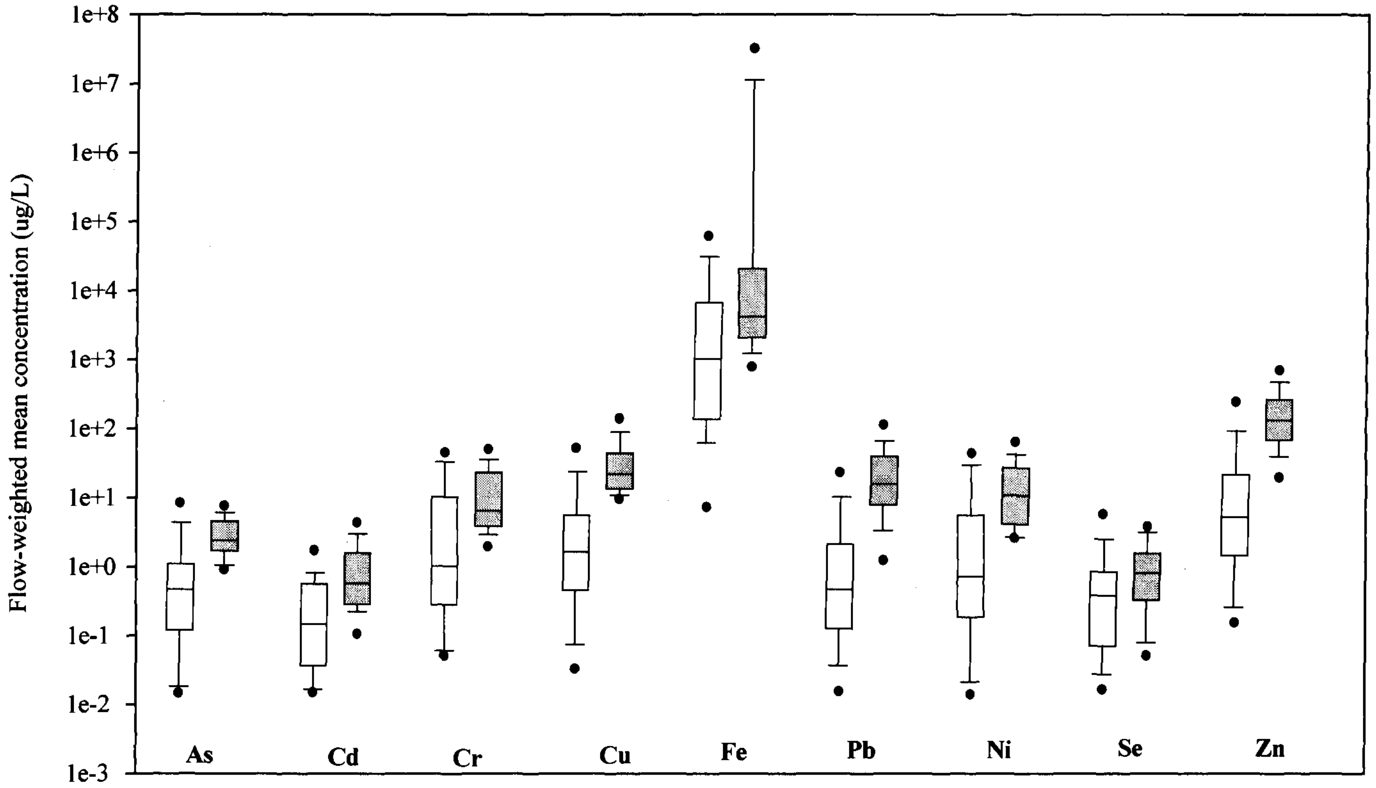

Figure 7. Comparison of wet-weather flow-weighted concentrations of metals between natural and developed catchments; white boxes represent natural catchments, while gray boxes represent developed catchments. Solid line is a median of all values in the category. A box indicates 25th and 75th percentile and error bars indicate 10th and 90th percentiles. Solid dots are for 5th and 95th percentiles. All concentrations are expressed in µg/L. Y-axis is in log scale.

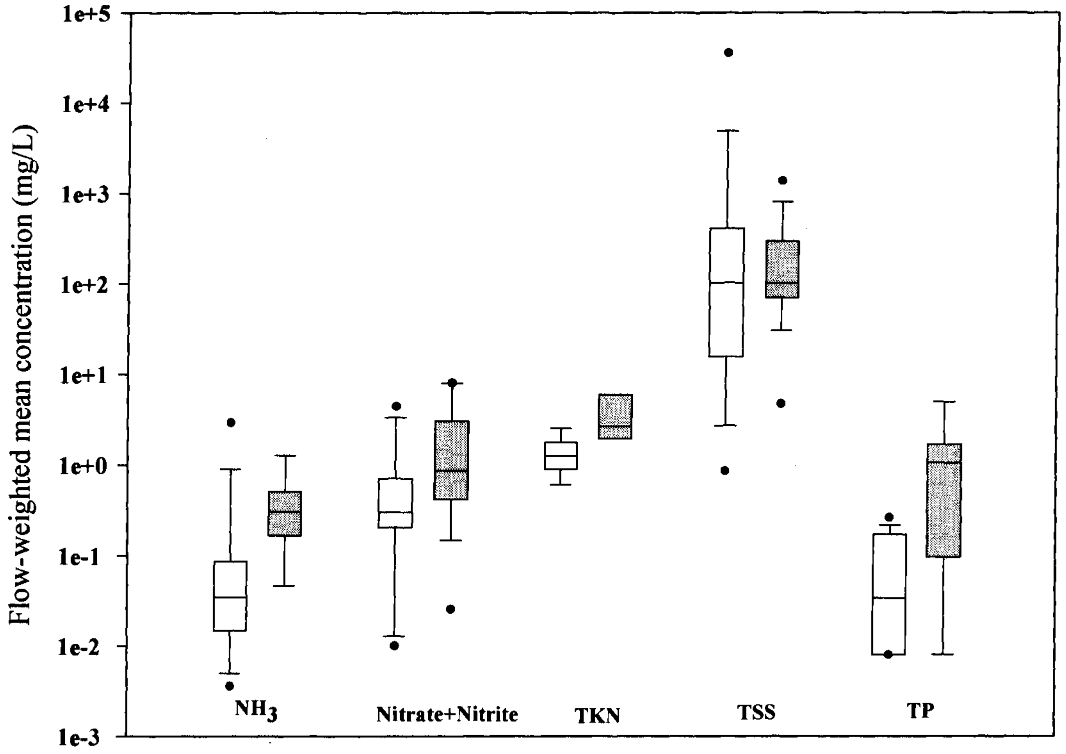

FIGURE 8. COMPARISON OF WET-WEATHER FLOW-WEIGHTED CONCENTRATIONS OF AMMONIA (NH_3), NITRATE+NITRITE, TOTAL KJELDAHL NITROGEN (TKN), TOTAL SUSPENDED SOLIDS (TSS), AND TOTAL PHOSPHOROUS (TP) BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL CATCHMENTS, WHILE GRAY BOXES REPRESENT DEVELOPED CATCHMENTS. ALL CONCENTRATIONS ARE EXPRESSED IN MG/L. Y-AXIS IS IN LOG SCALE.

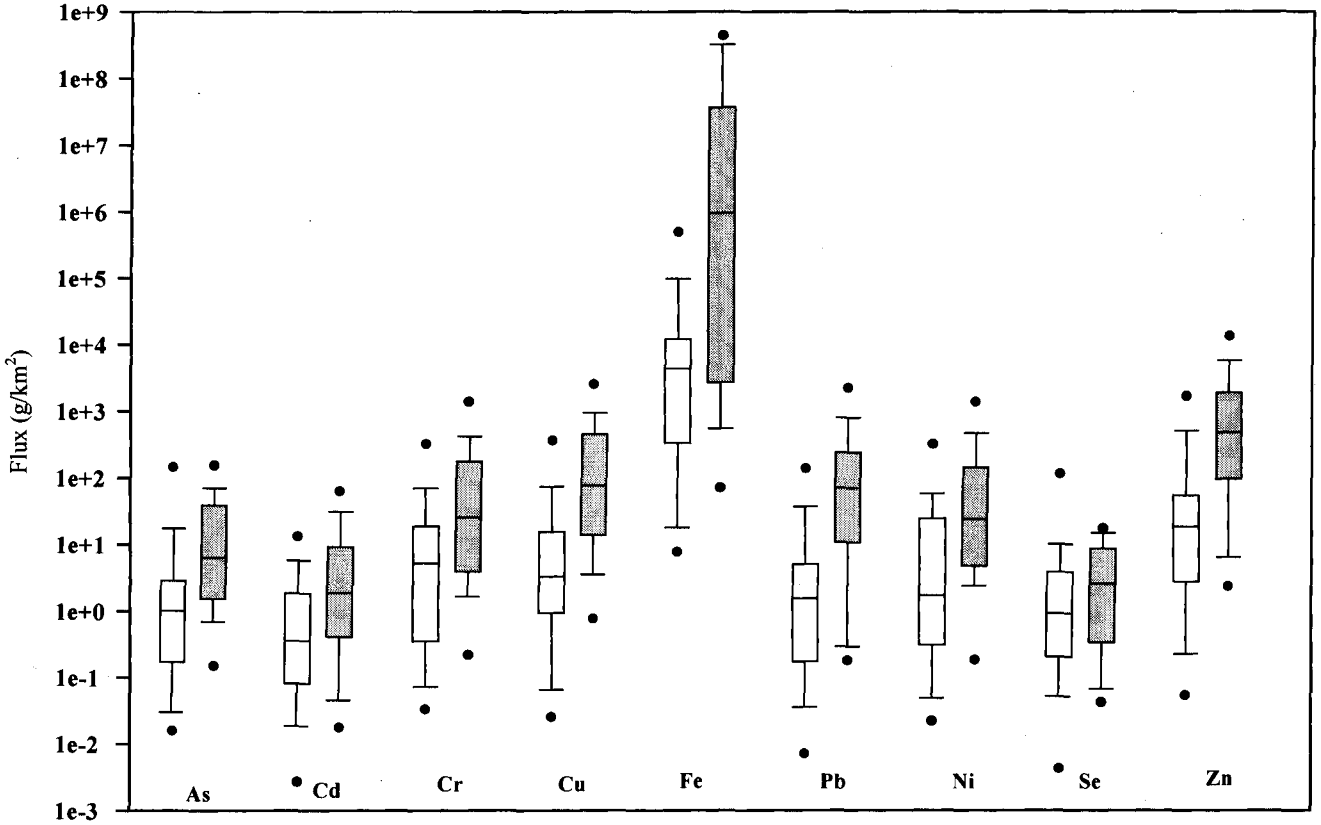

FIGURE 9. COMPARISON OF WET-WEATHER FLUXES OF METALS BETWEEN NATURAL AND DEVELOPED CATCHMENTS. WHITE BOXES REPRESENT NATURAL CATCHMENTS, WHILE GRAY BOXES REPRESENT DEVELOPED CATCHMENTS. ALL FLUXES ARE EXPRESSED IN G/KM^2. Y-AXIS IS IN LOG SCALE.

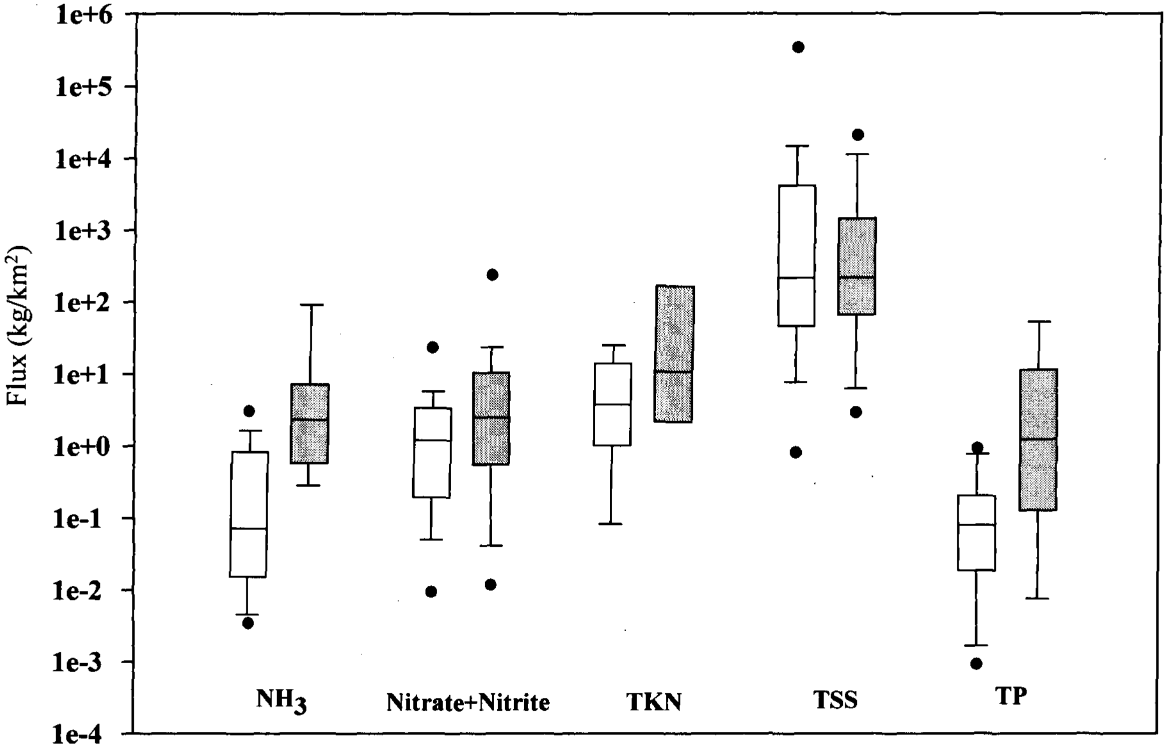

Figure 10. Comparison of wet-weather fluxes of ammonia (NH_3), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. All fluxes are expressed in kg/km^2. Y-axis is in log scale.

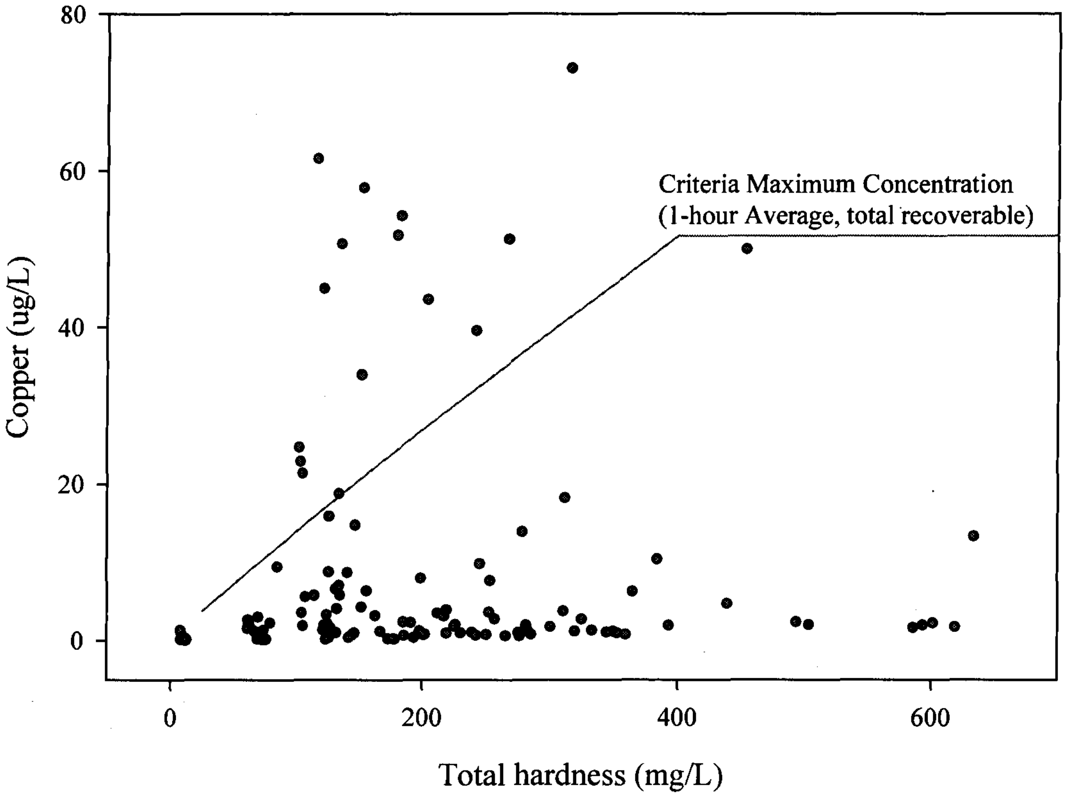

FIGURE 11. WET-WEATHER TOTAL RECOVERABLE COPPER CONCENTRATIONS AT NATURAL CATCHMENTS COMPARED WITH THE HARDNESS-ADJUSTED STANDARD UNDER THE CALIFORNIA TOXICS RULE (CTR). THE STORM WATER CONCENTRATIONS ARE COMPARED WITH THE ACUTE STANDARD.

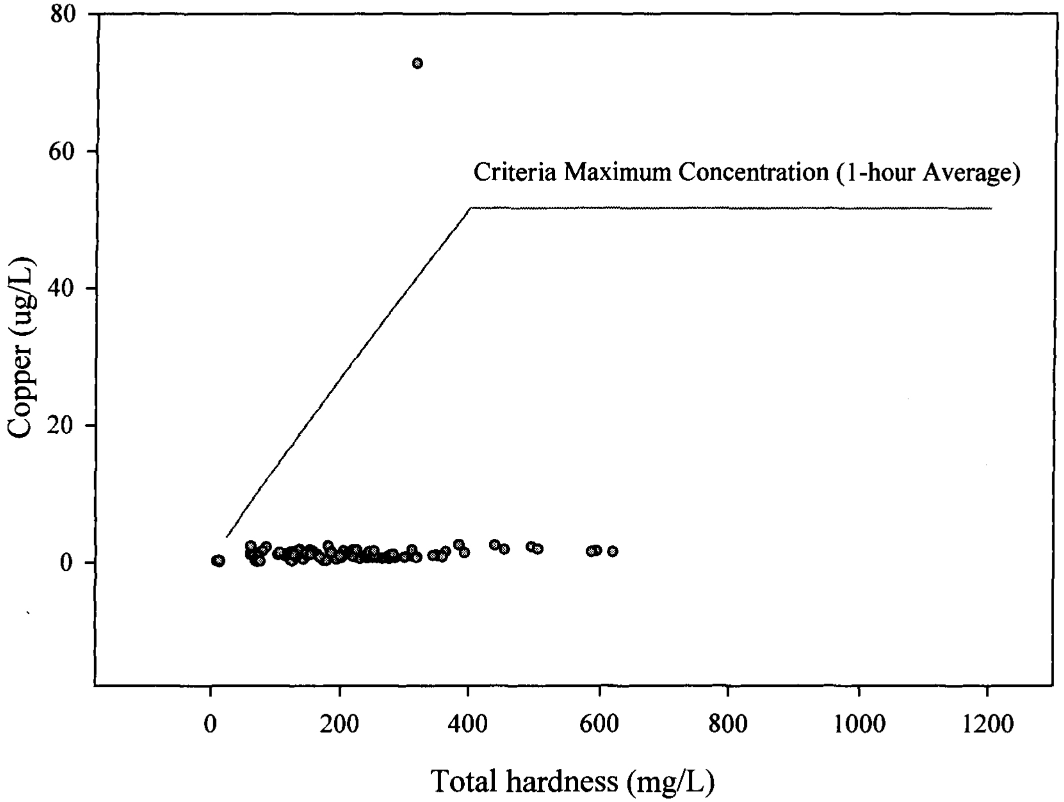

FIGURE 12. WET-WEATHER DISSOLVE COPPER CONCENTRATIONS AT NATURAL CATCHMENTS COMPARED WITH THE HARDNESS-ADJUSTED STANDARD UNDER THE CALIFORNIA TOXICS RULE (CTR). THE STORM WATER CONCENTRATIONS ARE COMPARED WITH THE ACUTE STANDARD.

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CHAPTER 4- ESTIMATION OF ANNUAL LOAIDNGS OF METALS, NUTRIENTS, AND SOLIDS FROM NATURAL CATCHMENTS IN SOUTHERN CALIFORNIA

Abstract

Coastal watersheds of southern California are some of the most highly urbanized areas in the United States. Continuing urbanization of the watersheds affects water quality, so considerable efforts have been made to assess and manage water quality in the urban watersheds. Most previous assessments have focused primarily on the evaluation of anthropogenic sources of constituents of concern. However, the majority of coastal watersheds contain considerable areas of open lands, with much of the upper watershed area being open and primarily natural. Therefore, it is important to evaluate the contribution of the relatively natural environments to water quality because both natural processes and anthropogenic activities will ultimately affect water quality in downstream receiving waters. This study estimated annual loadings of metals, nutrients, and solids from natural streams in southern California and compared the storm-flow load with the non-storm-flow load. Annual load estimation is derived from the flow and concentration data; thus, uncertainty that may reside in these flow and concentration data could result in uncertainty in the estimation of loadings. The limited availability of flow data for natural streams was the major issue in the load estimation for the natural systems. The water quality data were also not widely available for natural streams. Nonetheless, the results of this study yielded several conclusions regarding annual loadings of metals, nutrients, and solids from natural landscape. The non-storm flow accounts for more than half of the

annual discharges in the natural streams. The considerable portion of annual loadings was also resulted by the non-storm flow. Especially, annual loads for arsenic, cadmium, selenium, total organic carbons, orthophosphate, and total dissolved solids were largely contributed by the non-storm flow. For chromium, iron, lead, nickel, zinc, ammonia, and total suspended solids the dominant portion of annual loading was, however, from the storm flow. Considering the area of watersheds both the storm and non-storm loadings from the natural watersheds were significantly low compared with those from the urban systems. Results of this study may be helpful to environmental managers by providing estimates of annual flux from natural areas that can be used in TMDLs to assign reasonable contribution from natural areas.

1. Introduction

Coastal watersheds throughout the country are some of the most highly urbanized areas. Continuing urbanization of these watersheds affects water quality by increasing the amount of impervious area and changing the natural drainage system, as well as increasing anthropogenic inputs of pollutants (Roesner and Bledsoe 2003; Santa Monica Bay Restoration Project 1994; USEPA 1993). Because of the human and ecological health concerns, and the associated regulatory attention, a considerable effort has been made to assess and manage water quality in urban watersheds. Most previous assessments have focused primarily on the evaluation of anthropogenic sources of constituents of concern. However, most coastal watersheds contain considerable areas of open lands and in many watersheds, the upper portions are primarily natural. For example, in southern California, the natural areas in two densely populated watersheds, the Los Angeles River watershed and the Malibu Creek watershed, account for approximately 43% and 85% of each watershed, respectively (County of Los Angeles 2004). These natural areas could be significant sources for metals, nutrients and solids (Horowitz and Elrick 1987; Trefry and Metz 1985; Turekian and Wedepohl 1961). To evaluate the relative extent of anthropogenic activities, it is essential to assess the contribution of the relatively natural environments because both natural processes and anthropogenic activities will ultimately affect water quality in downstream receiving waters.

The contribution of undeveloped natural watersheds to overall pollutant loading depends on factors such as vegetation, atmospheric deposition, biological activity in soils, and weathering of soils and bedrocks (Horowitz and Elrick 1987; Trefry and Metz 1985; Turekian and Wedepohl 1961). For example, watersheds that are underlain by either marine shale or marine volcanic rocks are typically enriched in phosphorus and can be a natural source of phosphorus to receiving waters (Clark et al. 2000). Similarly, suspended solids can be produced from natural weathering and erosion of soil in natural areas. In southern California, high selenium concentrations in the San Diego Creek watershed was found to be caused by selenium-enriched groundwater discharge derived from the weathering of selenium–high Cretaceous marine sediments in the watershed (Hibbs and Lee 2000). In addition, atmospheric deposition can introduce sulfur, nitrogen, base cations, and acidity to relatively pristine watersheds (Likens et al. 1996).

Ranges of concentrations of water quality constituent from natural areas that were documented in the prior chapters (Chapter 2 and Chapter 3) provide valuable understanding on natural background water quality in southern California's coastal watersheds. However, estimates of watershed loading 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 of natural areas to total watershed loading requires estimates of annual loading 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, with only wet weather flow, not concentration data, being measured. Seldom are there sufficient flow and water chemistry data during both wet and dry seasons to fully estimate annual loading (Chapter 1.3. Present Conditions). Lack of distinct wet- and dry-weather data is particularly problematic in semi-arid climates, such as southern California. Chapters 2 and 3 indicated that most of constituent concentrations from natural areas during wet weather condition were about one order of magnitude higher than those during dry weather condition (Chapter 2 and 3 Table 3). However, non-storm flow can constitute a significant portion of the total annual flow, especially during years with low rainfall. As a result, 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 from a minor to an appreciable portion of 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 8-42% of the total annual 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. 2005; McPherson et al. 2002). These prior studies lack information on wet- and dry-weather concentrations and sufficient flow data to fully estimate loading.

This study estimated annual loadings of metals, nutrients, and solids from natural streams in southern California and compared the storm-originated load with the non-storm-originated load. The objectives of the study are: 1) to estimate annual flux and loading of metals, nutrients, and solids from a representative set of southern California's watersheds, 2) to compare the contribution to the total annual load of storm flow and non-storm flow, and 3) to compare the annual loads and fluxes from natural catchments with those from an urban developed catchment and other natural catchments.

2. Materials and Methods

2.1. Study sites

Five natural streams in natural areas were selected to represent the diversity in the sizes of catchments, geology and land cover types, and flow conditions in southern California (Figure 1). The study sites included three perennial streams and two intermittent streams whose catchment sizes ranged from 17 to 318 km^2 (Table 1). Arroyo Seco, Sespe Creek, and Piru Creek are perennial streams, where USGS flow-monitoring gauging stations are located. Santiago Creek, and Tenaja Creek are intermittent streams that flow only from the winter through the late summer, depending on the amount of rainfall in the preceding winter.

2.2. Flow data from USGS gaging 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 for the 2004 water year for Piru Creek and the 1998 and 2001 water years for Sespe Creek were unavailable. Flow data for the 2005 and 2006 water years were not available yet due to incomplete data quality checks by USGS.

2.3. Flow monitoring using water- level loggers

At the two ungauged intermittent streams, we installed pressure transducers to measure water surface elevation (i.e. level). 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 calculated based on the temperature logged with the pressure. Water level data were converted to flow using flow rating curves that were obtained from previous sampling events conducted during the dry and wet seasons of 2004 through 2006 (Chapters 2 and 3). 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.

2.4. Storm flow separation from non-storm flow

In this study storm flow was defined as rainfall-induced flow and non-storm flow was defined the rest of flow during both dry and wet weather. 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.

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

where: X_i is 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. Last, 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 stormevent.

Storm flows and non-storm flows were separately summed for the total discharge volume of the storm flow and the total discharge volume of the non-storm flow for each water year.

2.5. Water quality data

Water quality data for metals, nutrients, and solids (Table 2) were obtained from a related study conducted from December 2004 through June 2006 (Chapters 2 and 3), when water quality samples of both storm water and non-storm water were collected. The wet-weather concentrations are flow-weighted event mean concentrations (FWMC) that were computed according to

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

where FWMC = Flow-weighted event mean concentration for a particular storm; C_i = individual runoff sample concentration of *i*th sample; F_i = instantaneous flow at the time of *i*th sample; and n=Number of samples per event. The dry-weather concentrations are mean concentrations of three sampling events over a two-year period for each study site. 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.

2.6. Estimation of loads and fluxes

Load for each water quality constituent was estimated according to

$$W = \sum_j Cm \bullet Q_j \bullet K \qquad (3)$$

where W= load (mt or kg); Cm = FWMC for storm-flow load or mean concentration for non-storm-flow load (mg/L or ug/L); Q_j=total discharge volume (m^3)[16]; and K = unit conversion factor of 10^6.

Loadings were separately calculated based on storm volume and non-storm volume. A total of annual load for each water year was obtained by summing the storm load and non-storm load. A flux for each site was computed

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[16] The total discharge volume was flow (m^3/sec) multiplied by time (sec).

from a load divided by the size of drainage area in order to account for differences in catchment size.

3. Results

3.1. Flow and discharge volume

Three of the five streams studied flowed all year; Arroyo Seco, Sespe Creek, and Piru Creek. Santiago Creek and Tenaja Creek flowed until between mid-July and mid-August 2006 before drying up. Rating curves that were used in the conversion of water level into flows at the water-level logged sites, Santiago Creek and Tenaja Creek, are shown in Figure 2.

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 (1.37 m^3/sec). The difference between average storm and non-storm flow was much smaller at the intermittent streams, approximately one order of magnitude, than at the perennial streams (Table 3).

The relative volume discharged during the storm vs. non-storm periods varied largely based on whether the stream was perennial or intermittent. 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 lack of flow from late summer through the fall (Table 3). While, percent differences in total annual discharge volume were smaller among the perennial streams than between the intermittent streams.

Percent differences between storm and non-storm discharge volumes at perennial streams were greater in years with less overall discharge, which were dry years (1999-2004) (Figure 3). This implies that the contribution of the non-storm flow to annual discharge volume becomes more important in dry years. The annual discharge volume of non-storm flow was larger than the annual discharge volume of storm flow from 1995 through 2004 at Arroyo Seco and Piru Creek. The storm and non-storm volumes were similar at Sespe Creek except in the water year of 1995 (Figure 3).

3. 2. Average annual fluxes

Average annual fluxes of five natural streams for metals (except iron) ranged from tens to hundreds of grams/year km^2. Nutrient fluxes varied largely. Ammonia was at one digit level, orthophosphate and total phosphorus were one to two digits, and other nutrients were two to three or two to four digits (kg/year km^2). The median, minimum, and maximum values for each constituent are summarized in Table 4.

Storm flow contributed the majority of annual fluxes for most of constituents (Figure 4). Total suspended solids were almost entirely derived from storm runoff. However, a substantial portion of arsenic and TOC (60-70%) and cadmium, selenium, DOC, TOC, OP, TP, and TDS (40%-50%) were derived from non-storm flow. For nutrients, a substantial portion of total annual flux was contributed by non-storm flows. More than half of the annual flux of TOC and TDS came from non-storm flow.

3.3. Annual loads and fluxes for each stream

In the intermittent streams, storm flow was a major source for most metals, all nutrients, and solids (Table 5 and 6). More than 97% of total suspended solids load was contributed by storm flow. In perennial streams, even though the annual non-storm discharge accounted for more than half of the total annual discharge, a greater portion of the annual load was contributed by the storm flow because of high TSS concentrations in the storm flow. Non-storm flow contributed more to annual loads of metals at perennial streams than at the intermittent streams. For instance, the non-storm flow produced 53 to 82 % for cadmium at the perennial streams, while, the non-storm flow produced 10 to 21% for cadmium at the intermittent streams.

Annual flux was generally lower at the intermittent streams than at the perennial streams (Table 7). 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 from December 2005 through July 2006 because the streams dried up in July 2006, yet the annual fluxes at Arroyo Seco, Piru Creek, and Sespe Creek were derived from the annual loads of the entire year of 12 months.

4. Discussion

Annual flux rates were smaller at natural streams in natural catchments than in developed catchments in southern California (Table 7). This difference can be illustrated by comparing our results to data from the Ballona Creek catchment. Ballona Creek 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 covered by urban land uses (Wong et al. 1997). Annual loads of chromium, copper, lead, nickel, zinc, and total suspended solids, which were converted into flux values for the Ballona Creek watershed, were based on the values presented in studies by McPherson et al. (2005) and Tiefenthaler et al. (in review). Annual fluxes of chromium, copper, lead, nickel, and zinc were one to two orders of magnitude higher at Ballona Creek than at natural streams. The fluxes of total suspended solids (TSS) at the natural sites were one to two orders of magnitude higher at Piru Creek and Sespe Creek than that at Ballona Creek. This can be expected due to 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 open lands that can contribute large amounts of TSS. In addition, in-channel erosion in natural streams, which can be a substantial source of TSS (Pons 2003), does not occur in concrete lined channels such as Ballona Creek.

In the overall catchment context, natural streams natural catchment contribute proportionately less of the total annual catchment load to the receiving waters than would be expected based solely on catchment area. For example, Arroyo Seco is one of subwatersheds the Los Angeles River catchment. It occupies about 2% of the Los Angeles River catchment. Approximately 2,300kg of copper, 1,150kg of lead, 11,550kg of zinc are discharged from the mouth of the Los Angeles River watershed annually (Tiefenthaler et al. in review). According to the estimates of this study, Arroyo Seco contributed less than 0.4% of the total annual load of copper, lead, and zinc in the Los Angeles watershed.

Watershed geology has been shown to be a major factor that influences constituent concentrations (and hence loads) from natural catchments (Chapter 2 and 3). Flux of total suspended solids from Sespe and Piru Creeks are 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 dominant geologic type of Arroyo Seco is igneous. The flux of TSS at Arroyo Seco is only 4.75mt/year km^2, which is less than 0.5% of the flux at Sespe Creek. The difference in the geologic types also explains that the low concentration of TSS at Arroyo Seco during the dry weather compared with those at Piru Creek and Sespe Creek (Table 3). In addition to the geologic types, the magnitude of storm flow at Sespe Creek and Piru Creek were five times larger than that at Arroyo Seco. The effect of local 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 and others (2000). Clark and others' study 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 7). Nutrient fluxes were similar to the median values of Clark and other study in most cases except total nitrogen. Total annual fluxes of total nitrogen at all sites except Tenaja Creek were higher than the median value in Clark and other's study. Especially the flux of total nitrogen at Santiago Creek was more than five-fold higher than Clark and others' value. This study did not separate the possible contribution by atmospheric deposition from natural loadings, thus, this high total nitrogen may be due to higher nitrogen deposition rate in southern California than a nation-wide average rate (Bytnerowicz and Fenn 1996; Fenn et al. 2003; Fenn and Kiefer 1999).

The contribution of dry weather load was proportionately smaller in natural areas than in developed watersheds. Dry season load in the urbanized Ballona Creek watershed accounted for 54, 19, 33, and 44 % for chromium, copper, lead, and nickel, respectively (McPherson et al. 2002). In contrast, dry season load in the natural streams accounted for 7.6, 16.3, 4.1, and 21.0% of total annual chromium, copper, lead, and nickel, 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 discharged was derived from the non-storm flow. This difference likely results from the fact that dry weather flow (and loading) in urban watersheds in comprised almost entirely of urban runoff that continually washes pollutants off of developed surfaces.

Estimated differences between storm and non-storm flux could be influenced by two factors. First, the estimation of storm-flow loading is directly dependent on how to identify and to separate storm flow from non-storm flow. The estimation of storm-flow loadings is directly dependent on how to treat the prolonged tail part of storm hydrographs in the natural streams. For this study, the end of storm was defined as the 50% value of the peak flow. The degrees to which the choice of the 50% criterion influences general conclusions about the annual loadings was examined by estimating annual loadings with the 25% value of the peak flow. 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, when the 25% criterion was applied instead of the 50%. 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 total nitrogen increased from 43 to 54 mt/year and total suspended solids 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 total phosphorus at Arroyo Seco decreased from 40kg/year to 27kg/year with the 25% criterion. The increase in storm-flow load resulted in increase in total annual load for constituents that were contributed primarily from storm flow, yet decrease in total annual load for constituents that were contributed primarily from non-storm flow. For instance, the total annual load of total nitrogen at Arroyo Seco increased from 9.69 to 14.93 mt/year. Meanwhile the total annual load of the total phosphorus of which 88% was contributed by non-storm flow decreased from 0.22 to 0.135 mt/year.

Second, distribution of constituents between dissolved phase and particulate flow 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 and selenium exist mainly in dissolved phase in storm flow (Chapter 3 Figure 4). 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 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 concentrations of total suspended solids (McPherson et al. 2002; Stein and Ackerman In press). Preliminary data collected in the San Gabriel Watershed (Bernstein et al., in prep) suggest 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.

From a management perspective, there are several implications of this work. First, flux rates from natural areas are one to two orders of magnitude lower than in developed watersheds, and constituent flux tends to be proportionately smaller than expected based on watershed size. Therefore, control of this source would likely provide little overall benefit to downstream receiving waters. More significantly, substantial portions of the total annual load may occur during non-storm conditions and the difference between developed and natural watersheds is greater during non-storm seasons than during storm seasons. This suggests that management of non-storm loading in developed watersheds has the potential to provide proportionately greater benefit than management of storm water with respect to remediation toward baseline conditions. Furthermore, because non-storm loads occur predominantly in the dissolved phases, and are hence more bioavaliable, their control may provide a relatively larger environmental benefit.

TABLE 1. STUDY SITES

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	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	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

TABLE 2. 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 3. COMPARISON OF NON-STORM AND STORM FLOW; UNDERLINED VALUES ARE MEANS FOR INTERMITTENT STREAMS AND PERENNIAL STREAMS.

Site name	Non-storm flow		Storm flow	
	Mean flow (m^3/sec) ± standard deviation	Mean annual discharge volume (m^3)	Mean flow (m^3/sec) ± standard deviation	Mean annual discharge volume (m^3)
Intermittent	*0.11*	*1.55×10^6*	*1.37*	*3.86×10^6*
Santiago Creek	0.19 ± 0.045	2.53×10^6	0.92 ± 0.34	6.53×10^6
Tenaja Creek	0.03 ± 0.015	0.58×10^6	1.81 ± 0.41	1.19×10^6
Perennial	*0.63*	*14.14×10^6*	*10.27*	*10.62×10^6*
Arroyo Seco	0.16 ± 0.48	4.66×10^6	2.04 ± 3.90	3.43×10^6
Piru Creek	1.00 ± 2.19	29.86×10^6	10.73 ± 30.30	18.42×10^6
Sespe Creek	0.26 ± 0.93	7.94×10^6	9.81 ± 21.40	10.00×10^6

TABLE 4. RANGES OF AVERAGE ANNUAL FLUXES FOR METALS, NUTRIENTS, AND SOLIDS IN FIVE NATURAL STREAMS

	Unit	Median	Minimum	Maximum
Arsenic	g/year km^2	150	24	206
Cadmium		14	6	53
Chromium		127	67	319
Copper		202	54	213
Iron		103,823	65,691	222,316
Lead		46	34	102
Nickel		150	34	220
Selenium		65	19	539
Zinc		451	292	667
Ammonia	kg/year km^2	2	1	7
Total Nitrogen		103	38	445
Dissolved Organic Carbon		377	198	1,712
Total Organic Carbon		554	184	1,766
Orthophosphate		4	2	11
Total Phosphorus		6	4	28
Total Dissolved Solids	mt/year km^2	39	12	192
Total Suspended Solids		5	4	1154

TABLE 5. ANNUAL LOAD ESTIMATION OF METALS AND THE CONTRIBUTION OF THE DRY-WEATHER LOAD IN THE ANNUAL LOAD

			Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Zinc
Perennial	Arroyo Seco	Annual storm load (kg)	1.64	0.69	12.91	6.72	4196	4.18	4.08	0.96	23.41
		Annual non-storm load (kg)	6.80	0.89	0.37	1.82	118	0.08	0.49	2.43	2.20
		Total Annual load (kg)	**8.66**	**1.66**	**13.42**	**8.95**	**4360**	**4.29**	**4.71**	**3.50**	**26.32**
		% Non-storm load	*78.48*	*53.79*	*2.73*	*20.35*	*2.72*	*1.83*	*10.32*	*69.20*	*8.37*
	Piru Creek	Annual storm load (kg)	3.98	0.30	75.09	46.24	66852	15.55	48.35	4.43	135.23
		Annual non-storm load (kg)	42.99	1.60	4.94	15.67	3301	1.56	11.38	14.11	6.91
		Total Annual load (kg)	47.74	1.95	81.14	64.58	70918	17.45	61.87	19.26	143.74
		% Non-storm load	*90.05*	*82.04*	*6.08*	*24.27*	*4.66*	*8.94*	*18.39*	*73.26*	*4.81*
	Sespe Creek	Annual storm load (kg)	1.02	0.57	15.35	13.72	20616	4.36	15.23	1.96	40.80
		Annual non-storm load (kg)	1.89	1.07	0.31	3.87	443	0.10	2.96	5.91	1.49
		Total Annual load (kg)	**3.10**	**1.75**	**15.80**	**18.73**	**21265**	**4.51**	**19.19**	**8.28**	**42.96**
		% Non-storm load	*60.99*	*61.19*	*1.93*	*20.65*	*2.09*	*2.26*	*15.45*	*71.36*	*3.47*
Intermittent	Tenaja Creek	Annual storm load (kg)	0.87	0.4	3.35	2.77	3955	1.71	1.44	0.6	14.88
		Annual non-storm load (kg)	0.8	0.04	0.18	0.07	116	0.07	0.36	0.41	0.54
		Total Annual load (kg)	**1.66**	**0.44**	**3.53**	**2.84**	**4071**	**1.78**	**1.8**	**1.01**	**15.42**
		% Non-storm load	*47.9*	*9.8*	*5.0*	*2.5*	*2.8*	*3.9*	*19.8*	*40.9*	*3.5*
	Santiago Creek	Annual storm load (kg)	1.44	0.71	1.62	2.5	792	0.73	1.74	6.77	9.53
		Annual non-storm load (kg)	1.24	0.19	0.56	1.06	334	0.06	2.03	2.47	1.89
		Total Annual load (kg)	**2.68**	**0.9**	**2.18**	**3.56**	**1126**	**0.79**	**3.77**	**9.23**	**11.43**
		% Non-storm load	*46.4*	*21*	*25.8*	*29.8*	*29.7*	*8.0*	*53.9*	*26.7*	*16.6*

TABLE 6. ANNUAL LOAD ESTIMATION OF NUTRIENTS AND SOLIDS AND THE CONTRIBUTION OF THE NON-STORM FLOW LOAD IN THE ANNUAL LOAD

			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)	0.05	4.13	12.50	12.10	0.15	0.01	743.91	198
		Annual non-storm load (mt)	0.02	1.36	8.84	9.98	0.05	0.13	845.73	0.91
		Total Annual load (mt)	**0.07**	**5.77**	**22.50**	**23.27**	**0.21**	**0.15**	**1669.58**	**199**
		% Non-storm load	*25.70*	*23.62*	*39.27*	*42.88*	*25.11*	*88.61*	*50.66*	*0.46*
	Piru Creek	Annual storm load (mt)	0.22	19.72	48.72	56.35	0.47	-	-	45800
		Annual non-storm load (mt)	0.23	11.52	65.45	212.71	0.69	-	-	54.42
		Total Annual load (mt)	**0.47**	**32.86**	**120.19**	**278.53**	**1.22**	-	-	**45868**
		% Non-storm load	*48.90*	*35.07*	*54.46*	*76.37*	*56.57*	-	-	*0.12*
	Sespe Creek	Annual storm load (mt)	0.27	9.44	15.70	18.94	0.16	-	1186.78	147713
		Annual non-storm load (mt)	0.03	2.23	14.26	28.18	0.20	-	3543.51	1.53
		Total Annual load (mt)	**0.32**	**12.37**	**32.31**	**50.46**	**0.38**	-	**4975.90**	**147715**
		% Non-storm load	*10.74*	*18.00*	*44.13*	*55.86*	*51.84*	-	*71.21*	*0.00*
Intermittent	Tenaja Creek	Annual storm load (mt)	0.07	1.86	7.43	7.16	0.13	0.22	416	219
		Annual non-storm load (mt)	0.003	0.14	3.01	2.55	0.002	0.1	230	1
		Total Annual load (mt)	**0.07**	**1.99**	**10.44**	**9.71**	**0.13**	**0.32**	**646**	**221**
		% Non-storm load	*4.2*	*6.9*	*28.9*	*26.3*	*1.7*	*31.7*	*35.7*	*0.6*
	Santiago Creek	Annual storm load (mt)	0.11	6.6	21.41	21.02	0.09	0.37	2189	91
		Annual non-storm load (mt)	0.01	1.03	7.94	9.24	0.09	0.11	1114	2
		Total Annual load (mt)	**0.12**	**7.63**	**29.34**	**30.26**	**0.18**	**0.49**	**3302**	**94**
		% Non-storm load	*10.2*	*13.5*	*27*	*30.5*	*51.8*	*23.6*	*33.7*	*2.6*

TABLE 7. 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 AND COMPARISON OF FLUXES WITH OTHER URBAN STREAM (BALLONA CREEK) AND OTHER NATURAL STREAMS (NUMEROUS PERENNIAL STREAMS ACROSS THE NATION); '-', NO DATA AVAILABLE

	Arsenic	Cadmium	Chromium	Copper	Iron	Lead	Nickel	Selenium	Zinc
Arroyo Seco	0.21	0.04	0.32	0.21	103.82	0.10	0.11	0.08	0.63
Piru Creek	0.15	0.01	0.25	0.20	222.32	0.05	0.19	0.06	0.45
Sespe Creek	0.02	0.01	0.12	0.15	166.14	0.04	0.15	0.06	0.34
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
Developed stream	-	-	1.20[b]	4.00[b]	-	1.40[b]	1.10[b]	-	16.70 [c]

	Ammonia	Total Nitrogen	Dissolved Organic Carbon	Total Organic Carbon	Orthophosphate	Total Phosphorus	Total Dissolved Solids	Total Suspended Solids
Arroyo Seco	1.69	137.46	535.71	553.98	5.03	3.54	39.75	4.75
Piru Creek	1.48	103.01	376.76	873.13	3.82	-	-	143.79
Sespe Creek	2.47	96.62	252.45	394.18	2.96	-	38.87	1154.03
Santiago Creek [a]	7.0	450	1710	1770	11.0	28.0	192.6	5.4
Tenaja Creek [a]	1.0	40	200	180	2.0	6.0	12.2	4.2
Developed stream	-	-	-	-	-	-	-	15.3[b]
Natural streams [d]	8.1	86	-	-	2.8	8.5	-	-

[a] Total fluxes are only for the 8 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

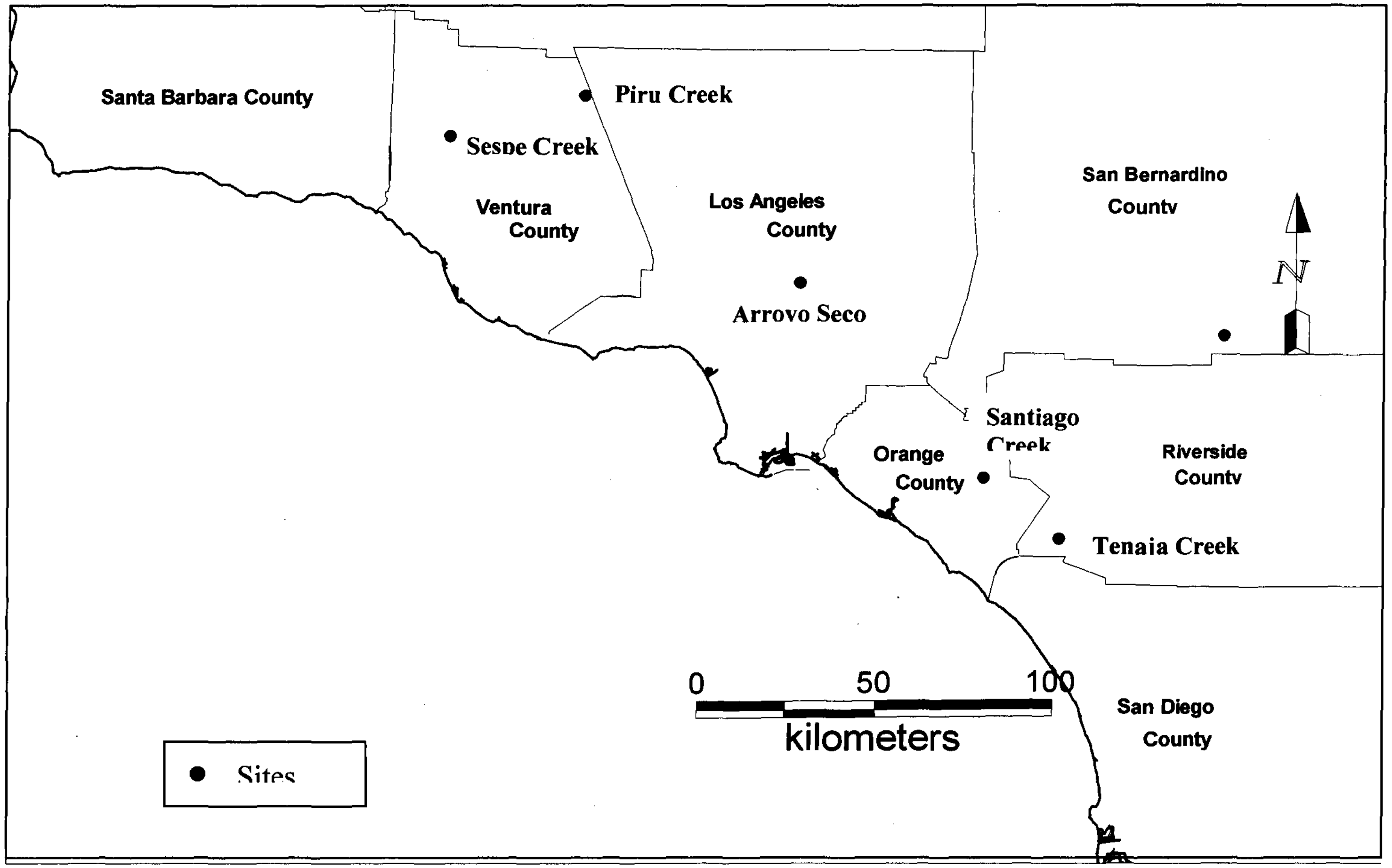

FIGURE 1. MAP OF STUDY SITES

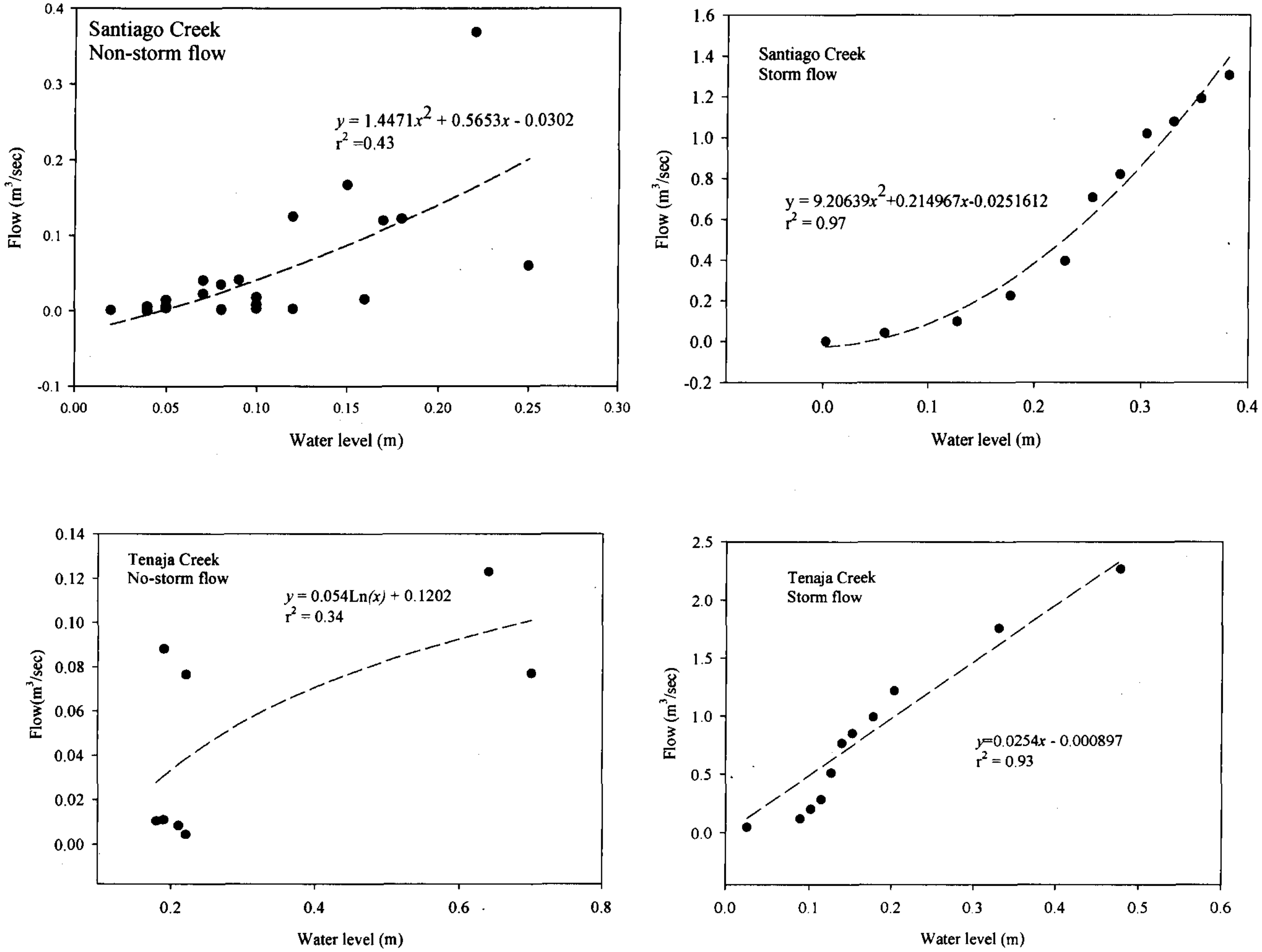

FIGURE 2. RATING CURVES AT SANTIAGO CREEK AND TENAJA CREEK FOR NON-STORM FLOW AND STORM FLOW

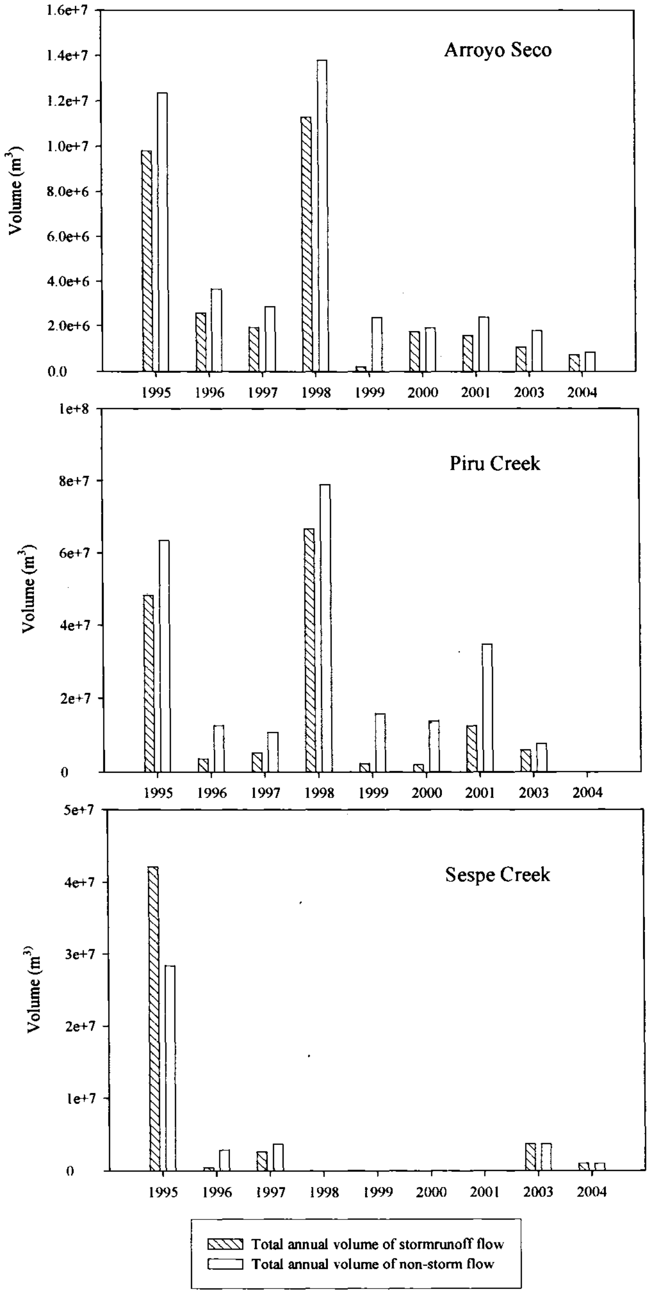

FIGURE 3. COMPARISON OF ANNUAL VOLUME OF STORM FLOW AND NON-STORM FLOW; THE FLOW DATA OF THE WATER YEAR 2004 FOR PIRU CREEK AND 1998-2001 FOR SESPE CREEK ARE NOT AVAILABLE. THE FLOW DATA OF THE WATER YEAR 2002 WERE NOT INCLUDED IN THE ANALYSIS DUE TO THE INSUFFICIENT QUALITY OF THE DATA SET.

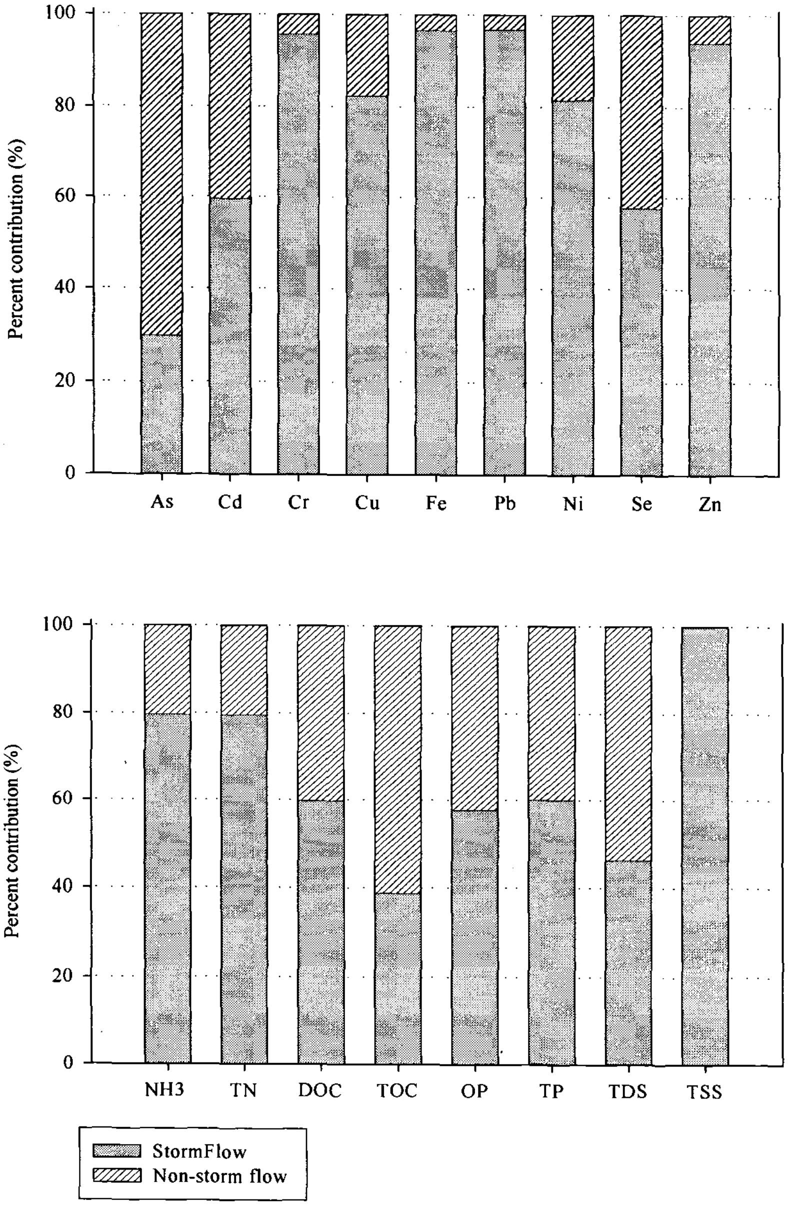

Figure 4. Average percent contribution of storm flow and non-storm flow to total annual fluxes of metals, nutrients, and solids in the natural streams; NH3, ammonia; TN, total nitrogen; DOC, dissolved organic carbon; TOC, total organic carbon; OP, orthophosphate; TP, total phosphorus; TDS, total dissolved solids; TSS, total suspended solids

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CHAPTER 5 – CONCLUSIONS

Ever-increasing urban development in southern California coastal watersheds has resulted in significant issues with their water quality. More than 100 waters in southern California were designated as impaired for their beneficial uses by the Clean Water Act 303 (d). However, we currently have no basis for differentiating water quality problems from natural variability. Higher levels of naturally occurring constituents observed in water do not automatically indicate that the water is polluted with the constituents without knowing the natural background water levels. This study presents that natural background water quality in southern California and environmental factors to the water quality. The results of this study yielded seven important conclusions;

- Concentrations in natural catchments are typically between one to two orders of magnitude lower than in developed watersheds.
- Wet weather fluxes of nutrients and TSS in natural catchments are not significantly different from those in developed catchments.
- Differences between natural and developed catchments are greater in dry weather than in wet weather.
- Dry weather loading can be a substantial portion of total annual load in natural catchments.
- Concentration and load peak later in a storm in natural catchments than in developed catchments and concentrations and loads spread out widely over the course of a storm.

- Metal concentrations in natural catchments are below existing water quality standards in both dry and wet weather
- Dry weather nutrient concentrations in natural catchments are lower, while wet-weather total nitrogen concentrations are higher than the EPA proposed nutrient criteria.
- Catchments underlain by sedimentary rock generally produce higher constituent concentrations than those underlain by igneous rock
- This study produces regionally applicable flux estimates for natural catchments during both storm and non-storm conditions.

1. Estimates of natural background water quality

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. The study shows that TSS concentrations in natural catchments are not different from those in developed catchments, which indicates that natural areas may be a substantial source of sediment to downstream areas. This finding suggests an important point on sediment in water, which is often blamed for degenerating benthic environments. In southern California, a number of watersheds are listed as impaired due to sediment and they are subject to sediment

TMDL[17] (State Water Resources Control Board 2003). The high level of TSS in natural catchments implies that significant amounts of sediment in the watersheds can be contributed by natural sources and a few of these watersheds may have to be taken off the list. This study also shows that natural background concentrations of metals in dry and wet weather are lower than the CTR standards. This implies that aquatic lives in southern California's watersheds may require lower levels of metals than the levels that are simply non-toxic to them. The CTR standards have been considered as a baseline for developing metal TMDLs. To assure the protection of sensitive lives such as endangered and threatened species more rigid baselines than the CTR, such as findings of this study, should be used for the development of the TMDLs.

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, and solids, the flux estimates from this study could be used to estimate the contribution of natural catchments 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

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[17] Under Section 303(d) of the 1972 Clean Water Act, states, territories and authorized tribes are required to develop a list of water quality limited segments. These waters on the list do not meet water quality standards, even after point sources of pollution have installed the minimum required levels of pollution control technology. The law requires that these jurisdictions establish priority rankings for water on the lists and develop action plans, called as Total Maximum Daily Loads (TMDL), to improve water quality.

natural catchments. 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 wet weather ranged from 0.3 (lower 95% confidence limit) to 1.8 g/stormevent· km^2 (upper 95% confidence limit). The area of Malibu Creek watershed is 285 km^2, and approximately 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.

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 catchments were derived from either open space in developed catchments or natural catchments from other regions. The flow-weighted mean concentrations of this study provide relevant background water quality concentrations for the southern California region.

Annual dry weather loading from natural catchments 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, the selenium flux ranged from 0.41g/km^2 day to 0.84g/km^2 day and the average of dry days in the Great Los

Angeles is 301. Thus, dry weather loading of selenium in the Malibu Creek watershed would be expected to range from 30 and 61kg/year. Total annual loading from natural catchments should account for contributions during both the wet and dry seasons.

Natural catchments in this study are relatively small because few large watersheds remain natural 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 nutrient mass as it travels downstream through stream channels (Alexander et al. 2000; Peterson et al. 2001). However, in this study no significant difference of natural background concentrations among catchments with different size was observed. This allows extrapolating the results of this study to natural background water quality for other larger or smaller developed watersheds.

2. Geology-specific loadings

Geology was shown to be the dominant factor that influenced the natural background water quality in this study. Most constituents were at higher levels in catchments underlain by sedimentary geologic material than in catchments underlain by igneous geologic material for both 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 catchments in a watershed of interest, average concentrations for each geology types can be used to estimate loadings from the natural catchments with different geologic types. For instance, each Malibu Creek subwatershed consists of different proportions of igneous and sedimentary rocks. The upper part of the watershed, which is north of Highway 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.

3. Dry weather vs. wet weather

In this study, concentrations of arsenic, selenium, dissolved organic carbon, total organic carbon, total phosphorus, and total dissolved solids were higher during the dry weather than during the wet weather. This resulted in the dry-weather flow comprising a larger proportion of the loadings than the storm flow for many constituents in natural watersheds. Knowledge of the relative contribution of dry-weather vs. wet-weather loading helps to plan for efficient management strategies, since storm water is typically much more difficult to manage than non-storm flows. For example, storm water management focuses on retention or detention, which can require commitment of large catchments. In contrast, management of non-storm (dry weather runoff) focuses on treatment, diversion, infiltration, and source control.

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APPENDICES FOR THE DISSERTATION

APPENDIX I, Review of existing data of water quality monitoring

1. Compilation of existing data sources

A number of ambient water quality monitoring programs and studies have been carried out across southern California to investigate impact of development on water quality. Most of these studies included water quality data in undeveloped areas as reference conditions. It is an important first step to compile these reference data and identify key data gaps in the existing databases. In addition, the data could provide guidelines for screening survey sites of the natural loadings project. The following monitoring programs were reviewed and summarized.

- Surface Water Ambient Monitoring Program (SWAMP)
- Environmental Monitoring and Assessment Program (EMAP)
- UCLA-Los Angeles Regional Water Quality Control Board (RWQCB) study
- Heal the Bay Stream Team Program Study
- USGS Hydrologic Benchmark Network
- USGS National Water Quality Assessment
- Santa Barbara Coastal Long Term Ecological Research Project (SBC-LTER)

- Water quality monitoring programs or/and bioassessment programs in local and state government agencies including U.S. Forest Service, RWQCB, Los Angeles, Orange, Ventura, San Diego, and San Bernardino counties and cities

Existing monitoring programs with data that were relevant to investigation of natural stream conditions in southern California were the SWAMP sampling conducted by the Los Angeles RWQCB, the EMAP sponsored by EPA Region 9, and the UCLA-Los Angeles RWQCB study, 'Environmental Monitoring and Bioassessment of Coastal Watersheds in Ventura and Los Angeles' sponsored by Los Angeles RWQCB. The other programs/studies did not contain usable data because either 1) they lacked sufficient water chemistry data, 2) the survey sites were not located in undeveloped areas, or 3) the sites were not located in southern California. Only data from the remaining studies were summarized and statistically analyzed.

The SWAMP program is designed to assess the conditions of surface waters throughout the state of California. The SWAMP water chemistry data obtained for this analysis were from the Santa Clara River watershed, and were collected from 2001 through 2003. EMAP is designed to monitor and assess national status and trends of ecological resources. The data used for this analysis were from the EMAP Western Pilot Study. The EMAP water quality data were collected from one-time samplings, carried out from 2000 through 2001. The UCLA-Los Angeles RWQCB study was carried out by UCLA during Fall 2001. The study included collection of water chemistry, physical, and biological data. The study contained relevant data from four reference sites. These three data sets contained concentrations for total suspended solids (TSS), dissolved organic carbon (DOC), total phosphorous (PTL), ammonium (NH_4), sulfate (SO_4), nitrate (NO_3), total nitrogen (NTL), selenium (Se), and zinc (Zn). Four survey sites from SWAMP, five reference sites from the UCLA study, and forty-five sites from EMAP were located in undeveloped areas and contained water chemistry data (Table 1).

2. ***Summary of existing water quality data***

2.1. Descriptive statistics

Descriptive statistics for each relevant water-quality parameter collected from existing studies are shown in Table 2. Although all the surveyed streams were in natural conditions, the water quality data varied. For instance, sulfate concentrations varied from 17.7 to 16788.4 mg/L. The concentrations of selenium were relatively more consistent than other water quality parameters, with the standard deviation of 0.94. These variations may have been due to effects of different land covers and geological settings in the catchments draining to each sampling site. A number of previous studies have shown that land cover types and geology types have the potential to affect water quality (Goodwin 1996;

Johnes et al. 1996; Larsen 1988; Pfeifer et al. 2000). Therefore, the existing data were also analyzed to investigate effects of different land cover and geology on water quality.

2.2. Impact of geology type and land cover type on water quality

Geology type and land cover type for each survey site were identified by plotting each sampling site in a GIS geology map (California Division of Mines and Geology, 1962) and a land cover map from Coastal Change Analysis Program (CCAP) (National Oceanographic and Atmospheric Administration 2003) (Table 3). Using the GIS-buffer zone technique, dominant types of geology and land cover within 1 km from each survey site was designated as a geology and a land cover. The data were analyzed to study the effect of geology and land cover on concentrations of total suspended solids (TSS), dissolved organic carbon (DOC), total phosphorous (PTL), ammonium (NH_4), sulfate (SO_4), nitrate (NO_3), total nitrogen (NTL), selenium (Se), and zinc (Zn) in water.

Two-way Analysis of Variance (ANOVA) with interaction was conducted to investigate effect of three types of geology and three types of land cover on nutrient and metal concentrations in water. Selenium levels in different geology types were significantly different ($p < 0.001$). There was not a statistically significant interaction between landcover and geology. The effect of different levels of geology on selenium did not depend on what level of landcover was present. (P = 0.154) (Table 4).

To isolate which geologic type differed from the others, a pair-wise multiple comparison procedure, Bonferroni t-test, was performed. The results of this analysis indicated that selenium concentrations in catchments draining sedimentary rocks groups were significantly higher than those draining metamorphic and igneous rocks ($p<0.05$) (Table 5; Figure 1).

Sulfate levels in water were significantly affected by geologic types (p = 0.006), but not by landcover types. There was no statistically significant interaction between landcover and geology. Therefore the effect of different levels of geology on selenium did not depend on what level of landcover was present (P = 0.154) (Table 6).

The sulfate concentrations in catchments draining sedimentary rocks was significantly higher from those draining metamorphic and igneous rocks and igneous rocks ($p<0.05$) (Table 7 and Figure 2).

The high selenium in the sedimentary rocks group may have been due to the fact that the group contains selenium-high Cretaceous rocks, which account for 70% of seleniferous across the United States (Trelease 1942) as well as Miocene rocks, which could be also seleniferous (Presser et al. 1994). USGS studies (Piper and Isaacs 1995) showed that the Miocene Monterey Formation, which is the major petroleum source rock in California, is also seleniferous. The Miocene Monterey Formation is broadly distributed in the southern San Joaquin Valley, San Francisco Bay area, central Coast Ranges including the Santa Maria Basin, and Los Angeles. Survey sites for the three studies were located across southern California, however, the sites whose geology types were sedimentary were dominantly in the Ventura County and Los Angeles basin area where soils were mainly sedimentary and potentially high in selenium.

High sulfur concentration in the sedimentary rocks group did not accord with the fact that sulfur was mainly associated with volcanic rocks such as pumice. However, sulfur could also occur in sedimentary rocks and the correlation of a geology type to sulfur levels were not as strong as selenium (Doherty 1971).

3. Conclusion

The analysis of the existing data suggested that loadings from undeveloped catchments may have been influenced by geology types, however, the data analyzed here contain several critical limitations. First, the data reviewed here were collected from one-time sampling. The result from one-time sampling should not be extrapolated for an entire season or a year. Second, samplings were conducted as part of separate studies and were collected neither in the same season nor in the same year. Third, samplings for some sites were conducted in dry season and for others in wet season. Third, the number of survey sites was not consistent across land cover and geologic types. For example, eleven of total twenty-three sites with the land cover of forest were in the sediment rocks group. In addition, not all land cover types paired with each geology type. Fourth, the methods to collect water samples were not consistent among the different studies. For example, a grab sampling method was used to collect the SWAMP data, while, a composite sampling method was used for the EMAP data.

Although limited the review of existing databases indicated that natural land covers and geology may affect water quality in undeveloped areas. However, the existing data are neither sufficient nor consistent enough to estimate ranges of expected loadings from undeveloped waterbodies in southern California. The "Assessment Of Water Quality Loadings From Natural Landscapes" study is designed to overcome the limitations of existing data, by sampling a series of sites over both wet and dry seasons and comparing the resultant runoff data to catchment characteristics, such as geology and land cover. The results of the study will allow a more precise estimation of background water quality in southern California.

Table 1. Sites with existing relevant data

Water Quality Monitoring Program	**Number of site**
SWAMP	5
RWQCB_UCLA Study	4
EMAP (2000-2002)	45

Table 2. Descriptive statistics of relevant water chemistry data from the existing water quality monitoring programs

Parameter (mg/L)	TSS	DOC	PTL	Se (ug/L)	NH4	SO4	NO3	NTL	Zn
Size	54	54	54	52	54	54	54	54	54
Missing	9	9	6	18	0	4	4	6	4
Mean	4.663	2.026	39.515	0.719	6.597	3472.876	1079.777	685.292	5.06
Std Dev	7.182	1.001	85.1	0.935	38.996	4189.175	2129.563	1734.932	4.121
Std. Error	1.071	0.149	12.283	0.16	5.307	592.439	301.166	250.416	0.583
C.I. of Mean	2.158	0.301	24.711	0.326	10.644	1190.55	605.215	503.772	1.171
Range	35	3.97	566	4.035	287.436	16770.72	6948.5	8732	15
Max	35.1	4.61	568	4.035	287.446	16788.42	6948.5	8756	15
Min	0.1	0.64	2	0	0.01	17.7	0	24	0
Median	2.5	1.81	16.5	0.72	0.585	1570.56	3.925	179.5	5
25%	1	1.348	8.5	0	0.43	257.13	0	110	1.9
75%	4.73	2.725	34.5	1	0.93	6299.3	588.6	302.01	8
Skewness	3.007	0.734	5.433	1.838	7.316	1.498	1.917	4.044	0.633
Kurtosis	9.259	-0.139	33.029	4.145	53.67	1.88	2.345	16.264	-0.461
K-S Dist.	0.281	0.148	0.33	0.264	0.455	0.207	0.39	0.404	0.113
K-S Prob.	<0.001	0.014	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.11
Sum	209.82	91.15	1896.7	24.454	356.245	173643.809	53988.845	32894	253.02
Sum of Squares	3247.724	228.702	415325.23	46.438	82947.511	1462953771	280512695	164011393	2112.48

*TSS, Total suspended solids; DOC, Dissolved organic carbon; PTL, Total phosphate; Se, Selenium; NH4, Ammonium; SO4, Sulfate; NO3, Nitrate; NTL, Total nitrogen; Zn, Zinc

Table 3. Survey sites with geology and land cover

Land cover	Geology	No. of sites	Total
Forest	Igneous Rocks	3	18
	Metamorphic Rocks	4	
	Sedimentary Rocks	11	
Shrub	Igneous Rocks	9	30
	Metamorphic Rocks	9	
	Sedimentary Rocks	12	
Grassland	Igneous Rocks	2	6
	Metamorphic Rocks	2	
	Sedimentary Rocks	2	

Table 4. Two-way ANOVA analysis, effect of 3 land cover types and 3 geology types on selenium levels in water

Source of Variation	DF	SS	MS	F	P
Landcover	2	2.235	1.117	1.944	0.164
Geology	2	11.139	5.569	9.69	<0.001
Landcover x Geology	4	4.214	1.054	1.833	0.154
Residual	25	14.369	0.575		
Total	33	28.85	0.874		

*DF, degree of freedom; SS, sum of square; MS, mean square; F, fixed effect; P, probability

Table 5. Results of the pairwise multiple comparison procedures (Bonferroni t-test)

Comparison	Diff of Means	t	P	P<0.05
Sedimentary Rocks vs. Metamorphic Rocks	1.429	3.625	0.004	Yes
Sedimentary Rocks vs. Igneous Rocks	1.327	3.697	0.003	Yes
Igneous Rocks vs. Metamorphic Rocks	1.02E-01	0.244	1	No

*Diff of Means, difference in means; t, t-test statistic value; P, probability

Table 6. Two-way ANOVA analysis, effect of 3 land cover types and 3 geology types on sulfate levels in water

Source of Variation	DF	SS	MS	F	P
Landcover	2	1E+07	5E+06	0.358	0.701
Geology	2	2E+08	8E+07	5.817	0.006
Landcover x Geology	4	6E+06	1E+06	0.103	0.981
Residual	41	6E+08	1E+07		
Total	49	9E+08	2E+07		

Table 7. All pair wise multiple comparison procedures (Bonferroni t-test)

Comparison	Diff of Means	t	P	P<0.050
Sedimentary Rocks vs. Metamorphic Rocks	4580.77	2.933	0.016	Yes
Sedimentary Rocks vs. Igneous Rocks	4540.423	2.833	0.021	Yes
Igneous Rocks vs. Metamorphic Rocks	40.347	0.0239	1	No

*Diff of Means, difference in means; t, t-test statistic value; P, probability

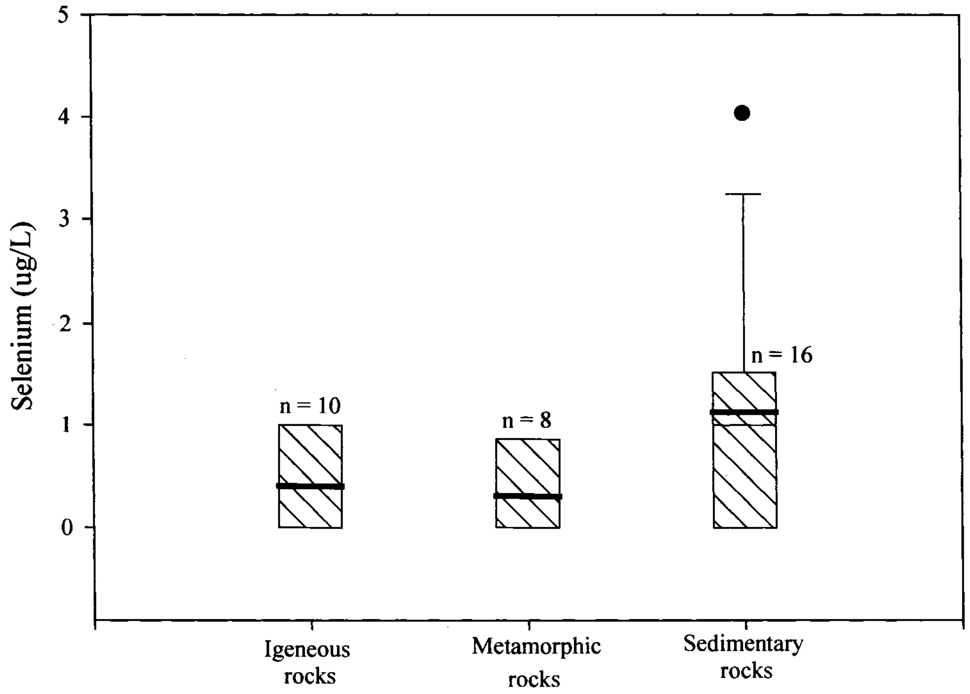

Figure 1. Selenium levels in different geology types; thicker solid lines indicate mean values in groups and the thinner ones indicate median values

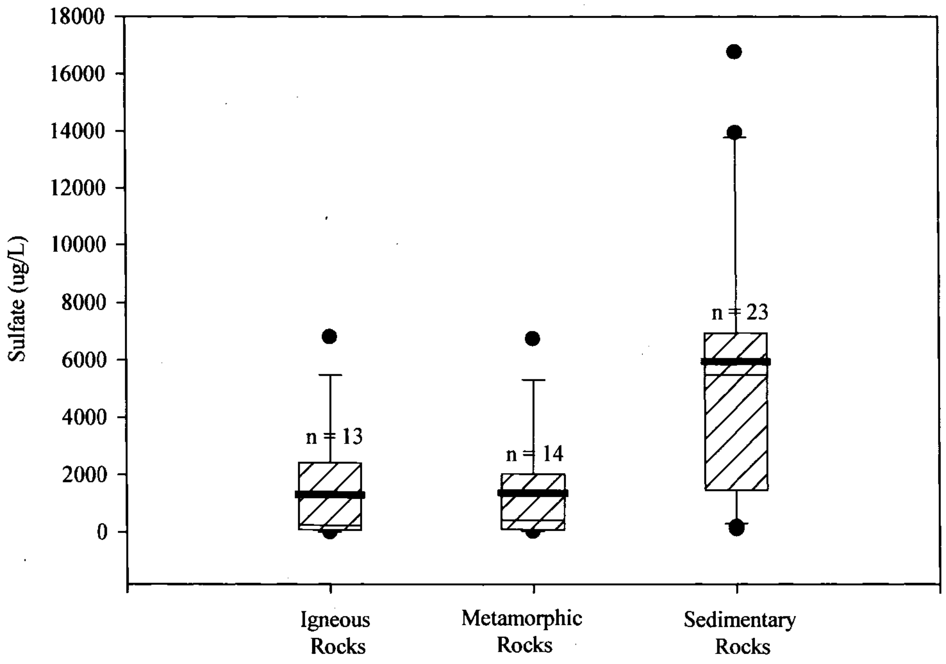

Figure 2. Sulfate levels in different geology types, the thicker solid lines indicate mean values in groups and the thinner ones indicate median values

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APPENDIX II, Characterization of coastal watersheds in southern California by geology and land use types

Table 1. a. Characterization of coastal watersheds by land use types; HUNAME=Hydrologic Unit Name, HANAME=Hydrologic Area Name, HSANAME = Hydrologic Sub-Area Name

HUNAME	HANAME	HSANAME	%Dev	%Undev	%Grassland	%Forest	%Shrub
CALLEGUAS	Oxnard Plain	Oxnard Plain	77.82	22.18	1.11	1.39	12.40
CALLEGUAS	Piru	Hungry Valley	1.14	98.86	17.98	10.36	59.62
CALLEGUAS	Piru	Santa Felicia	10.23	89.77	24.05	11.47	50.80
CALLEGUAS	Piru	Stauffer	0.75	99.25	6.55	41.71	49.47
CALLEGUAS	Piru	Upper Piru	0.38	99.62	8.66	35.95	52.65
CALLEGUAS	Santa Paula	Sisar	1.37	98.63	8.04	39.03	51.24
CALLEGUAS	Santa Paula	Sulfur Springs	25.42	74.58	8.00	16.96	47.62
CALLEGUAS	Sespe	Fillmore	36.83	63.17	11.45	8.30	40.04
CALLEGUAS	Sespe	Topa Topa	0.15	99.85	4.38	42.64	51.92
CALLEGUAS	Upper Santa Clara	Acton	2.20	97.80	15.18	6.07	70.96
CALLEGUAS	Upper Santa Clara	Bouquet	0.24	99.76	1.34	28.47	62.75
CALLEGUAS	Upper Santa Clara	Eastern	15.07	84.93	8.90	13.41	59.31
CALLEGUAS	Upper Santa Clara	Mint Canyon	4.15	95.85	3.37	0.77	91.41
CALLEGUAS	Upper Santa Clara	Sierra Pelona	16.51	83.49	12.11	0.91	68.75
CARLSBAD	Escondido Creek	Escondido	48.33	51.67	2.06	2.03	46.91
CARLSBAD	Escondido Creek	Lake Wohlford	8.59	91.41	11.33	3.13	73.30
CARLSBAD	Escondido Creek	San Elijo	49.73	50.27	0.73	3.17	39.07
LOS ANGELES RIVER	Los Angeles	Los Angeles	94.06	5.94	0.00	1.26	3.80
LOS ANGELES RIVER	Raymond	Monk Hill	17.66	82.34	0.74	18.88	61.18
LOS ANGELES RIVER	Raymond	Pasadena	72.30	27.70	0.36	5.63	19.49
LOS ANGELES RIVER	Raymond	Santa Anita	0.14	99.86	0.22	49.26	50.06
LOS ANGELES RIVER	San Fernando	Bull Canyon	68.66	31.34	2.98	3.99	23.01
LOS ANGELES RIVER	San Fernando	Eagle Rock	69.37	30.63	0.00	4.43	26.19
LOS ANGELES RIVER	San Fernando	Sylmar	17.80	82.20	1.01	13.33	67.26
LOS ANGELES RIVER	San Fernando	Tujunga	6.55	93.45	4.59	15.56	71.69
LOS ANGELES RIVER	San Fernando	Verdugo	35.78	64.22	0.46	8.82	54.41
OTAY	Coronado	Coronado	83.96	16.04	0.00	0.04	1.96
OTAY	Dulzura	Engineer Springs	0.70	99.30	25.74	0.14	71.80
OTAY	Dulzura	Hollenbeck	0.99	99.01	9.79	2.28	86.02
OTAY	Dulzura	Jamul	23.64	76.36	9.89	0.50	64.79
OTAY	Dulzura	Lee	9.22	90.78	8.12	0.72	81.91
OTAY	Dulzura	Lyon	2.10	97.90	6.25	4.11	87.40
OTAY	Dulzura	Proctor	25.46	74.54	7.77	0.07	65.02
OTAY	Dulzura	Savage	2.74	97.26	15.52	1.05	69.29
OTAY	Otay Valley	Otay Valley	49.10	50.90	15.66	0.20	22.08
PENASQUITOS	Fiesta Island	Fiesta Island	74.99	25.01	0.00	0.38	0.19
PENASQUITOS	Miramar	Miramar	56.76	43.24	0.03	1.88	38.64
PENASQUITOS	Miramar Reservoir	Miramar Reservoir	57.29	42.71	0.87	2.31	31.38
PENASQUITOS	Mission Bay	Mission Bay	9.98	90.02	0.00	0.01	0.27
PENASQUITOS	Poway	Poway	40.62	59.38	0.70	1.48	56.10
PENASQUITOS	Scripps	Scripps	76.91	23.09	0.04	3.88	16.11
PENASQUITOS	Tecolote	Tecolote	78.64	21.36	0.00	2.26	17.59
PENASQUITOS	Vacation Isle	Vacation Isle	91.50	8.50	0.00	0.88	0.35

Table 1.b. Characterization of coastal watersheds by land use types; HUNAME=Hydrologic Unit Name, HANAME=Hydrologic Area Name, HSANAME = Hydrologic Sub-Area Name

HUNAME	HANAME	HSANAME	%Dev	%Undev	%Grassland	%Forest	%Shrub
SAN DIEGO	Boulder Creek	Cuyamaca	1.72	98.28	23.99	36.15	35.55
SAN DIEGO	Boulder Creek	Inaja	2.13	97.87	8.88	24.47	64.32
SAN DIEGO	Boulder Creek	Spencer	3.55	96.45	33.62	20.52	42.21
SAN DIEGO	El Capitan	Alpine	43.50	56.50	0.00	3.35	52.59
SAN DIEGO	El Capitan	Conejos Creek	1.29	98.71	2.98	5.65	86.65
SAN DIEGO	Lower San Diego	Coches	42.95	57.05	2.95	0.85	52.20
SAN DIEGO	Lower San Diego	El Cajon	77.46	22.54	0.02	2.28	19.52
SAN DIEGO	Lower San Diego	El Monte	17.18	82.82	4.29	0.99	75.39
SAN DIEGO	Lower San Diego	Mission San Diego	64.97	35.03	0.08	1.76	29.74
SAN DIEGO	Lower San Diego	Santee	33.21	66.79	2.75	0.70	60.67
SAN DIEGO	San Vicente	Barona	6.64	93.36	11.79	2.75	78.64
SAN DIEGO	San Vicente	Fernbrook	3.63	96.37	3.45	1.36	84.21
SAN DIEGO	San Vicente	Gower	19.22	80.78	6.27	1.58	72.62
SAN DIEGO	San Vicente	Kimball	6.93	93.07	13.08	1.13	78.57
SAN DIEGUITO	Hodges	Bear	80.52	19.48	0.00	3.46	15.57
SAN DIEGUITO	Hodges	Del Dios	37.24	62.76	0.61	2.89	52.21
SAN DIEGUITO	Hodges	Felicita	77.57	22.43	0.00	4.51	17.54
SAN DIEGUITO	Hodges	Green	82.92	17.08	0.00	3.84	12.74
SAN DIEGUITO	San Pasqual	Guejito	0.82	99.18	25.19	10.77	63.08
SAN DIEGUITO	San Pasqual	Hidden	2.07	97.93	21.37	1.82	74.63
SAN DIEGUITO	San Pasqual	Highland	44.25	55.75	4.99	0.53	49.36
SAN DIEGUITO	San Pasqual	Las Lomas Muertas	32.39	67.61	2.64	1.60	62.15
SAN DIEGUITO	San Pasqual	Reed	3.71	96.29	3.47	1.78	90.73
SAN DIEGUITO	San Pasqual	Vineyard	0.00	100.00	51.14	2.81	46.03
SAN DIEGUITO	Santa Maria Valley	Ballena	0.83	99.17	51.93	0.61	46.56
SAN DIEGUITO	Santa Maria Valley	East Santa Teresa	0.28	99.72	68.84	0.78	28.21
SAN DIEGUITO	Santa Maria Valley	Lower Hatfield	3.46	96.54	24.88	1.47	69.85
SAN DIEGUITO	Santa Maria Valley	Ramona	38.78	61.22	22.32	1.45	37.23
SAN DIEGUITO	Santa Maria Valley	Upper Hatfield	0.61	99.39	26.75	1.42	70.96
SAN DIEGUITO	Santa Maria Valley	Wash Hollow	1.66	98.34	19.10	1.46	77.56
SAN DIEGUITO	Santa Maria Valley	West Santa Teresa	0.17	99.83	33.35	1.48	64.85
SAN DIEGUITO	Santa Ysabel	Boden	10.65	89.35	6.57	1.48	80.89
SAN DIEGUITO	Santa Ysabel	Pamo	0.68	99.32	12.98	18.61	67.49
SAN DIEGUITO	Santa Ysabel	Sutherland	1.08	98.92	24.82	10.35	62.60
SAN DIEGUITO	Santa Ysabel	Witch Creek	0.85	99.15	29.61	28.57	40.87
SAN DIEGUITO	Solana Beach	La Jolla	53.82	46.18	5.22	0.66	34.99
SAN DIEGUITO	Solana Beach	Rancho Santa Fe	62.03	37.97	0.88	3.34	24.61
SAN GABRIEL R.	Anaheim	Anaheim	96.27	3.73	0.15	0.45	2.45
SAN GABRIEL R.	Anaheim	La Habra (Split)	55.18	44.82	8.38	9.31	25.73
SAN GABRIEL R.	Lower San Gabriel	Alamitos Bay	59.52	40.48	0.00	0.04	0.29
SAN GABRIEL R.	Lower San Gabriel	Central (Split)	92.68	7.32	0.08	1.80	4.23
SAN GABRIEL R.	San Gabriel Valley	Foothill	2.42	97.58	1.10	19.19	76.77
SAN GABRIEL R.	San Gabriel Valley	Lower Canyon	29.15	70.85	1.15	4.58	50.88
SAN GABRIEL R.	San Gabriel Valley	Upper Canyon	0.21	99.79	2.28	34.76	60.93
SAN GABRIEL R.	Spadra	Live Oak	43.15	56.85	2.83	6.72	45.58
SAN GABRIEL R.	Spadra	Pomona	80.95	19.05	0.44	3.01	9.43
SAN GABRIEL R.	Spadra	San Jose	77.06	22.94	3.82	2.96	15.72
SAN GABRIEL R.	Upper San Gabriel	Upper San Gabriel	72.09	27.91	1.26	5.60	18.47

Table 1.c. Characterization of coastal watersheds by land use types; HUNAME=Hydrologic Unit Name, HANAME=Hydrologic Area Name, HSANAME = Hydrologic Sub-Area Name

HUNAME	HANAME	HSANAME	%Dev	%Undev	%Grassland	%Forest	%Shrub
SAN JUAN	Laguna	Aliso	57.98	42.02	1.04	7.48	29.71
SAN JUAN	Laguna	Dana Point	59.21	40.79	0.01	10.78	27.79
SAN JUAN	Laguna	Laguna Beach	25.06	74.94	1.06	8.74	62.75
SAN JUAN	Laguna	San Joaquin Hills	12.10	87.90	4.12	4.11	78.31
SAN JUAN	Mission Viejo	Gobernadora	23.94	76.06	17.92	2.07	49.75
SAN JUAN	Mission Viejo	Lower San Juan	57.48	42.52	9.41	1.97	17.29
SAN JUAN	Mission Viejo	Middle San Juan	27.33	72.67	8.47	4.71	52.63
SAN JUAN	Mission Viejo	Middle Trabuco	58.25	41.75	2.66	2.17	30.96
SAN JUAN	Mission Viejo	Ortega	40.30	59.70	21.58	1.85	31.99
SAN JUAN	Mission Viejo	Oso	67.13	32.87	0.79	8.48	20.96
SAN JUAN	Mission Viejo	Upper San Juan	2.05	97.95	1.46	4.99	89.57
SAN JUAN	Mission Viejo	Upper Trabuco	2.19	97.81	0.09	15.18	82.22
SAN JUAN	San Clemente	Prima Deshecha	56.87	43.13	12.97	2.08	24.81
SAN JUAN	San Clemente	Segunda Deshecha	57.88	42.12	8.95	3.42	26.48
SAN JUAN	San Mateo Canyon	San Mateo Canyon	5.63	94.37	2.49	2.96	83.98
SAN JUAN	San Onofre	Las Pulgas	2.07	97.93	5.12	1.25	53.80
SAN JUAN	San Onofre	San Onofre Valley	3.27	96.73	8.54	3.16	71.72
SAN JUAN	San Onofre	Stuart	7.66	92.34	1.72	0.53	50.49
SANTA ANA RIVER	Colton-Rialto	Colton	85.24	14.76	7.28	0.17	3.49
SANTA ANA RIVER	Colton-Rialto	Lower Lytle	15.92	84.08	5.06	12.27	52.80
SANTA ANA RIVER	Colton-Rialto	Reche	4.72	95.28	21.01	0.84	57.26
SANTA ANA RIVER	Colton-Rialto	Rialto	15.38	84.62	45.80	1.29	36.40
SANTA ANA RIVER	Colton-Rialto	Upper Lytle	0.78	99.22	2.11	48.10	44.62

Table 1.d. Characterization of coastal watersheds by land use types; HUNAME=Hydrologic Unit Name, HANAME=Hydrologic Area Name, HSANAME = Hydrologic Sub-Area Name

HUNAME	HANAME	HSANAME	%Dev	%Undev	%Grassland	%Forest	%Shrub
SANTA MARGARITA	Aguanga	Devils Hole	0.78	99.22	1.08	42.26	55.76
SANTA MARGARITA	Aguanga	Redec	2.61	97.39	2.65	42.02	52.01
SANTA MARGARITA	Aguanga	Tule Creek	8.01	91.99	11.54	10.52	69.13
SANTA MARGARITA	Aguanga	Vail	6.53	93.47	22.50	6.26	59.25
SANTA MARGARITA	Auld	Bachelor Mountain	7.73	92.27	22.14	0.10	63.64
SANTA MARGARITA	Auld	Gertrudis	38.85	61.15	33.68	0.48	26.01
SANTA MARGARITA	Auld	Lower Tucalota	6.55	93.45	19.88	0.06	71.27
SANTA MARGARITA	Auld	Tucalota	2.96	97.04	9.75	0.21	85.31
SANTA MARGARITA	Cave Rocks	Anza	2.08	97.92	33.24	3.35	59.49
SANTA MARGARITA	Cave Rocks	Burnt	0.16	99.84	5.17	4.58	89.28
SANTA MARGARITA	Cave Rocks	Lower Coahuila	10.67	89.33	15.62	0.55	72.37
SANTA MARGARITA	Cave Rocks	Upper Coahuila	0.32	99.68	19.38	0.98	77.10
SANTA MARGARITA	DeLuz	Deluz Creek	16.17	83.83	2.38	5.07	73.73
SANTA MARGARITA	DeLuz	Gavilan	31.03	68.97	0.79	4.41	63.02
SANTA MARGARITA	DeLuz	Vallecitos	21.81	78.19	0.06	2.99	74.61
SANTA MARGARITA	Murrieta	Diamond	1.36	98.64	14.39	0.07	47.58
SANTA MARGARITA	Murrieta	Domenigoni	18.24	81.76	17.71	0.01	29.19
SANTA MARGARITA	Murrieta	French	28.63	71.37	35.78	0.15	32.96
SANTA MARGARITA	Murrieta	Lower Domenigoni	42.98	57.02	48.13	0.01	8.75
SANTA MARGARITA	Murrieta	Murrieta	44.87	55.13	15.53	1.23	36.93
SANTA MARGARITA	Murrieta	Wildomar	35.24	64.76	16.49	1.88	46.02
SANTA MARGARITA	Oakgrove	Chihuahua	1.20	98.80	9.68	4.83	84.15

Table 1.e. Characterization of coastal watersheds by land use types; HUNAME=Hydrologic Unit Name, HANAME=Hydrologic Area Name, HSANAME = Hydrologic Sub-Area Name

HUNAME	HANAME	HSANAME	%Dev	%Undev	%Grassland	%Forest	%Shrub
SANTA MARGARITA	Oakgrove	Dodge	0.41	99.59	6.91	33.07	59.26
SANTA MARGARITA	Oakgrove	Lower Culp	5.54	94.46	13.56	1.35	78.99
SANTA MARGARITA	Oakgrove	Previtt Canyon	2.29	97.71	6.36	7.93	83.02
SANTA MARGARITA	Pechanga	Pauba	35.54	64.46	25.83	0.72	36.20
SANTA MARGARITA	Pechanga	Wolf	21.62	78.38	12.76	2.06	63.00
SANTA MARGARITA	Wilson	Lancaster Valley	15.14	84.86	21.44	0.05	62.48
SANTA MARGARITA	Wilson	Lewis	6.94	93.06	30.19	0.05	61.64
SANTA MARGARITA	Wilson	Reed Valley	3.81	96.19	8.19	3.62	84.00
SANTA MARGARITA	Ysidora	Chappo	14.31	85.69	0.85	0.58	61.41
SANTA MARGARITA	Ysidora	Lower Ysidora	30.56	69.44	2.32	0.54	35.90
SANTA MARGARITA	Ysidora	Upper Ysidora	19.98	80.02	0.91	0.94	60.09
SANTA MONICA BAY	Malibu Creek	La Virgenes Canyon	15.37	84.63	24.77	3.16	54.54
SANTA MONICA BAY	Malibu Creek	Lindero Canyon	28.61	71.39	16.87	1.73	51.80
SANTA MONICA BAY	Malibu Creek	Monte Nido	7.97	92.03	2.79	14.27	73.09
SANTA MONICA BAY	Malibu Creek	Russell Valley	47.54	52.46	5.90	3.77	41.22
SANTA MONICA BAY	Malibu Creek	Sherwood	21.17	78.83	4.83	7.81	64.62
SANTA MONICA BAY	Malibu Creek	Triunfo Canyon	10.68	89.32	2.58	7.41	76.61
SUN LUIS REY	Lower San Luis	Bonsall	55.35	44.65	0.40	1.86	40.35
SUN LUIS REY	Lower San Luis	Mission	56.00	44.00	1.17	1.17	29.39
SUN LUIS REY	Lower San Luis	Moosa	33.58	66.42	0.16	2.03	63.61
SUN LUIS REY	Lower San Luis	Rincon	59.94	40.06	0.00	4.06	35.63
SUN LUIS REY	Lower San Luis	Valley Center	34.13	65.87	7.24	4.15	54.11
SUN LUIS REY	Lower San Luis	Woods	24.78	75.22	0.52	4.75	69.05
SUN LUIS REY	Monserate	La Jolla Amago	1.56	98.44	7.74	40.99	49.28
SUN LUIS REY	Monserate	Pala	17.39	82.61	2.84	2.62	76.02
SUN LUIS REY	Monserate	Pauma	16.83	83.17	6.08	25.95	50.78
SUN LUIS REY	Warner Valler	Combs	1.72	98.28	1.46	18.92	77.84
SUN LUIS REY	Warner Valler	Warner	1.24	98.76	25.53	17.37	54.27
SWEETWATER	Lower Sweetwater	La Nacion	72.95	27.05	0.13	2.20	21.02
SWEETWATER	Lower Sweetwater	Telegraph	86.96	13.04	0.09	0.57	3.69
SWEETWATER	Middle Sweetwater	Alpine Heights	32.39	67.61	0.01	1.90	65.62
SWEETWATER	Middle Sweetwater	Dehesa	23.40	76.60	0.02	1.22	72.49
SWEETWATER	Middle Sweetwater	Galloway	14.57	85.43	0.16	1.22	83.96
SWEETWATER	Middle Sweetwater	Hillsdale	79.82	20.18	0.00	2.18	17.11
SWEETWATER	Middle Sweetwater	Jamacha	20.37	79.63	4.80	1.49	69.50
SWEETWATER	Middle Sweetwater	Sequan	22.42	77.58	1.24	0.66	73.68
SWEETWATER	Upper Sweetwater	Descanso	0.98	99.02	7.56	13.08	78.20
SWEETWATER	Upper Sweetwater	Garnet	1.08	98.92	4.79	43.88	50.14
SWEETWATER	Upper Sweetwater	Japatul	5.18	94.82	21.98	0.57	71.83
SWEETWATER	Upper Sweetwater	Loveland	5.30	94.70	7.29	1.25	84.26
SWEETWATER	Upper Sweetwater	Viejas	7.19	92.81	15.73	1.13	75.77
VENTURA RIVER	Lower Ventura River	Lower Ventura River	16.02	83.98	9.13	12.63	59.51
VENTURA RIVER	Ojai	Ojai Valley	20.10	79.90	3.76	35.90	39.73
VENTURA RIVER	Ojai	Upper Ojai	4.26	95.74	18.65	43.17	33.55
VENTURA RIVER	Upper Ventura River	Upper Ventura River	5.62	94.38	4.32	47.43	39.19

Table 2. Characterization of coastal watersheds by geology types

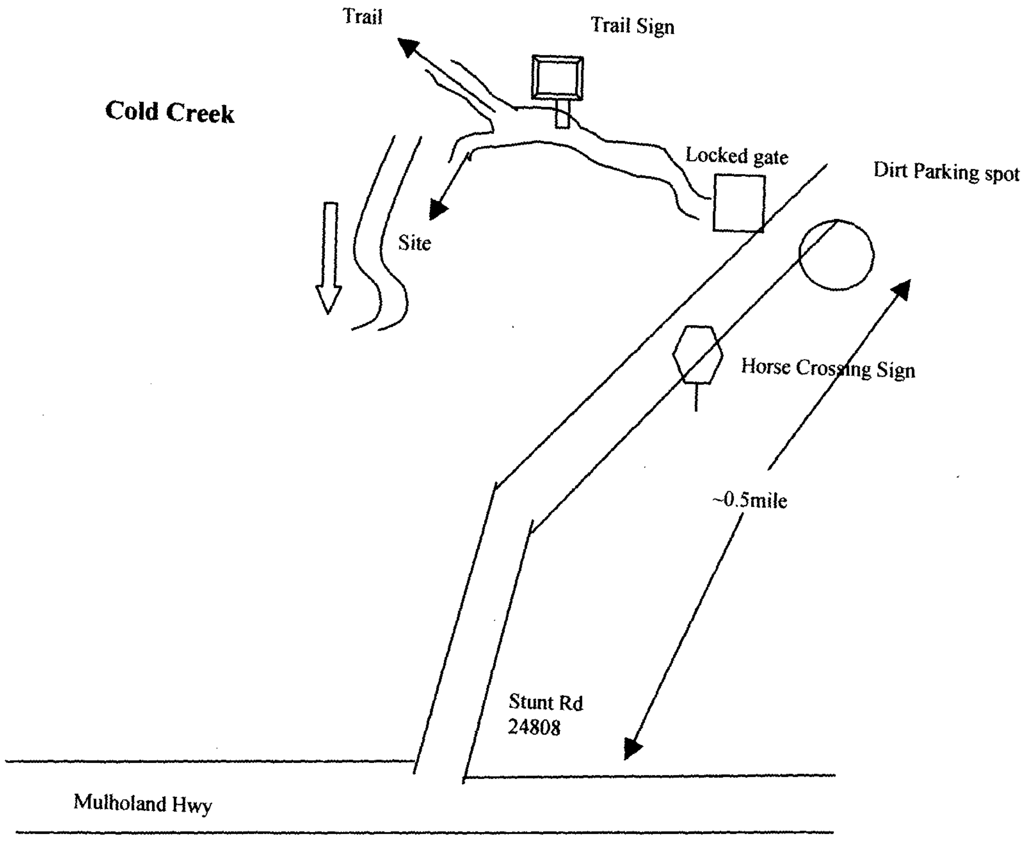
Watershed	Dominant Geology	Description
Ventura River Watershed	Sedimentary Rocks	Permian marine, Oligocene nonmarine
Santa Clara River Watershed	Sedimentary Rocks	Oligocene nonmarine, Miocene marine, Pliocene nonmarine (<10% Precambrian metamorphic & Igneous rocks)
San Diego Watershed	No Geology information available	
Santa Ana River Watershed	Sedimentary Rocks	Only 1/2 part (SW) of the WS has geo info/ SW, Alluvium/SE, Miocene marine, Oligocene nonmarine
Los Angeles River Watershed	Sedimentary Rocks	NE 1/5 of the WS is Metamorphic rocks
San Juan River Watershed	Sedimentary Rocks	NE (mountain area), granitic rocks
Aliso Creek Watershed (part of San Juan Watershed)	Sedimentary Rocks	Quaternary nonmarine, Miocene marine
San Mateo Watershed (part of San Juan Watershed)	Sedimentary Rocks/Metavolcanic/Granitic rocks	Upper WS(NE) granitic-metavolcanic-sediment Lower (SW), >50% Sed
Santa Monica Watershed	Volcanic/Sedimentary rocks	Malibu Creek WS, Volcanic/ the rest of WS Sedimentary
Malibu Creek (part of Santa Monica Watershed)	Volcanic(N) - Sedimentary (S)	Miocene volcanic (major) / Miocene marine rocks (minor)
San Gabriel Watershed	Sedimentary Rocks	No geo info for 2/3 N of the WS, !/3 S of the WS- sedimentary rocks
Santa Margarita Watershed	Granitic	portion of N is sedimentary rocks/ dominantly granitic rocks
San Luis Rey	Granitic	mainly granitic/ small portion of lower WS, around Lake Henshaw - sedimentary

APPENDIX III, Description of study sites

1. Site-specific information for Los Angeles County sites

1.1 Cold Creek

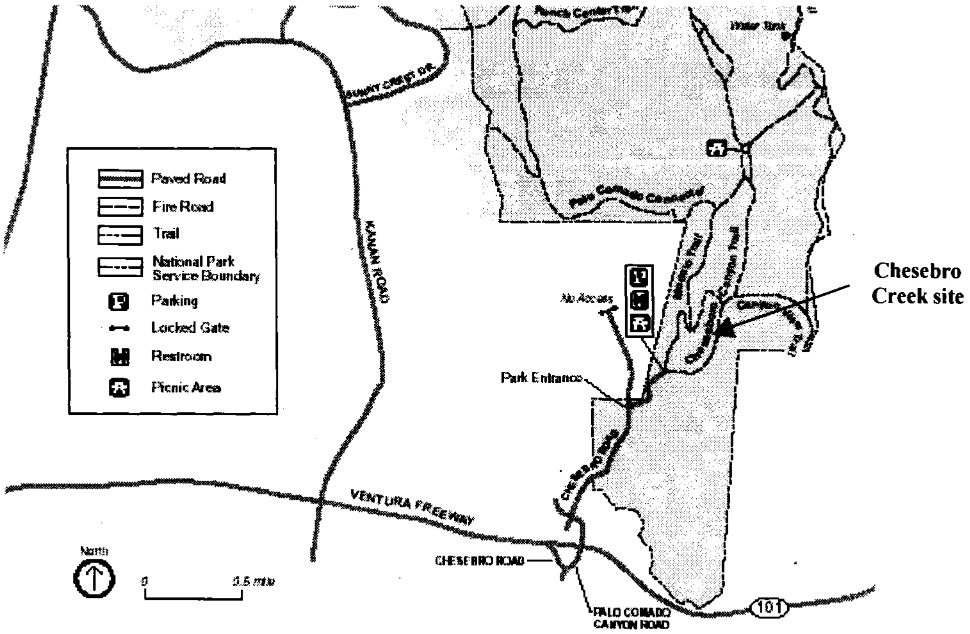
Location: Cold Creek, Los Angeles
Description:
Site name: Cold Creek
Coordinate: 34.09273N 118.64811W
Watershed: Malibu Creek Watershed
Geology: Sedimentary/Igneous
Landcover: Shrub/Forest
Sampling Season: Dry season only
Previous study done: Heal the Bay reference site/ UCLA Study reference site
Direction: 101(N)- Mulholland Dr/Valley Circle Blvd exit- Left on Valley Circle Blvd- continue on Mulholland Dr 1.5miles - Left onto Stunt Rd
~200 m upstream of the Stunt Rd over crossing / 1.3miles on Stunt Rd behind 1st lower gate on the left side-Park on the right side dirt parking lot
Thomas Guide: 589 E6
Dry season flow: Yes
Cell signal reception: No
Note: It is hard to rate the stream and not possible to access during storm. This sites should be considered as a dry season only site. Wildfire broke out in 1993. The site is closed with a locked gate.
Health and safety concern:
Hard to access to the site during storm – dry weather sampling only
Poison Oaks are abundant along the trail down to the site - surgical gloves and long sleeves should be worn. The unpaved trail to the site is very steep.



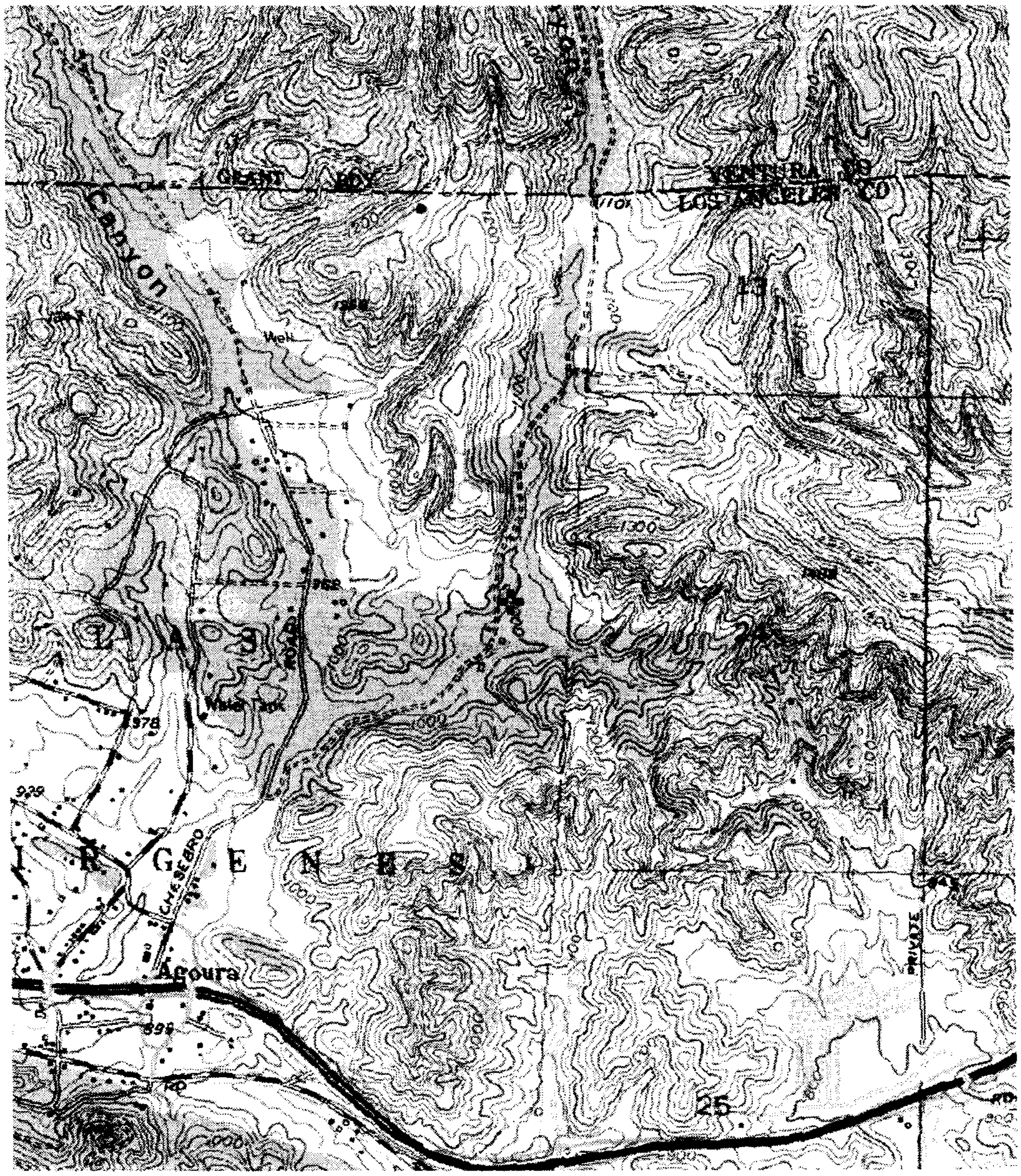
Cold Creek site

Cold Creek 34.0908°N, 118.6463°W (NAD27)

1.2 Chesebro Creek
Location: Chesebro Creek, Los Angeles
Description:
Site Name: Chesebro Creek
Coordinate: 36.0586N 119.65 181W 978FT(upstream)
34.15568N 118.72544W 975FT(downstream road crossing)
Watershed: Malibu Creek Watershed
Geology: Sedimentary
Landcover: Shrub
Access contact info:
Permit # SAMO-2004-SCI-0010
National Park Service Santa Monica Mountains NRA
enter through the Liberty Canyon gate (using the combo lock) and set up in Chesebro Creek near the Morrison House
Sampling Season: Wet/Dry
Previous study done: UCLA Study reference site
Direction: Park down at parking lot and hike up on the trail
Chesebro exit Parlo Comado Rd Chesebro Cyn
Thomas Guide: 558 E5
Dry season flow: no
Cell signal reception: Yes
Note: Need a key for the gate from the Park Service.
In general, the stream flows in dry season. It was dry in August 2004 but found to be damp and there was a ground water pool in upstream site. Upstream site is not good for wet season. Downstream road crossing is ratable and it is feasible for storm water sampling.
Combination lock for the main gate at the entrance of Chesebro trail.
No driving is allowed on the Parlo Comado Rd during storm.
There is an outer gate with a lock that will be closed after hour. Contact John before each sampling.
The Creek flew after the first storm in Oct 2004.
* The groundwater contamination by landfill nearby
Liberty canyon that is located next to the Chesebro canyon is the LA County landfill. The creek that flows from the east hill and merges into the Chesebro Creek at the downstream of the site was polluted possibly by the landfill. The Chesebro creek may be affected by the possible groundwater contamination. The Chesebro Creek may not be appropriate for a reference site.
Safety tips: Poison oaks are abundant. Ticks were found. The area is a mountain lion habitat.

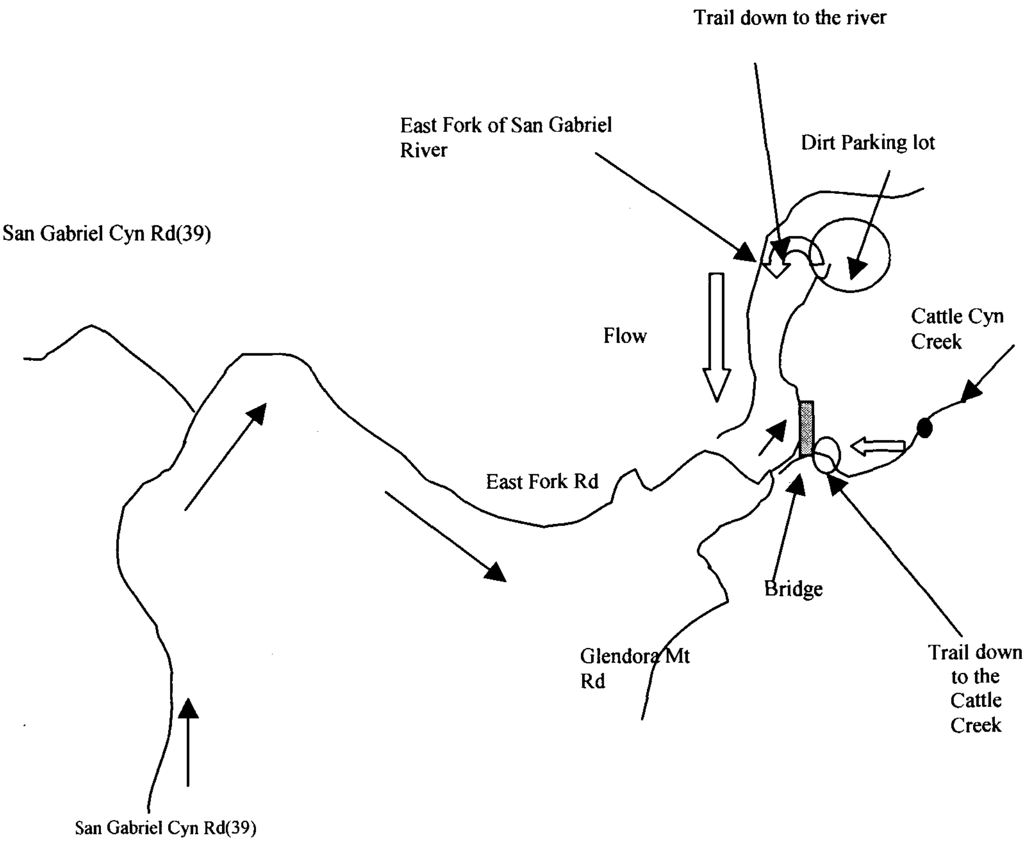


Chesebro Creek

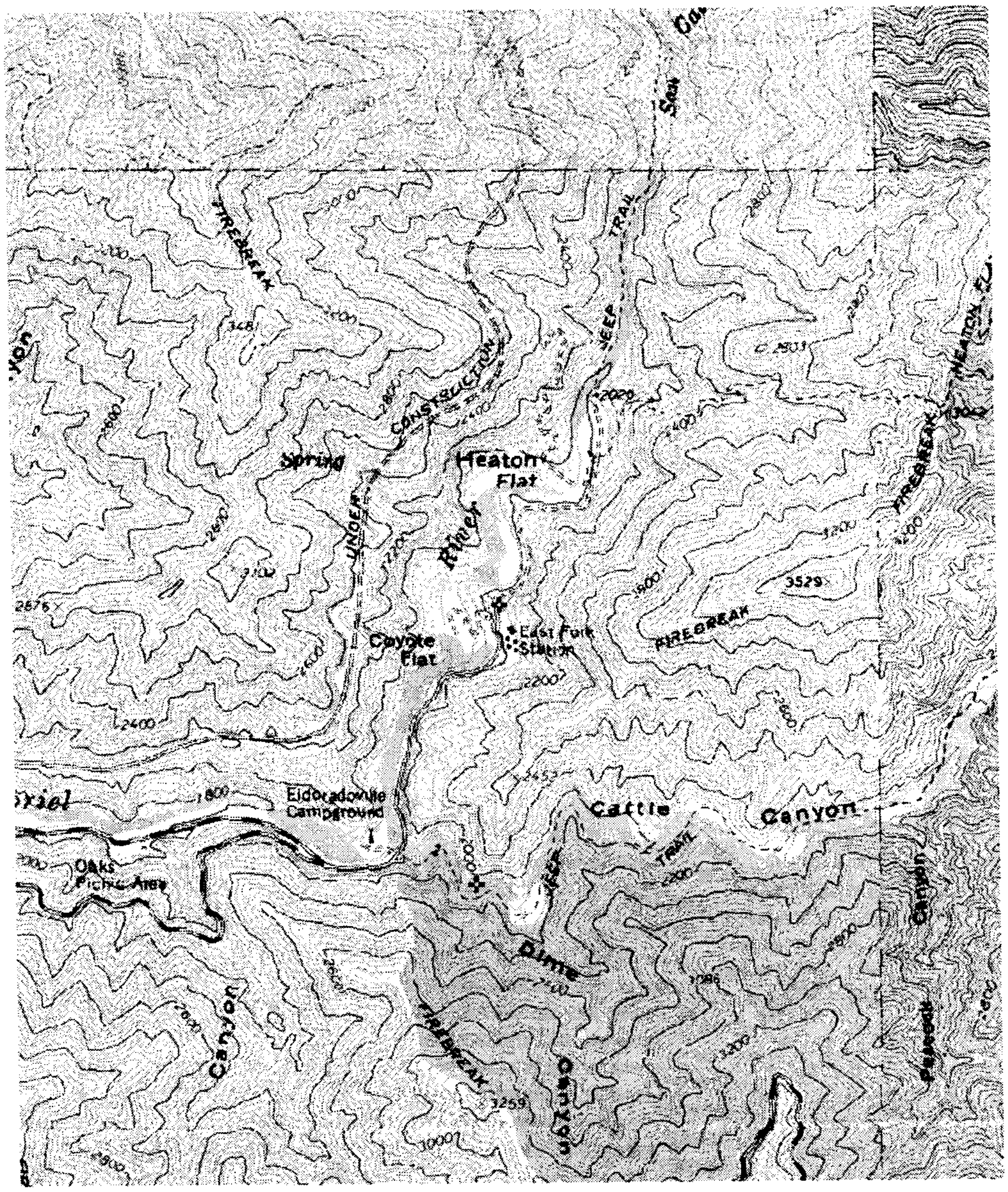


Topographical map of Chesebro Creek

1.3 Cattle Canyon Creek, a tributary to East Fork San Gabriel River
Location: Cattle Canyon Creek, Los Angeles
Description:
Site Name: Cattle Canyon Creek
Coordinate: 34.23707N 117.76483W (at the parking lot)
34.22891N 117.76610W (2nd trail crossing)
34.22830N 117.76593W (3rdk trail crossing)
Watershed: San Gabriel River Watershed
Geology: Igneous/Sediment
Landcover: Shrub
Sheep Mt. Wilderness Park
Sampling season: Wet/Dry
Previous study done: FS/DWR
Direction: 210 – San Gabriel Cyn Rd (39) exit - San Gabriel Cyn Rd (39) – Right onto East Fork Rd-pass the bridge over East Fork parking lot at the end of East Fork Rd
Right side right before the bridge there is a trail down to the creek
Thomas Guide:
Dry season flow: Yes
Cell signal: Yes
Note: Need a key for the gate on the trail down to the Creek
East Fork is highly used recreation area. The sampling site is upstream and less accessible to crowd.
Safety tips: The sampling site is not far from the road. It takes a few minute hike from the road where you may park your car to the sampling site. No special safety concern exists for the site.

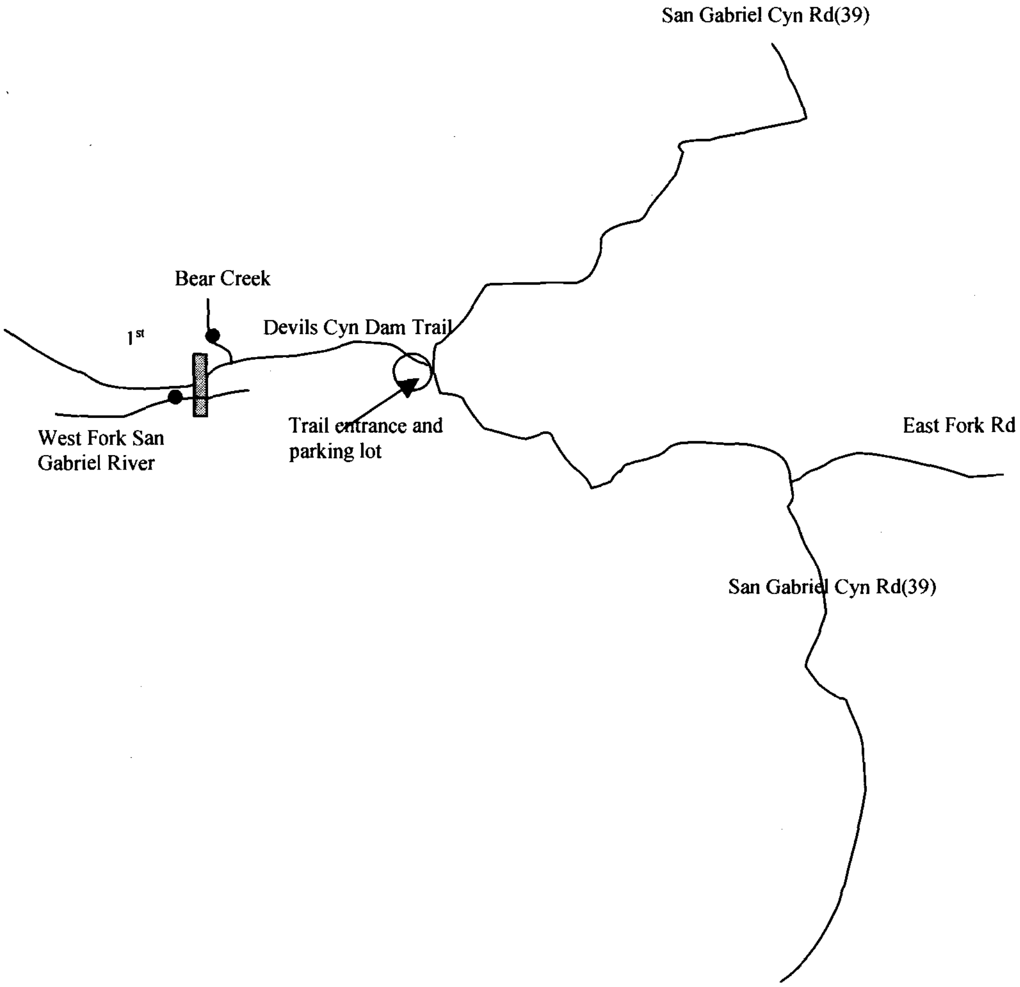


Cattle Canyon Creek, East Fork San Gabriel River

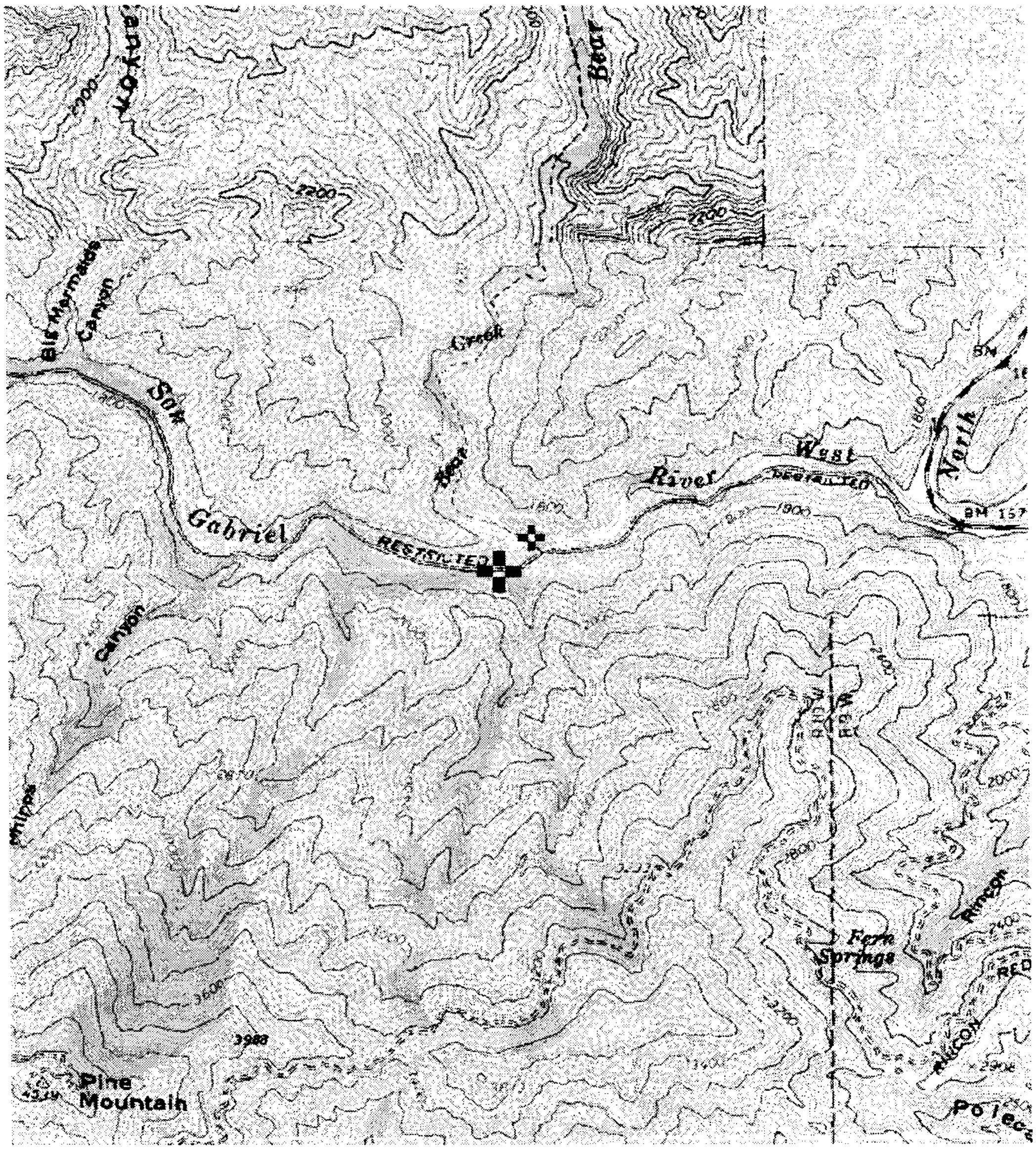


Topographical map of Cattle Canyon Creek,

1.4 West Fork San Gabriel River
Location: West Fork San Gabriel River, Los Angeles
Description:
Site Name: West Fork San Gabriel River
Coordinate: 34.23953N 117.88378W 1908FT
Watershed: San Gabriel River Watershed
Geology: Igneous/Sediment
Landcover: Shrub/Forest
Access contact info: Angeles National Forest
Administration pass and a key were granted.
Sampling season: Wet/Dry
Previous study done: FS/DWR
Direction: West Fork Trail 1st bridge-20min hike from the trail entrance-
A key is required for the gate to drive into the bridge. 39 to Devils Cyn Dam Trail entrance
Thomas Guide:
Dry season flow: Yes
Cell signal reception: No
Note: Storm water sampling can be conducted near the bridge.
Bear Creek, a tributary to West Fork (34.24057N 117.88318 W 1659FT) is not affected by Cogswell dam and it may be a candidate for a dry weather-sampling site even though it is not easy to rate.
Algae were present in the stream. The stream under the bridge is ratable. The sampling site is downstream of Cogswell dam. Minimum recreation activity was observed
Safety tips: No specific concern for safety exists.

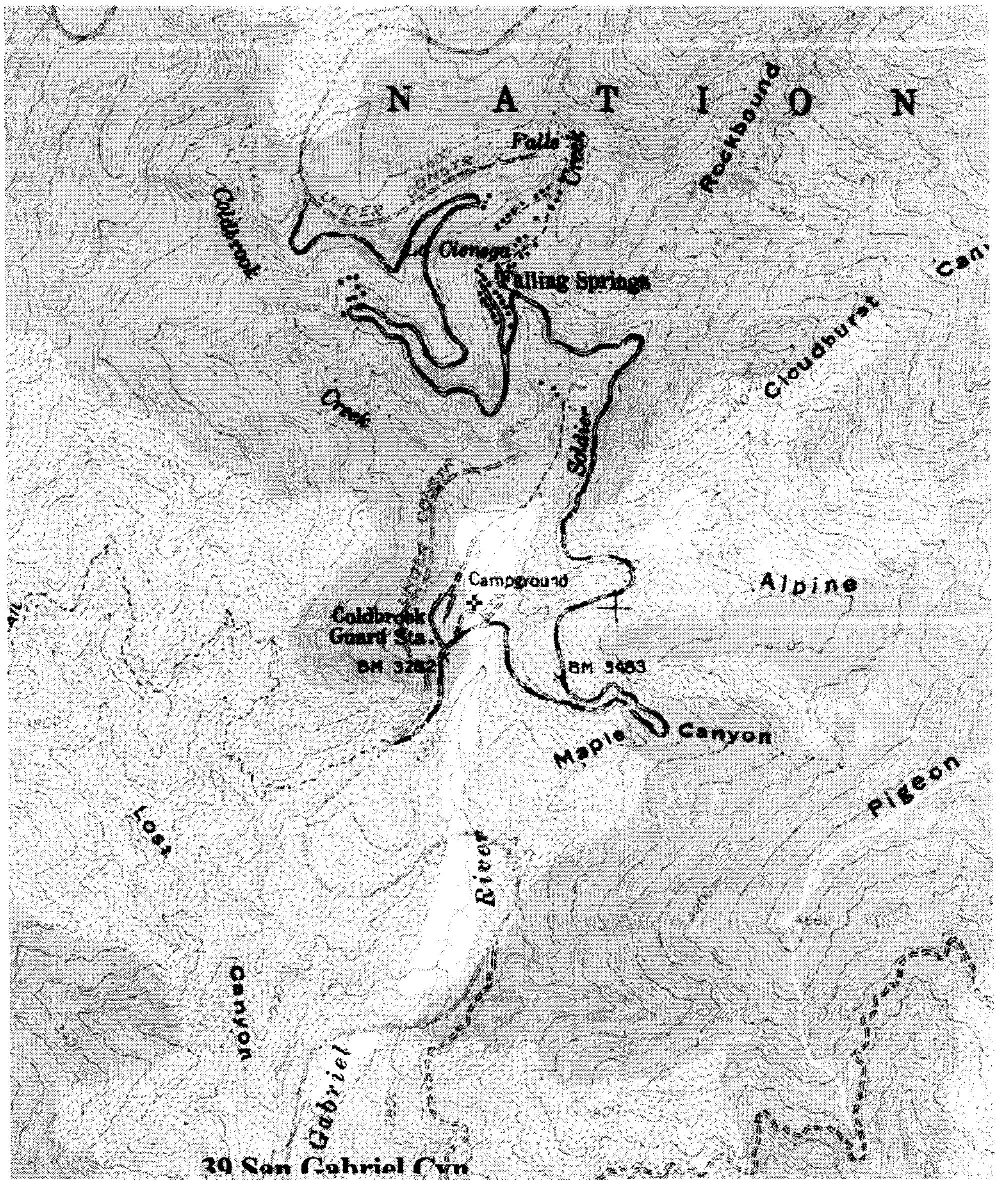


West Fork San Gabriel River



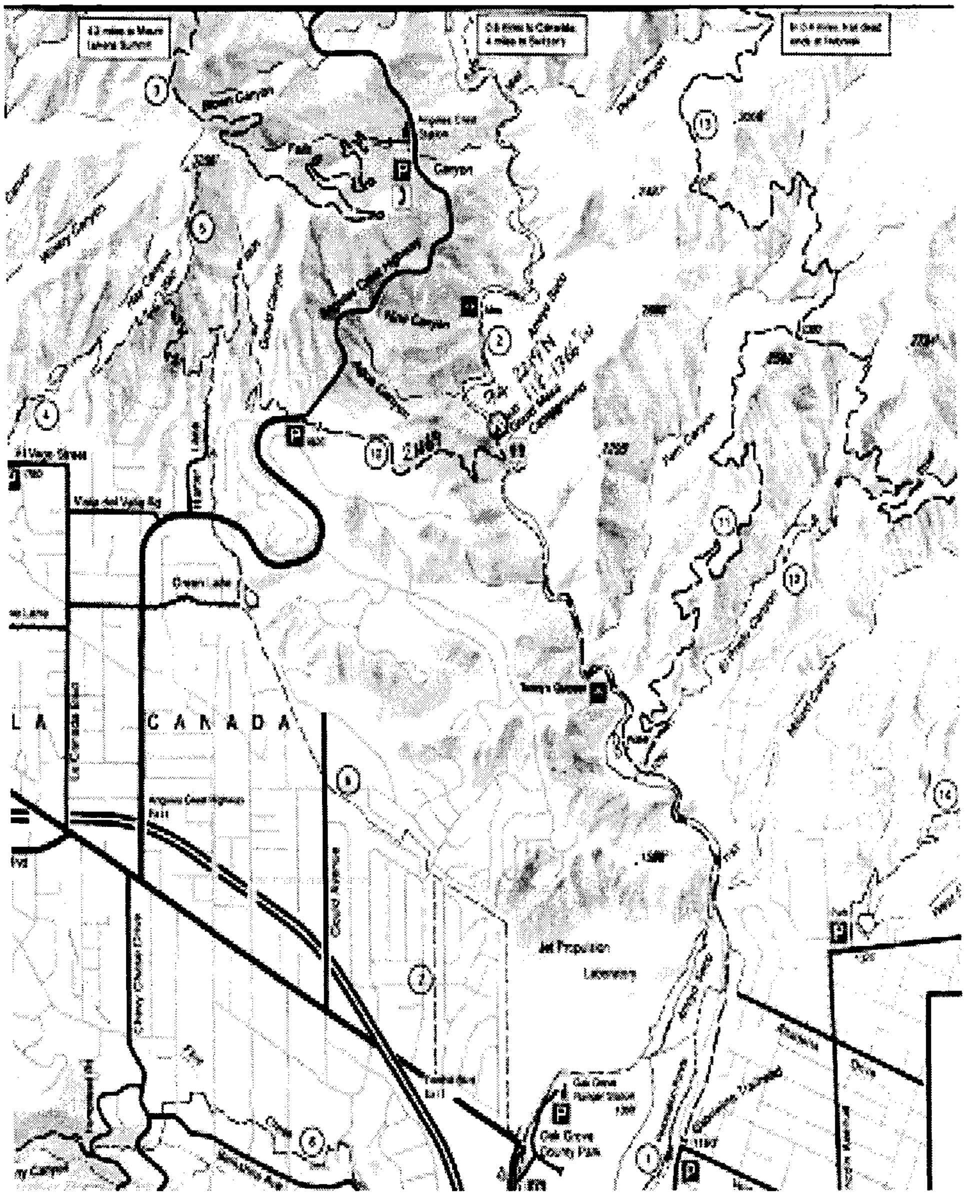
Topographical map of West Fork and Bear Creek

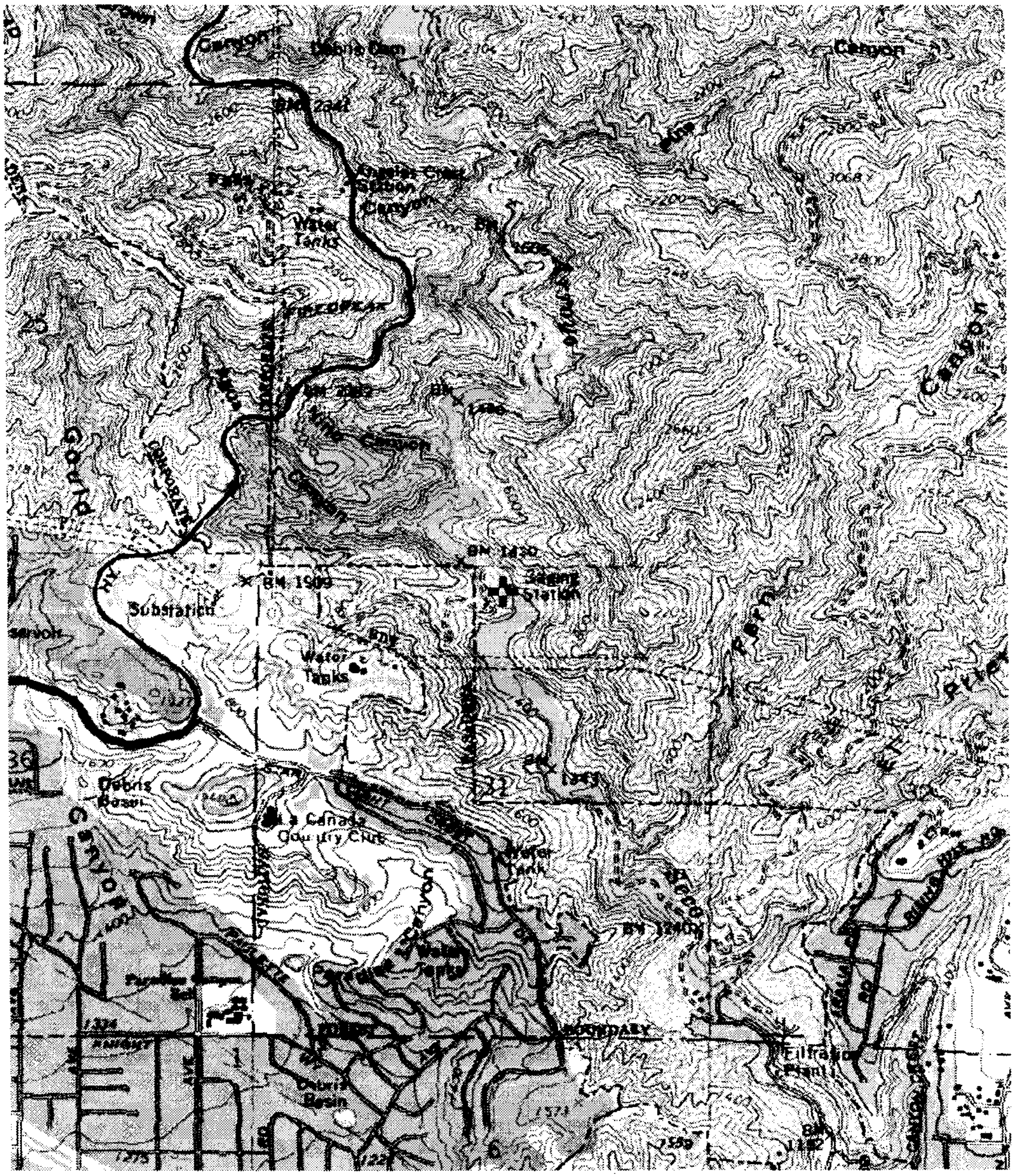
1.5 Coldbrook Campground, a tributary to North Fork San Gabriel River
Location: Coldbrook Creek, Los Angeles
Description:
Site Name: Coldbrook Campground
Coordinate: 4th stream crossing
34.292163N 117.83856W 3297FT
Watershed: San Gabriel River Watershed
Geology: Igneous/Sediment
Landcover: Shrub
Access contact info: Angeles National Forest
Sampling season: Wet/Dry
Previous study done: FS/DWR
Direction: 39 toward North Fork/Crystal Lake -Coldbrook Campground
Thomas Guide:
Dry season flow: Yes
Cell signal reception: Yes
Note: Restrooms, picnic areas and camping area downstream of sampling site. There are several tributaries to North Fork San Gabriel River in the campground. Sampling site is upstream of road crossings in the campground.
Safety tips: The site is within the campground.



Topographical map of Coldbrook Creek, a tributary to North Fork San Gabriel River

1.6 Arroyo Seco
Location: Arroyo Seco, City of Pasadena
Description
Site Name: Arroyo Seco
Coordinate: USGS gaging station 34.2220N 118.1778W
Watershed: LA River Watershed
Geology: Igneous/Sediment
Landcover: Forest
Sampling season: Wet/Dry
Previous study done: USGS, two USGS gaging stations
Direction: 210 – 2 Angeles Crest Hwy – FS road 2N69- Gould Mesa Campground –USGS gaging station
Thomas Guide:
Dry season flow: Yes
Cell signal reception: No
Note: The site is located within Angeles National Forest
Safety tips: It is not safe to drive on the FS road during the storm. Field crew should hike on the road to the site if there is need to change sampling bottles of automatic sampler. Poison oaks are abundant. Bears were seen before.


Brown Canyon
Falls
Canyon
Angeles Crest Highway
Vista del Valle Rd
Green Lake
LA CANADA
Angeles Crest Highway
Jet Propulsion
Laboratory
Fern Canyon
Oak Grove
Ranger Station
Oak Grove
County Park

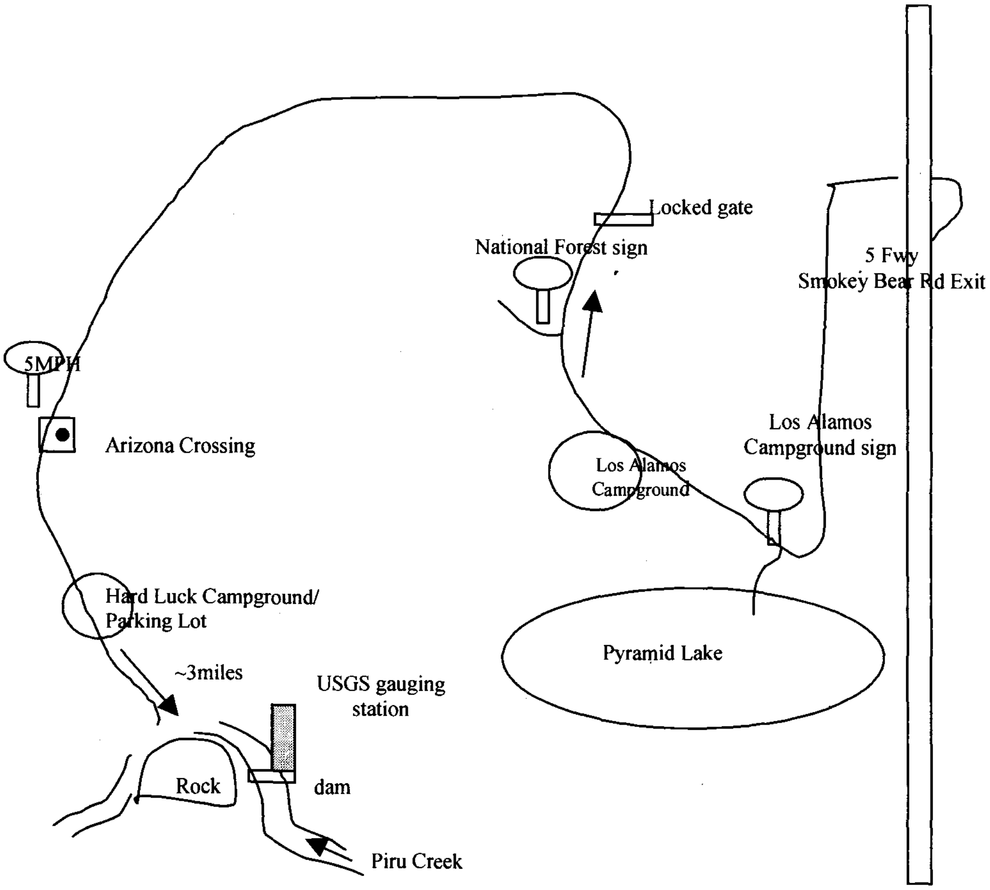


Arroyo Seco, Gould Mesa campground & USGS gaging station
34.2220°N, 118.1769°W (NAD27)

2 Site-specific SOPs for sampling sites in Ventura County

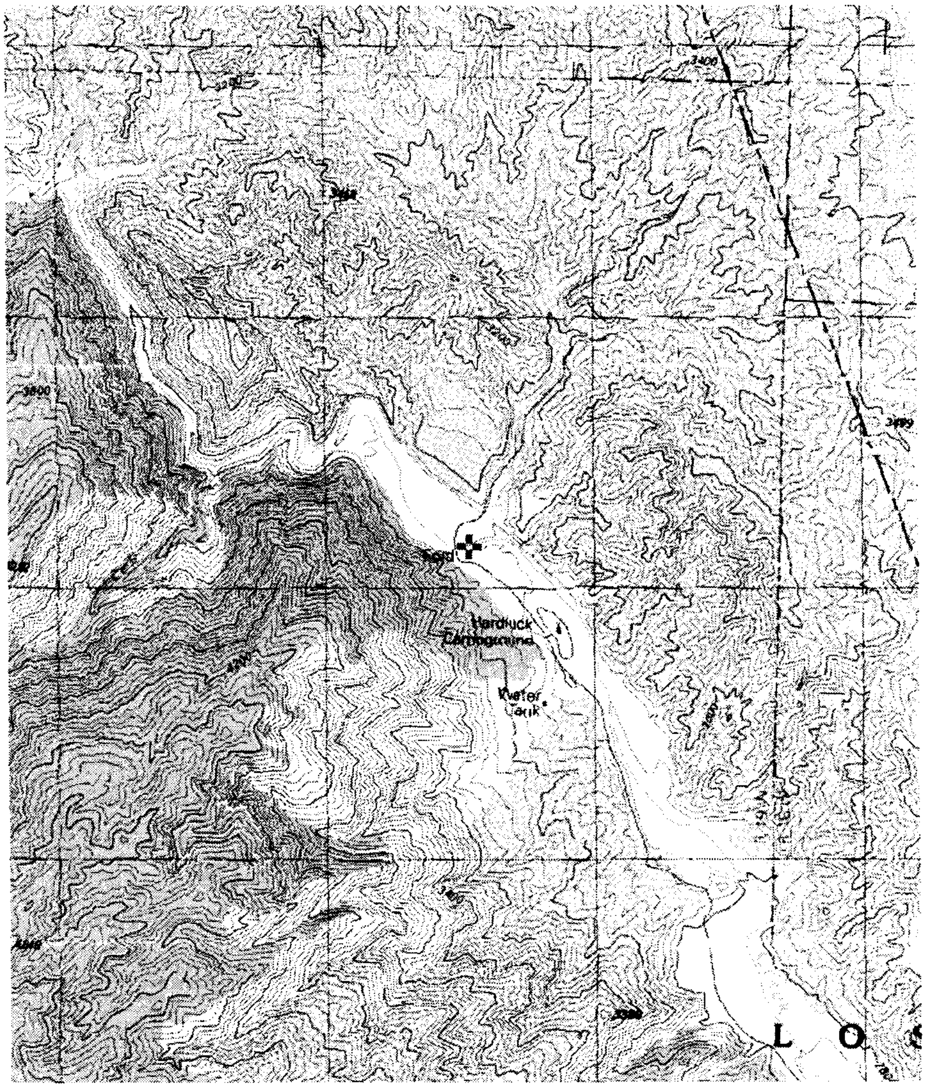
2.1 Piru Creek at Arizona Crossing (1^{st} road crossing)

Location: Piru Creek, Ventura
Description:
Site Name: Piru Creek Arizona Crossing
Coordinate: 34.69114N 118.85026W below Buck Creek
Watershed: Santa Clara River
Geology: Sedimentary
Landcover: Shrub
Sampling Season: Dry/Wet
Previous study done: DWR site/USGS gauging station upstream, Ventura County monitoring the site
Direction: 5 Fwy (N) - Smokey Bear Rd – Left onto Pyramid Lake Rd –Pass the abandoned lake check point and right turn to Los Alamos Campground –Pass Los Alamos Campground – Take the right fork at the National Forest sign - Locked gate – drive on dirt road - Pass 5MPH sigh – park cars before the Arizona Crossing
Thomas Guide: 367
Dry weather flow: Yes
Cell signal reception: Yes but weak
Note: USGS Gauging station and teleport are located upstream of the crossing. Accessibility might be an issue for stormwater sampling. The crossing is a habitat for Arroyo toad *Bufo californicus*. Extreme care is required not to disturb the toad population. No driving is allowed above the road crossing.
John Madden from the USFS would like to accompany us when we sample to ensure that impacts to sensitive species are being addressed.
The hardluck campground is open November through February.
Safety Tips: There are poison oaks, yucca plants, and snakes. Bear, deer and mountain lions have been observed in the area.



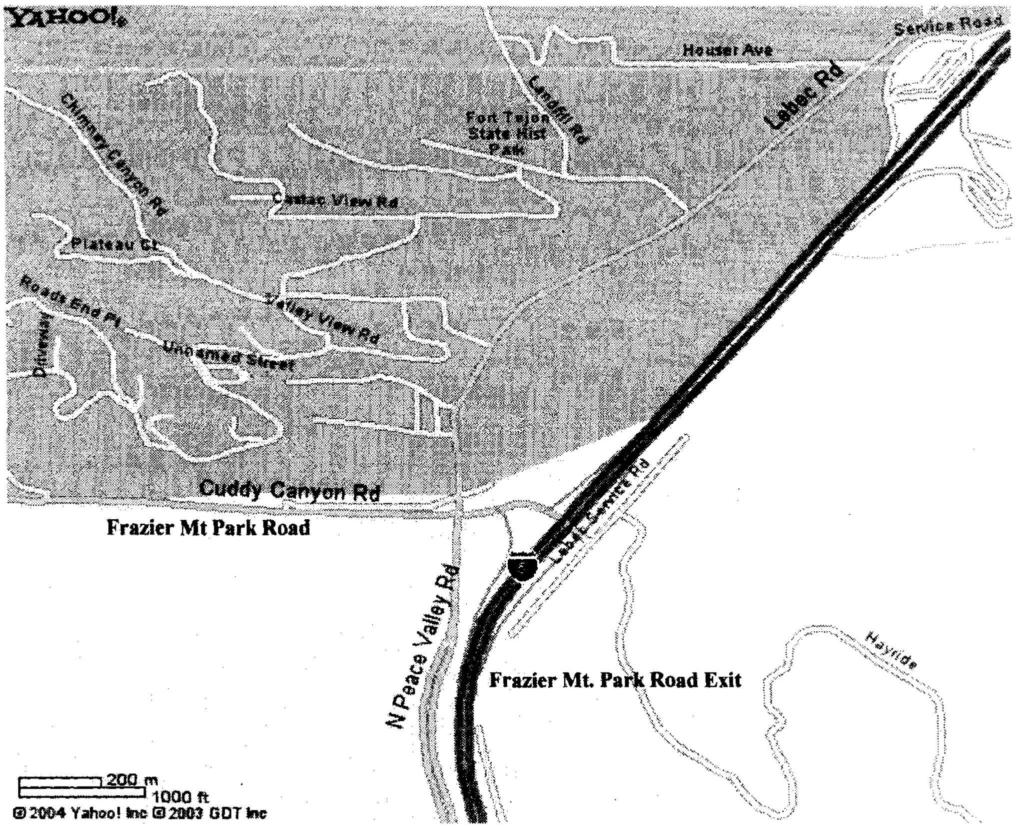
Piru Creek at Arizona crossing

Arizona Crossing on Piru Creek 34.6911°N, 118.8503°W (NAD27)



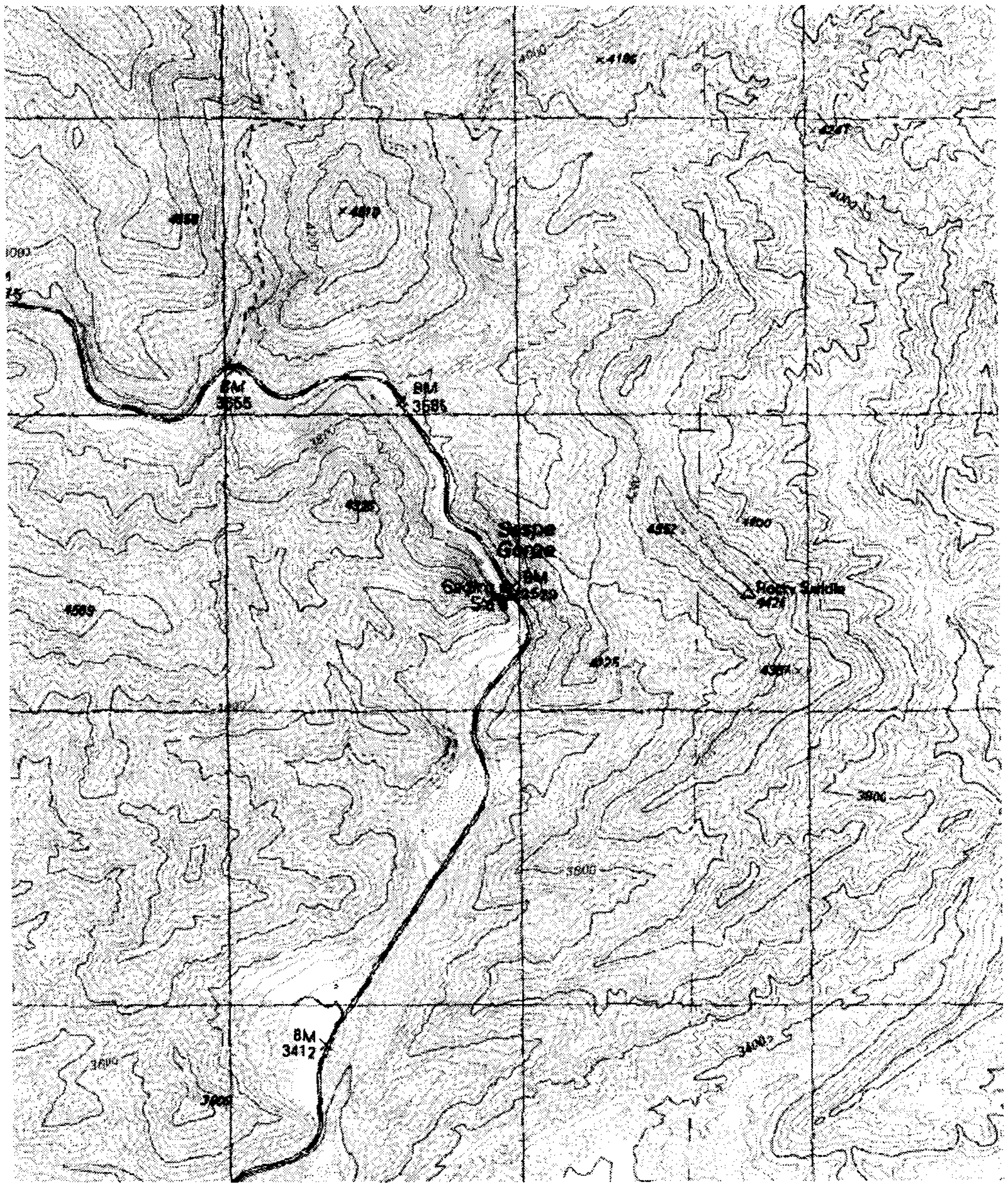
2.2 Sespe Creek

Location: Sespe Creek, Ventura
Description:
Site Name: Sespe Creek at Sespe Gorge
Coordinate: 34.57880N 119.25692W 2891FT
Watershed: Santa Clara River
Geology: Sedimentary
Landcover: Shrub
Access Contact Info: Los Padres National Forest
Sampling Season: Wet/Dry
Previous study done: USGS
Direction: 5(N) – Frazier exit – left turn onto Frazier Park Rd – Left onto Lockwood Valley Rd (~45-min drive)– Left on 33 W/S (Ojai/Ventura) – Pass Godwin Cyn, Munson Cyn,…-Parking space right side of the road after Derry Dale Creek in front of the antennae – Trail down to the site behind the antennae
Thomas Guide: 366
Dry season flow: Yes
Cell signal: No
Note: small fish, cattails (*Typha angustifolia*), and monkey flower (*Mimulus ringens*) were observed.
USGS gauging station is located in the stream.
Safety Tips: The trail down to the stream is steep and poison oaks are present along the trail. For winter sampling, 4x4 with chain is required due to snow. During storm, sampling crew should take 33 from 101 to reach the site instead of taking Lockwood Valley Road due to flooding.



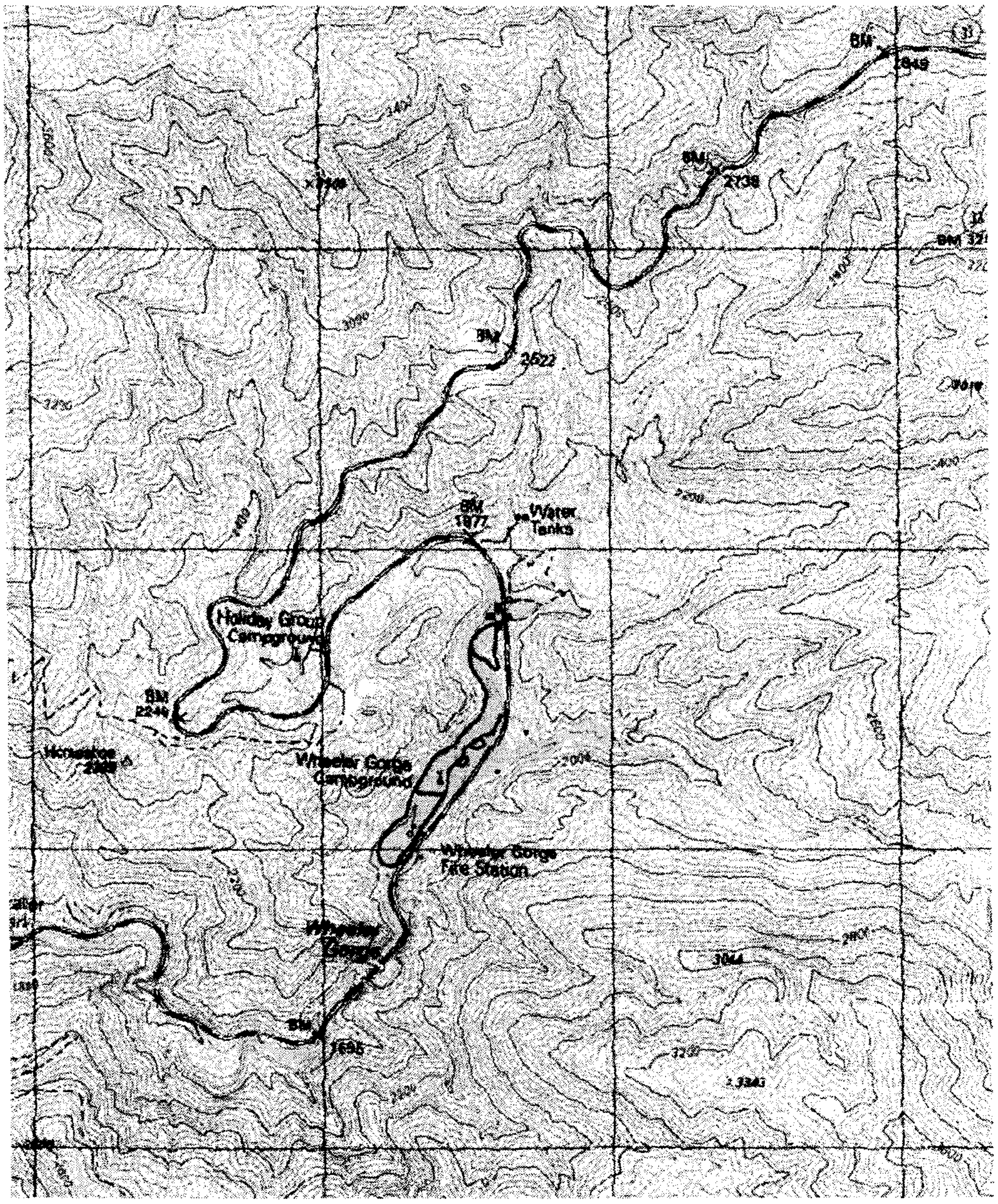
Frazier Mountain Park Road to Sespe Creek

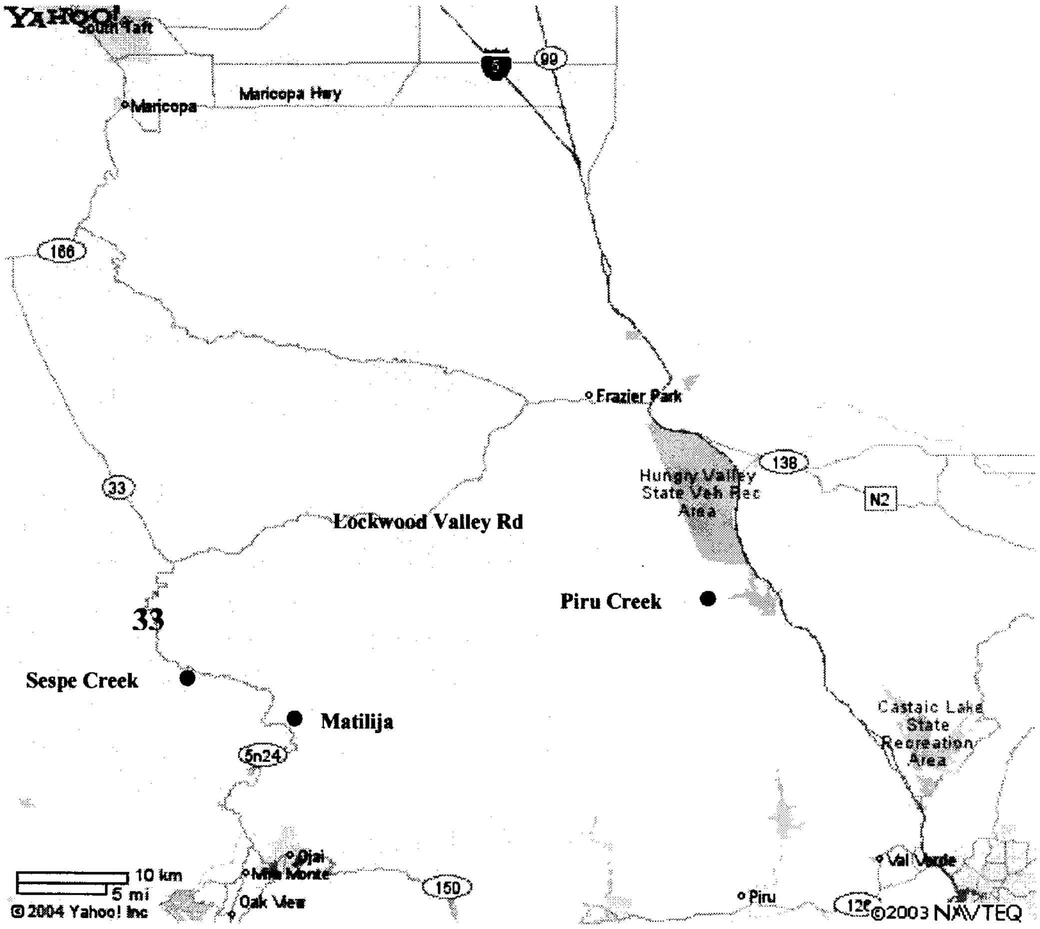
Sespe Creek at Sespe Gorge, USGS gaging station 34.5782°N, 119.2571°W (NAD27)



2.3 Bear Creek, a tributary to North Fork Matilija
Location: Bear Creek, Ventura
Description:
Site Name: Bear Creek, a North Fork Matilija
Coordinate: 34.51630N 119.27078W
Watershed: Ventura River
Geology: Sedimentary
Landcover: Forest
Access Contact Info: Los Padres National Forest Ventura County Watershed Protection District holds a permit.
Sampling Season: Dry/Wet
Previous study done: VCWPD gauging site is nearby.
Direction: 33 E between Sespe and Matilija – Bridge (North Fork Matilija Creek Bd. No.52-453 - right next to the Wheeler Gorge Natural Trail entrance/ near Campground – before pass the Forest Office
Thomas Guide: 366
Flow: Yes
Cell signal: No. Higher area between Matilija and Sespe receives cell signal
Note: VCWPD site is not suitable for sampling due to algae bloom.
The stream is clean but it is hard to rate. For stormwater sampling, pollutograph sampling from the bridge or next to the Wheeler Gorge trail may be feasible.
Safety Tips: Poison oaks all over on the trail down to the site

Bear Creek, Tributary to North Fork Matilija 34.5184°N, 119.2698°W

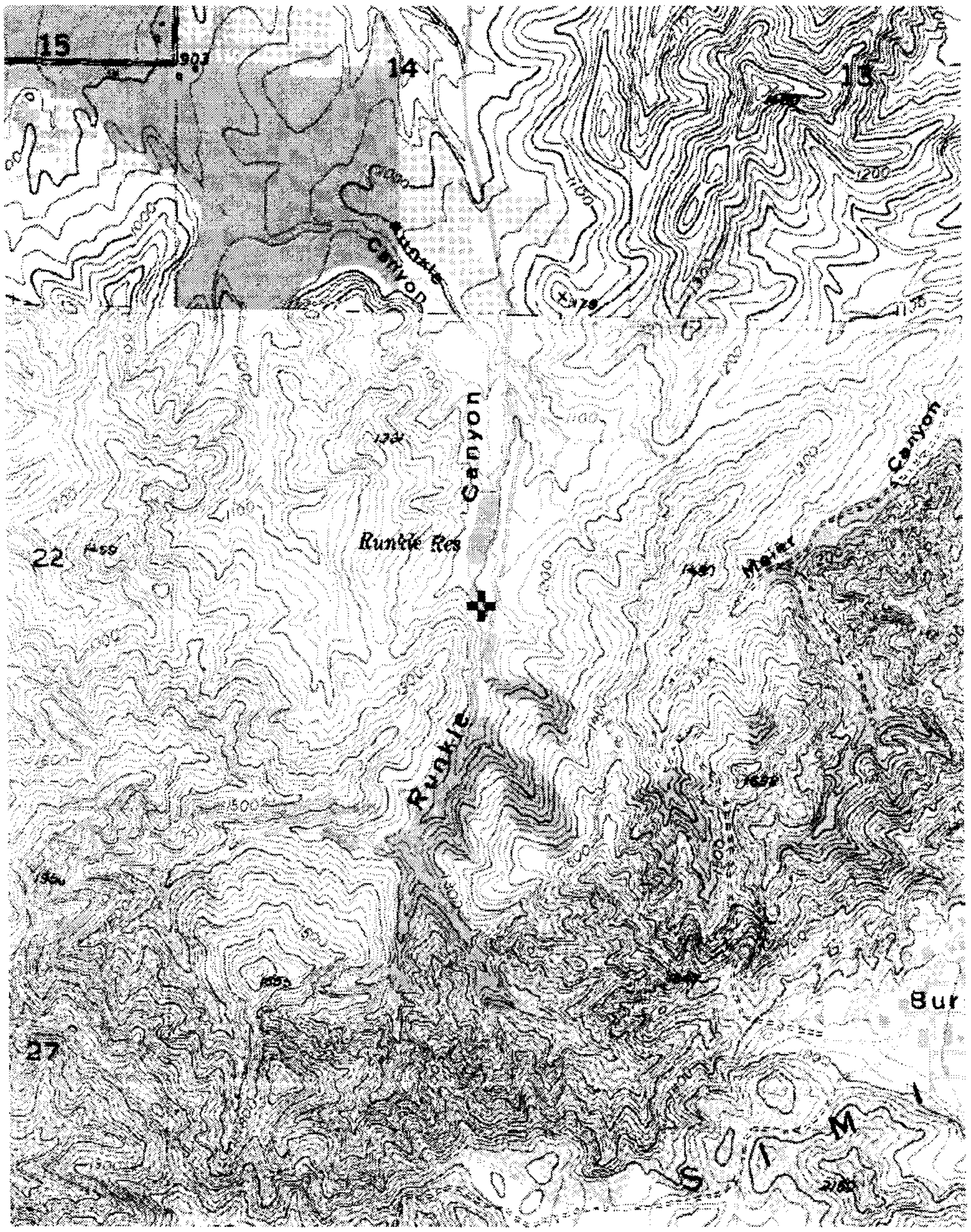




Piru Creek, Sespe Creek, and Matilija

2.4. Runkle Canyon

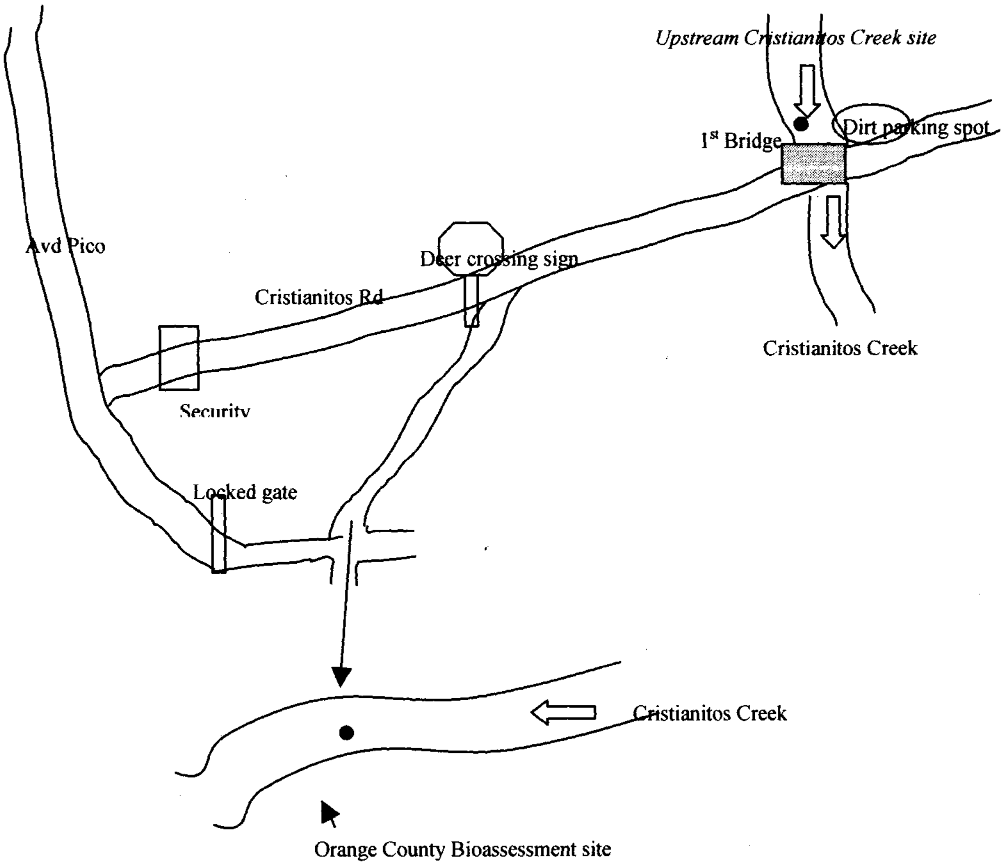
Runkle Canyon 34.2411°N, 118.7307°W (NAD27)



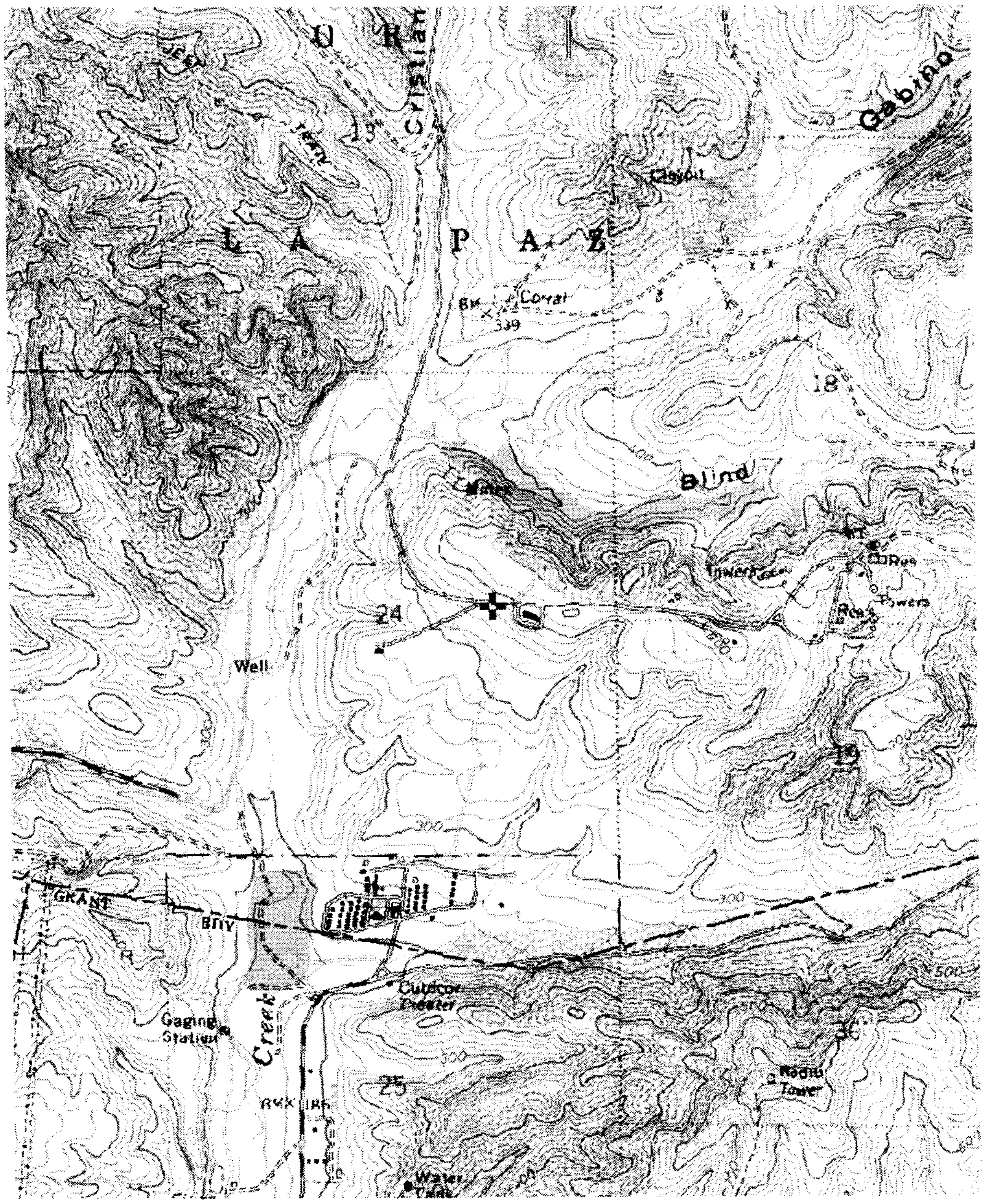
3. Site-Specific Standard Operating Procedures for sampling sites in Orange County

3.1 Cristianitos Creek

Description:
Site Name: Cristianitos Creek at Cristianitos Rd
Coordinate: 33.46206N 117.55995W 2890FT (1st bridge, upstream)
Watershed: San Mateo Watershed
Geology: Sedimentary
Landcover: Shrub/Grassland
Safety training – we were viewed on December 22, 2004.
Sampling Season: Dry/Wet
Previous study done: Orange County Bioassessment site
Direction: 5(S) – Avenida Pico Exit – Left on to Avd Pico – continue on the end of Avd Pico – left onto Cristianitos Creek Rd and security checkpoint
Thomas Guide: 973
Flow: No but in general it flows in the late spring.
Cell signal: Yes
Note: It has sandy streambed. Cattails are abundant. The stream is ratable. Teleport is located nearby.
Orange County Bioassessment site downstream near the locked gate at the end of Avd Pico - Gravel streambed - 33.45589N 117.57118W 2890FT - check for potential drainage from development nearby.
The sampling site is upstream at the 1st bridge.
Safety Tips: Mountain lions, bobcats, and coyotes are abundant in the area. Special caution for wild animals is required. Carry a bear spray in handy with your all the time.



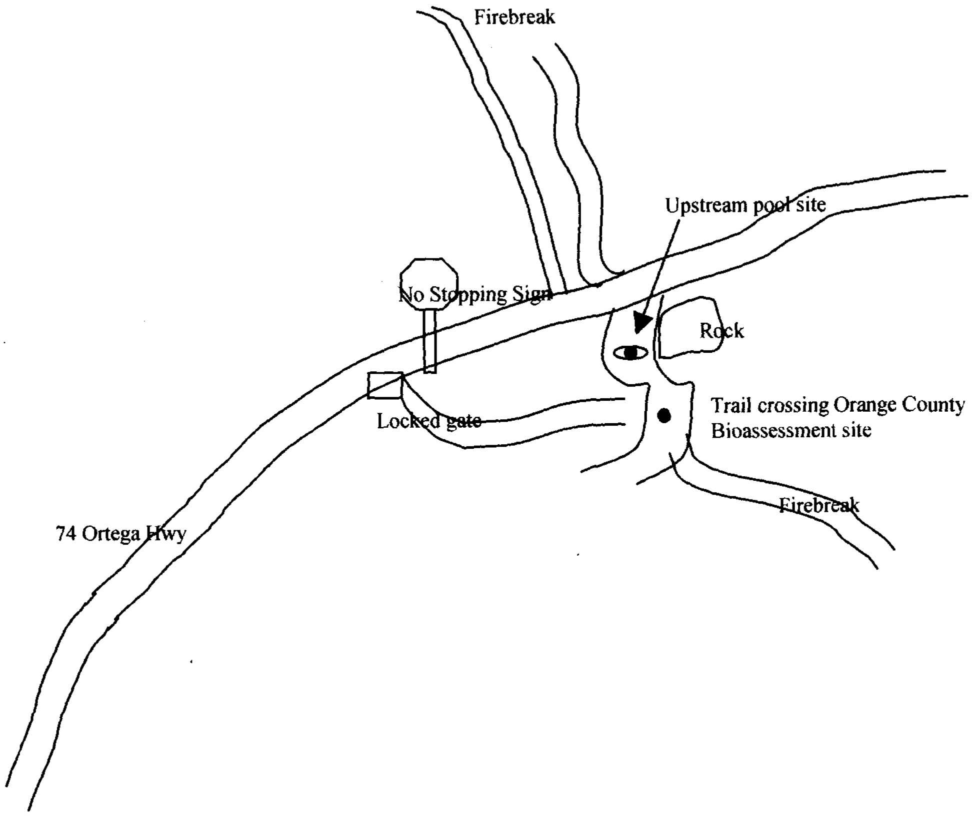
Cristianitos Creek at Cristianitos road



Topographical map of Cristianitos Creek

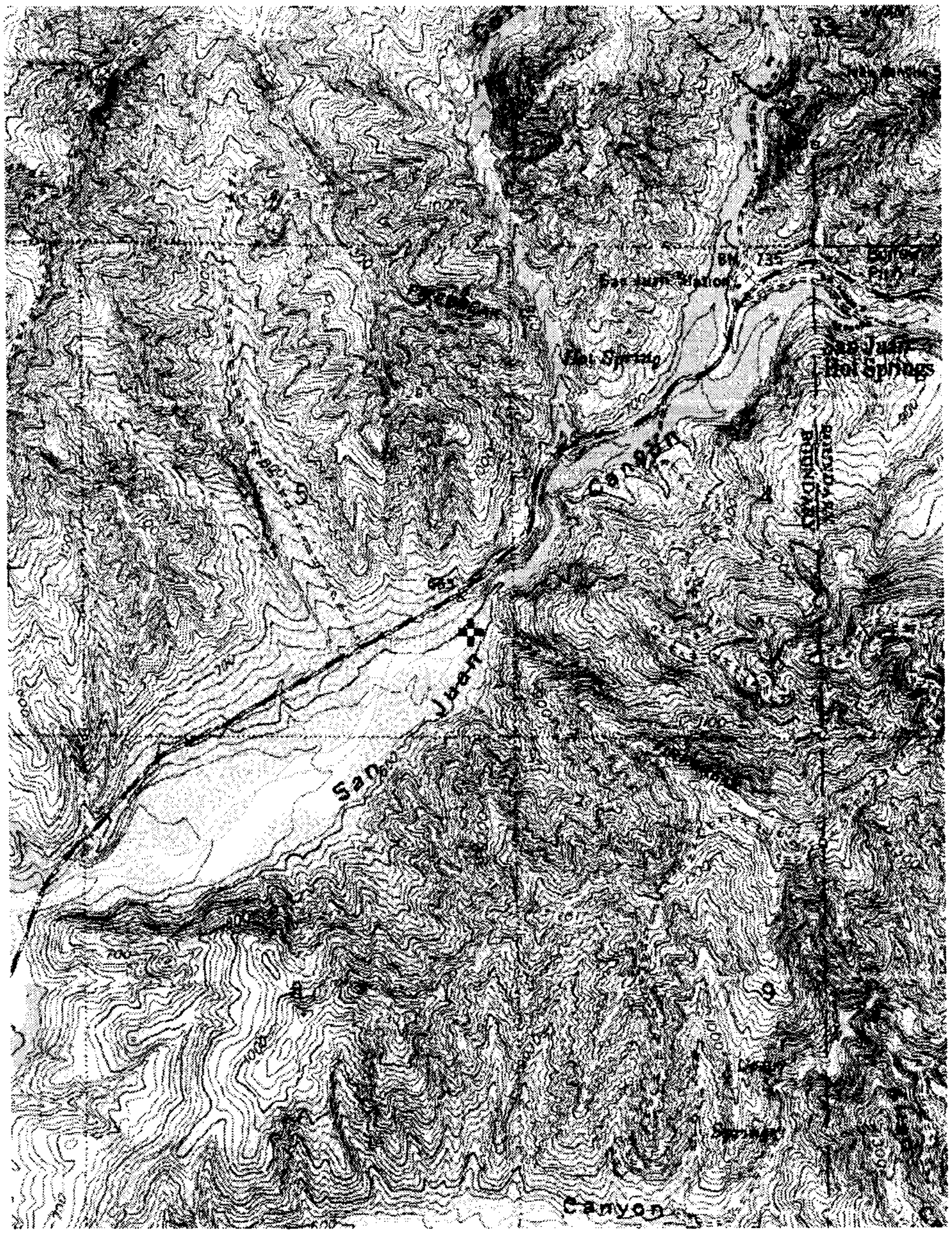
3.2 San Juan Creek at Cold Spring

Description:
Site Name: San Juan Creek at Cold Spring
Coordinate: 33.5819N 117.52333W 581FT
Watershed: San Juan
Geology: Sedimentary/igneous
Landcover: Shrub
Access Contact Info: Orange County, Casper Wildlife Park
Sampling Season: Dry season only
Previous study done: Orange County
Direction: 5 Fwy – 74 Ortega Hwy – locked gate on the right just before fire break – drive on dirt road down to the stream
Thomas Guide: 924
Description: Dry season flow: no but there was a pool 10 feet upstream.
Cell signal reception: Yes
Note: The County of Orange bioassessment sampling is conducted on Oct and April. It has gravel streambed. Ratability is an issue. During storm, it is hard to access the site. There is water upstream (33.58274N 117.52251W 577FT).
Safety Tips: The steep unpaved trail requires 4x4 to drive on. It is a mountain lion habitat. On 74 hwy, speed limit strongly enforced by cops!



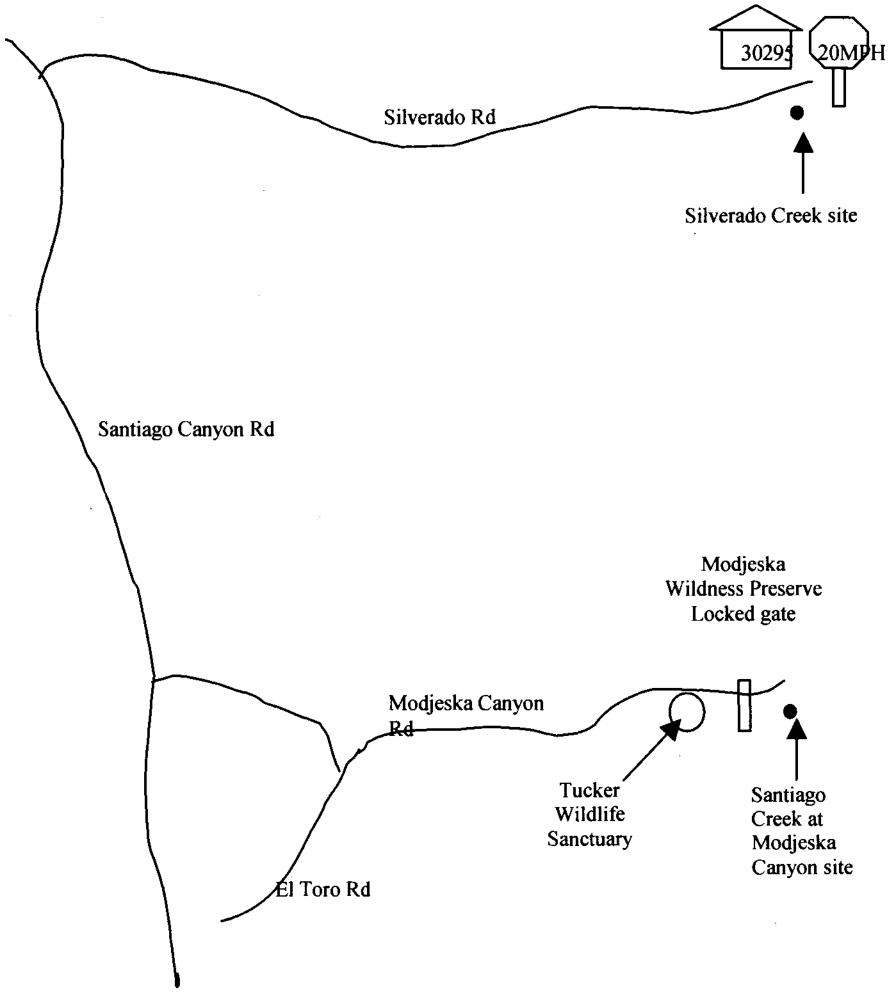
San Juan Creek at Cold Spring

San Juan Creek at Hot Spring 33.5819°N, 117.5233°W (NAD27)

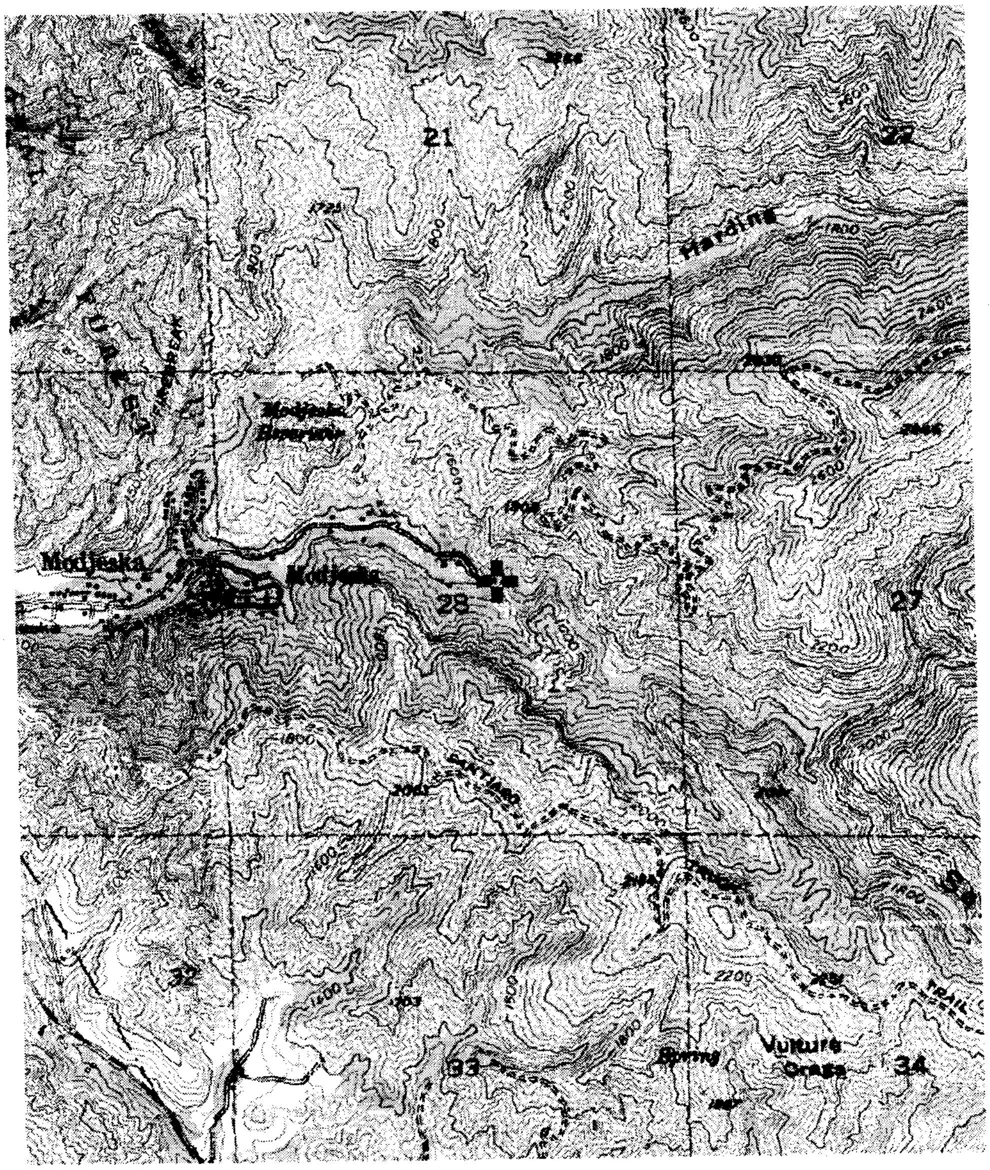


3.3 Santiago Creek at Modjeska Canyon

Description:
Site Name: Santiago Creek at Modjeska Canyon
Coordinate: 33.70855N 117.61392W 597FT
Watershed: Santa Ana River Watershed
Geology: Sediment
Landcover: Forest/shrub
Sampling Season: dry/wet
Previous study done: Orange County Bioassessment Reference site
Direction: Ortega Hwy (W) from the San Juan Creek site – right turn onto Antonio Pk Rd – Pass 241 – Left on Santa Margarita – Right on El Toro Rd – Left on Modjeska Canyon Rd – Pass by Turker Wildlife Sanctuary on the right – Mojeska Wilderness Preserve (locked gate)
Thomas Guide: 832
Flow: dry
Cell signal: no
Note: Good for stormwater sampling, good to install an autosampler, toilet, picnic table
Safety Tips: Mountain lion habitat



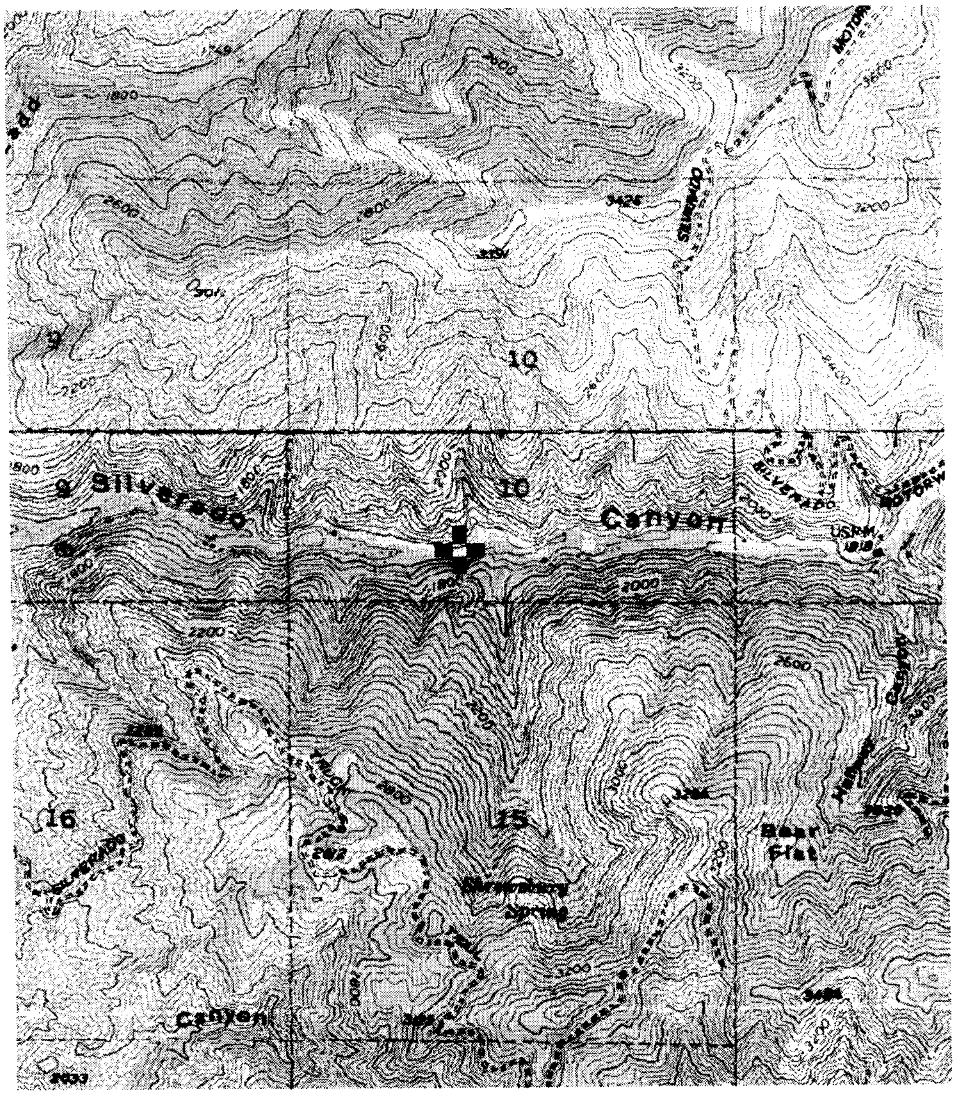
Santiago Creek and Silverado Creek



Topographical map of Santiago Creek at Modjeska Canyon

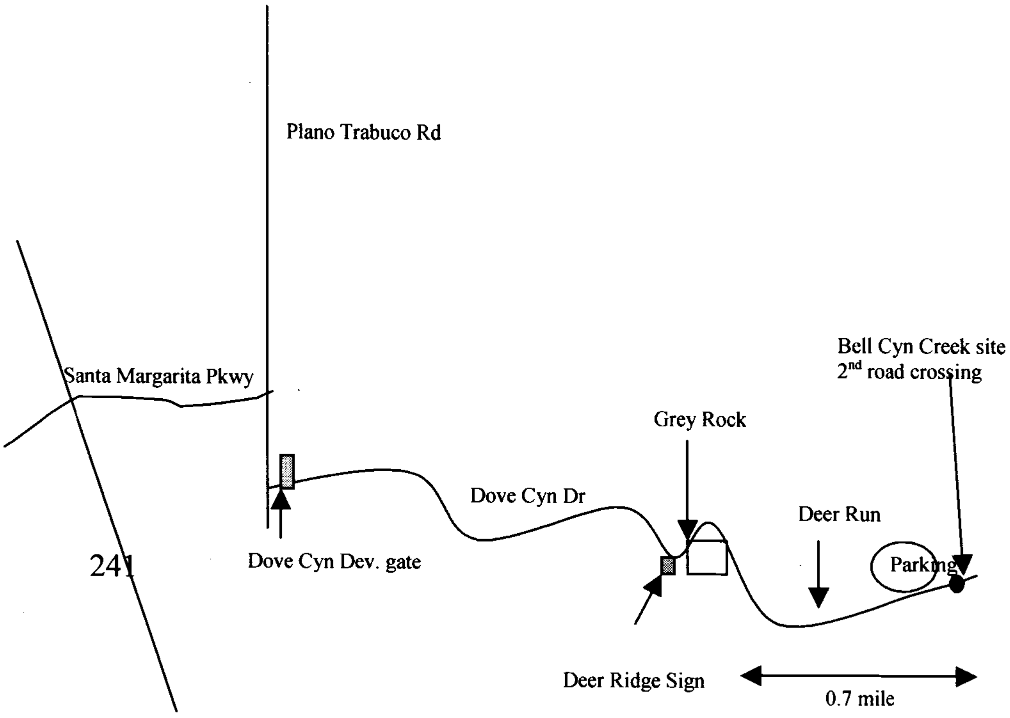
3.4 Silverado Creek

Description:
Site Name: Silverado Creek
Coordinate: 33.74612N 117.59974W 667FT
Watershed: Santa Ana River Watershed
Geology: Sediment
Landcover: Shrub
Access Contact Info: Orange County
Sampling Season: Dry/Wet
Previous study done: Orange County Bioassessment Reference site
Direction: Santiago Canyon Rd – 30295 Silverado Rd
Thomas Guide: 832
Flow: Yes
Cell signal: Yes
Note: Park in front of the 20MPH sign, not good access down to the Creek especially for storm season. Alternative site for wet weather
Safety Tips: Mountain lions habitat

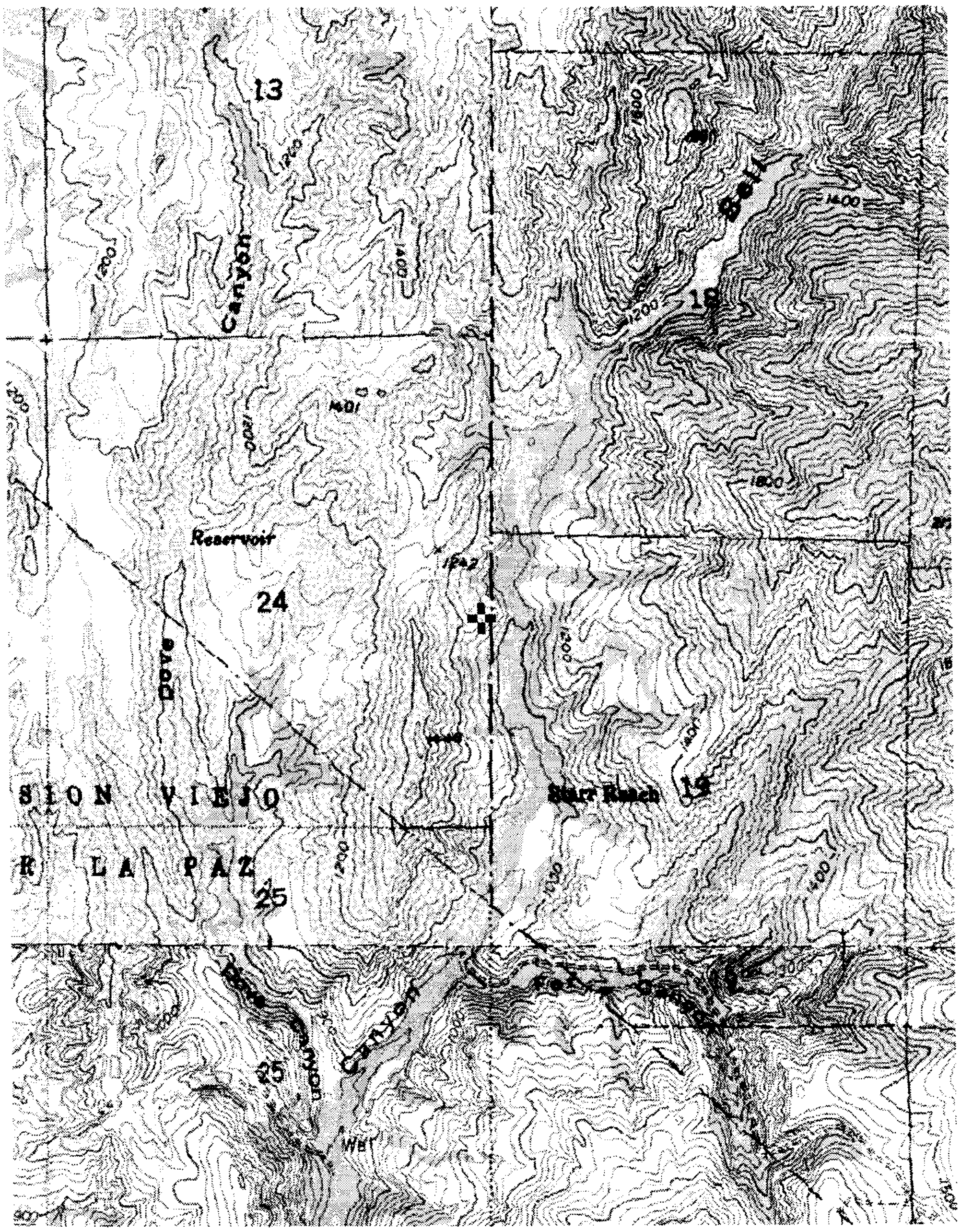


Silverado Creek

3.5 Bell Canyon Creek
Description:
Site Name: Bell Canyon Creek
Coordinate: 33.63467N 117.55573W 3300FT
Watershed: San Juan
Geology: Sediment
Landcover: Shrub
Access Contact Info: Audubon California Starr Ranch Sanctuary
www.starrranch.org
Ask Starr Ranch to make a call to inform the security guy that we are coming for sampling
Sampling Season: Wet/Dry
Previous study done: Orange County Bioassessment site
Direction: 5(S) or 241(Toll road) – Alicia Pkwy exit- Left onto Alicia – Right on Santa Margarita Pkwy- Right onto Plano Trabuco Rd – Left onto Dove Canyon Rd – Dove Canyon Development gate – continue on Dove Canyon Rd – Left onto Grey Rock – Right onto Deer Run – paved trail to the Sanctuary - 0.7 mile – 2nd road crossing
Thomas Guide: 893 F3
Flow: Dry
Cell signal: No
Note: Ratable, easy to access, monkey flowers, dried algae on rocks of stream bed
Safety Tips: Bob cats, mountain lions, snakes, and poison oaks



Bell Canyon Creek



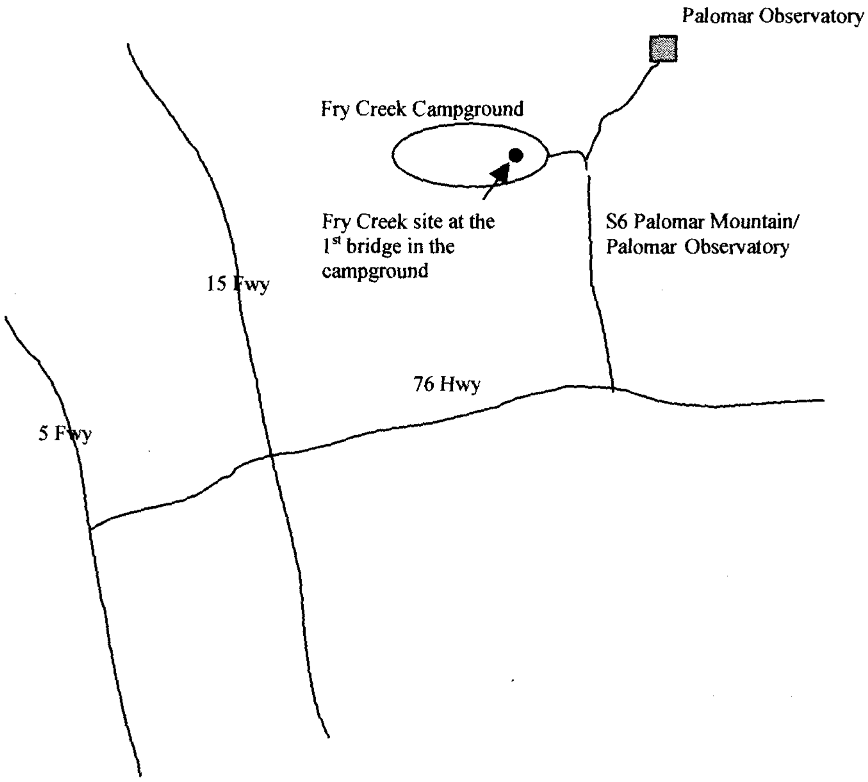
Topographical map of Bell Creek

4 Site-Specific Standard Operating Procedures for sampling sites in San Diego County

4.1 Fry Creek at Fry Creek Campground

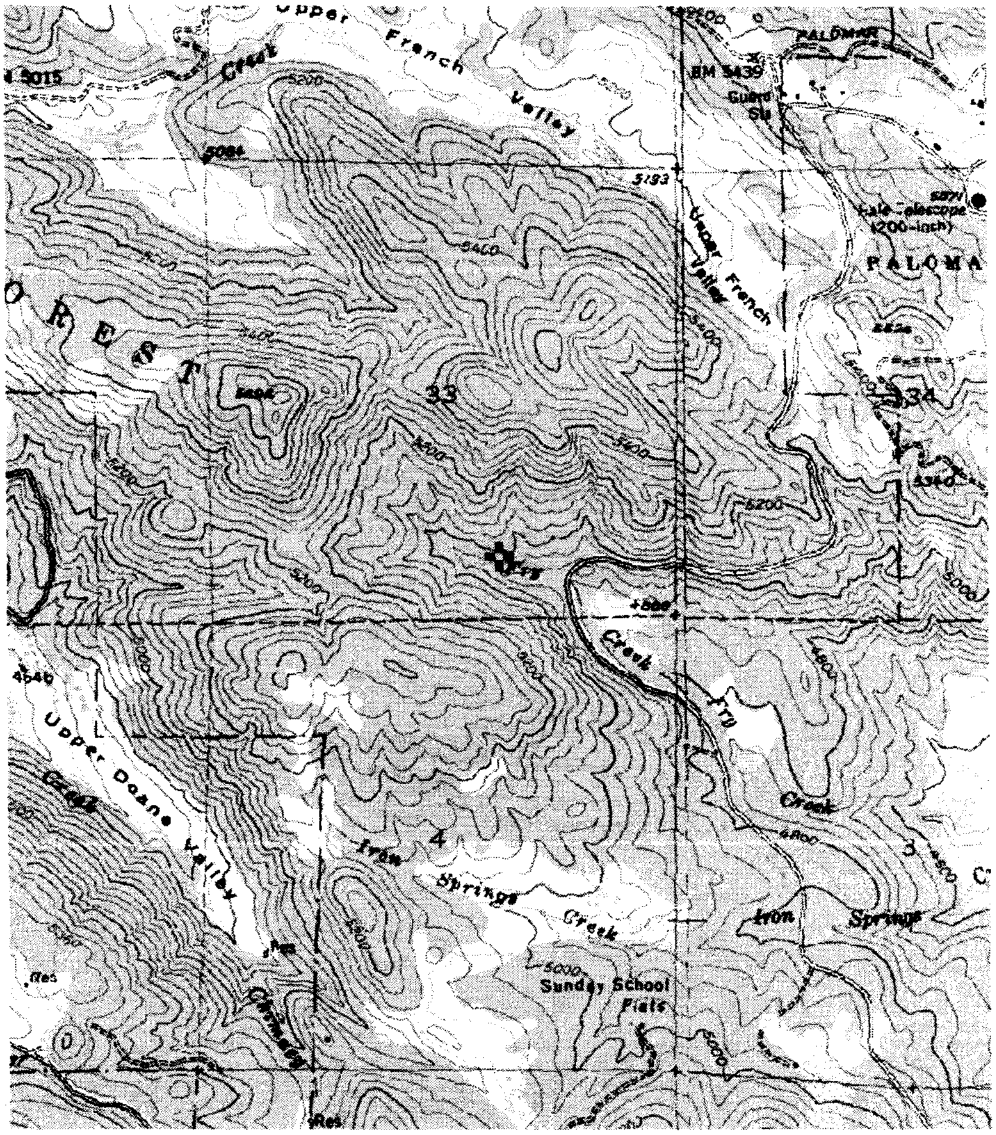
Description

Site Name: Fry Creek
Coordinate: 33.3421N 116.88216W
Watershed: San Luis Rey
Geology: Igneous
Landcover: Forest
Access Contact Info: Cleveland National Forest Palomar Ranger District Jeff Wells District Wildlife Biologist Cleveland National Forest
Palomar Ranger District 1634 Black Canyon Rd. Ramona, CA 92065
(760) 788-0250 ext. 3342 (760) 788-6130 fax
Sampling Season: Dry/Wet
Previous study done:
Direction: 76 Hwy (Pala Rd) – S6 (N) Palomar Mountain/Palomar Observatory – Fry Creek Campground
Thomas Guide: 409 G6
Flow: no but it flows until early summer
Cell signal: No
Note: monkey flowers, cattails
Stormwater sampling should be fully automated due to possible snow during a storm even.
Good access, campground is closed, locked gate – 0253 for a combo lock (contact Jeff), ratable, a bridge
Safety Tips: many dead trees in the campground (it's why the campground is closed), be careful with in case dead trees falls down over you. Be careful with poison oaks.


Palomar Observatory
Fry Creek Campground
Fry Creek site at the 1st bridge in the campground
S6 Palomar Mountain/ Palomar Observatory
15 Fwy
76 Hwy
5 Fwy

Fry Creek

Fry Creek at Fry Creek Campground 33.3445°N, 116.8819°W (NAD27)



4.3. Tenaja Canyon

Description

Site Name: Tenaja Creek
Coordinate: 33.5508N 117.3833W
Watershed: San Mateo
Geology: Igneous
Landcover: Shrub
Access Contact Info: Cleveland National Forest Palomar Ranger District Mary Thomas District Wildlife Biologist Cleveland National Forest
Sampling Season: Dry/Wet
Previous study done:
Direction: 15 FWY(S) –Clinton Keith Rd exit – Right on Clinton – Right on Tenaja Rd – Right on Cleveland Forest Rd – Truck trail -1st road crossing
Thomas Guide:
Flow: no but it flows until early summer
Cell signal: No
Note:

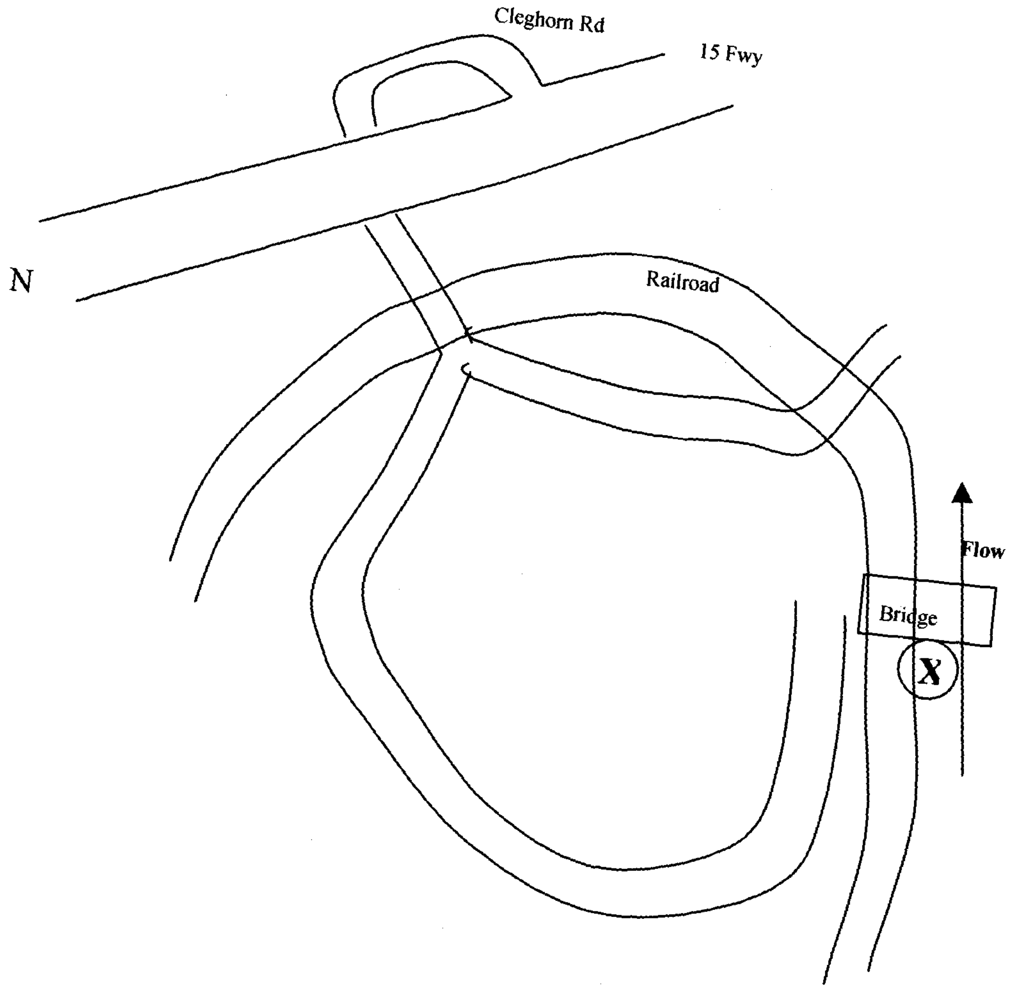
Stormwater sampling should be fully automated due to possible flooding during a storm even. Good access, open to public in the summer

5. Site-Specific Standard Operating Procedures for sampling sites in San Bernardino County

5.1 Cajon Creek

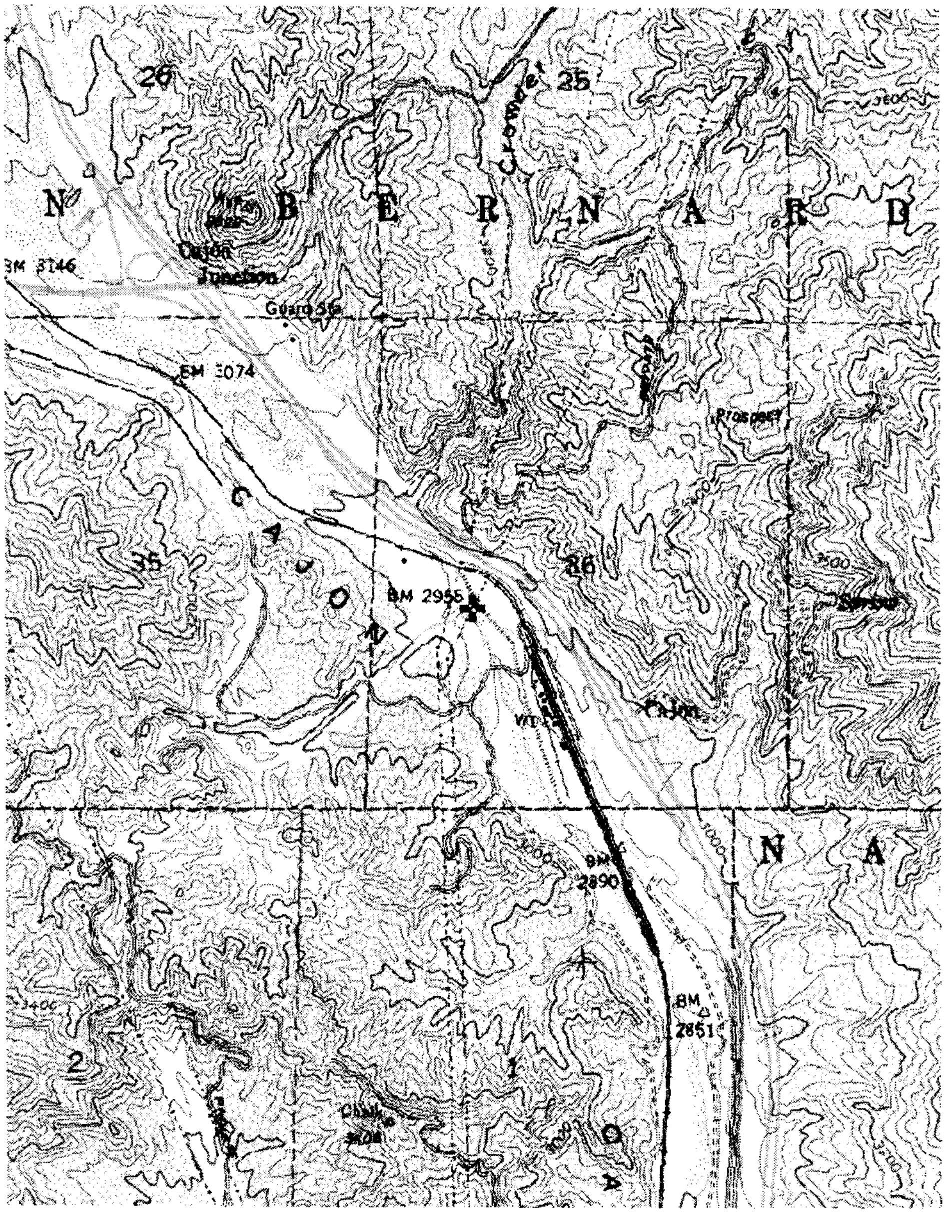
Description:

Site Name: Cajon Creek
Coordinate: 34.30226N 117.46262W
Watershed: Santa Ana River
Geology: Igneous
Landcover: Shrub
Sampling Season: Dry
Previous study done: No
Direction: 15(N) – Cleghorn Fire Road exit (Before Silverwood Lake) – left turn – cross rail Rd – right fork of dirt road - site is upstream of 1st bridge crossing
Thomas Guide: 544
Flow: Yes
Cell signal: No
Note: Near a railroad
Safety Tips: The section of 15 between 60 and 215 is under construction and extremely congested. Use 91 and 215 to get to the site.



Cajon Creek

Cajon 34.3023°N, 117.4626°W (NAD27)



5.2 Seven Oaks Dam

Description:

Site Name: Santa Ana River above Seven Oaks Dam

Coordinate: W34.145966 N117.061433

Watershed: Santa Ana River

Geology: Igenous

Landcover: Shrub/forest

Sampling Season: Dry/Wet

Previous study done: San Bernardino County Bio-monitoring site

Direction: 215(S) – 30(E) –5th street exit – left turn (North) – pass through Boulder Ave –continue on 5th street becomes Green Spot – Left on Santa Ana Cyn Rd – drive up on the dam zigzag pass – behind the right side of dam there is a road down to the stream above dam – pass a yellow bridge – power house – continue on the dirt Rd – a pond with a channel

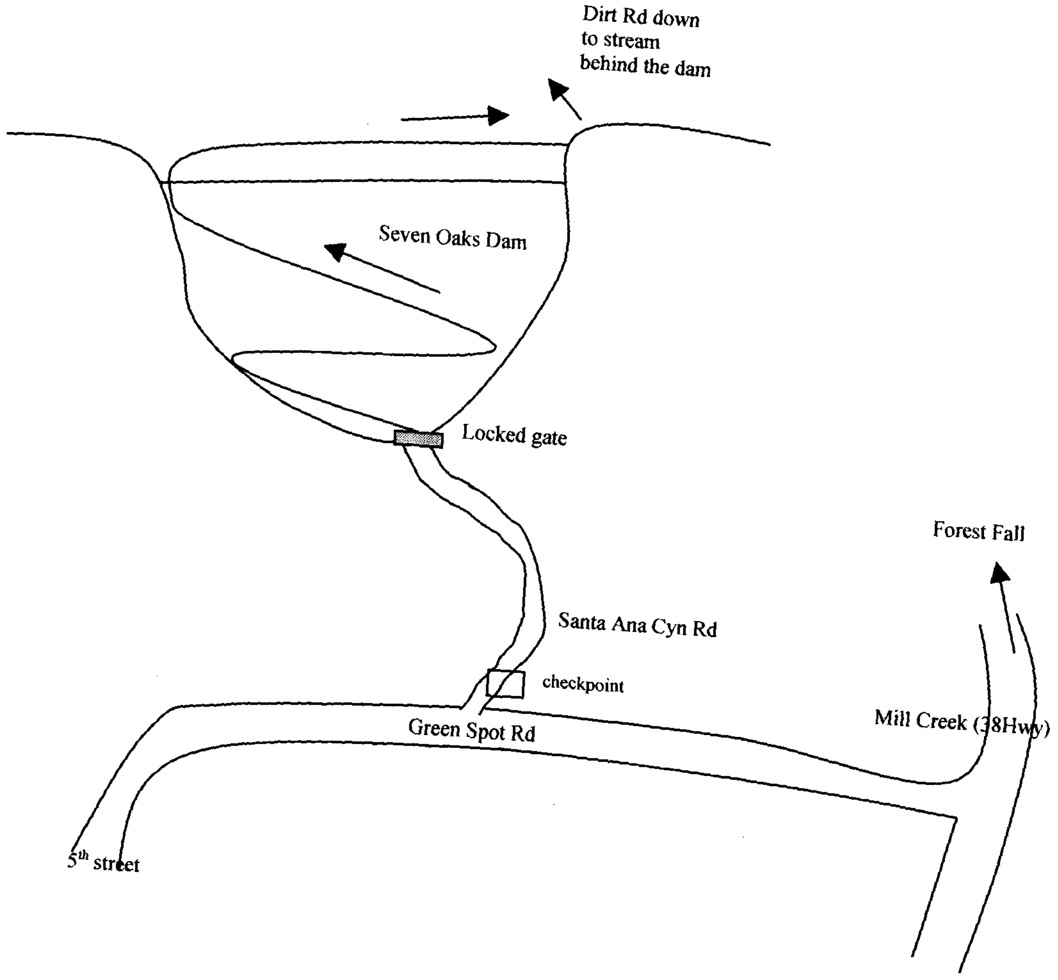
Thomas Guide: 389

Flow: Yes

Cell signal: No

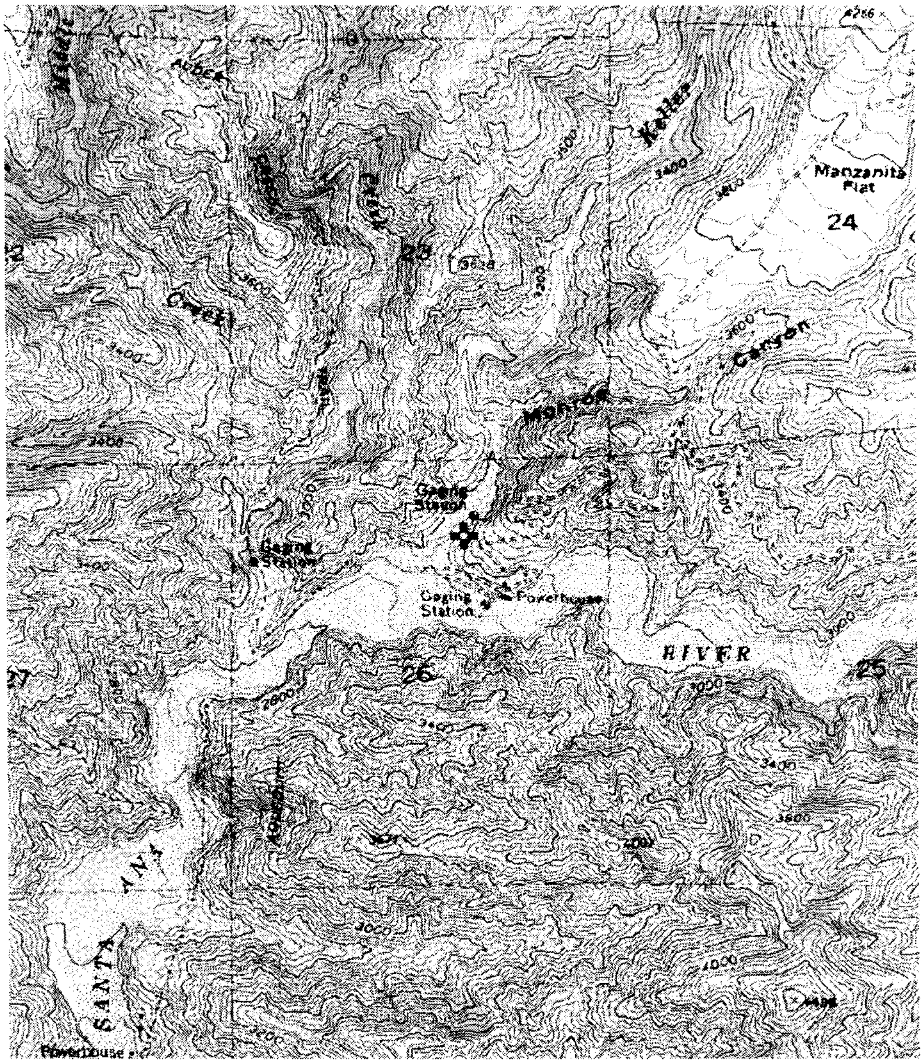
Note: Gate keys required, upstream of the pond is a sampling site, dry/wet

Safety Tips: Poison oaks are abundant. 4x4 drive is required for both dry and wet seasons.



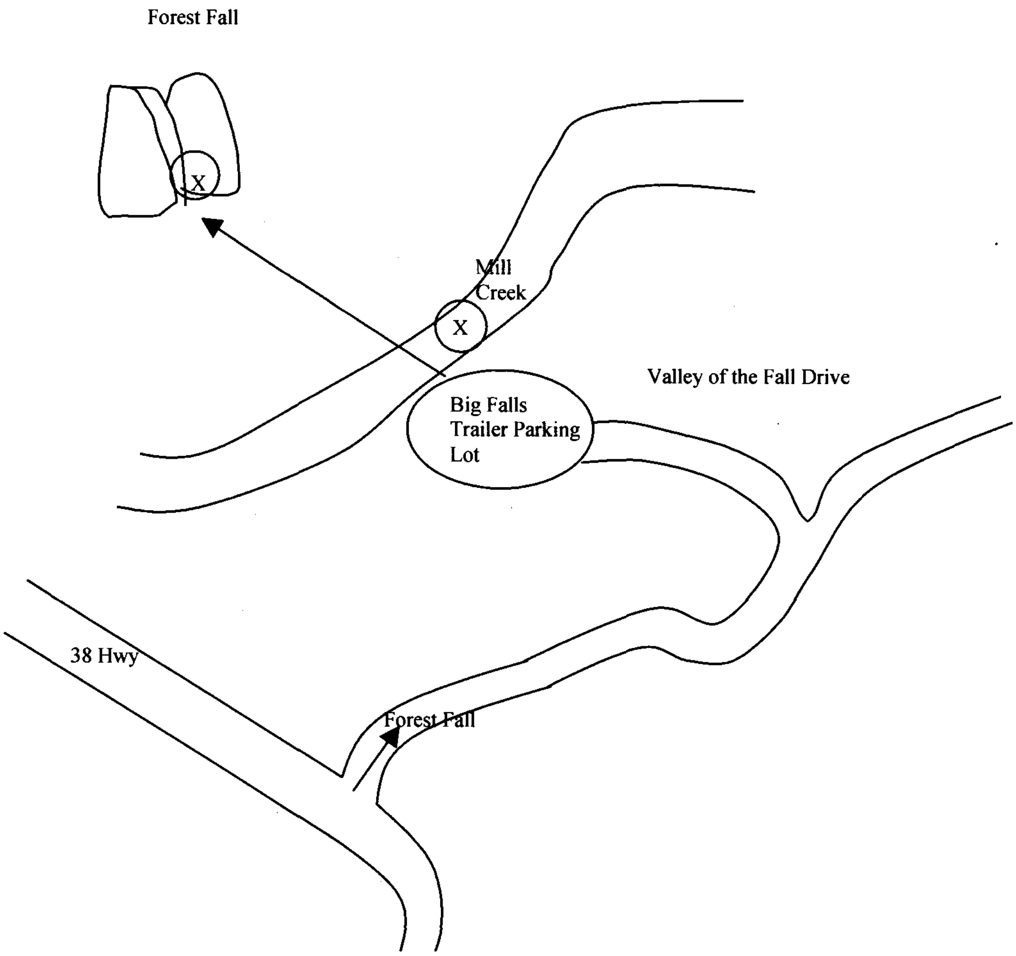
Santa Ana River above Seven Oaks Dam

Santa Ana River at Seven Oaks Dam 34.1477°N, 117.0591°W (NAD27



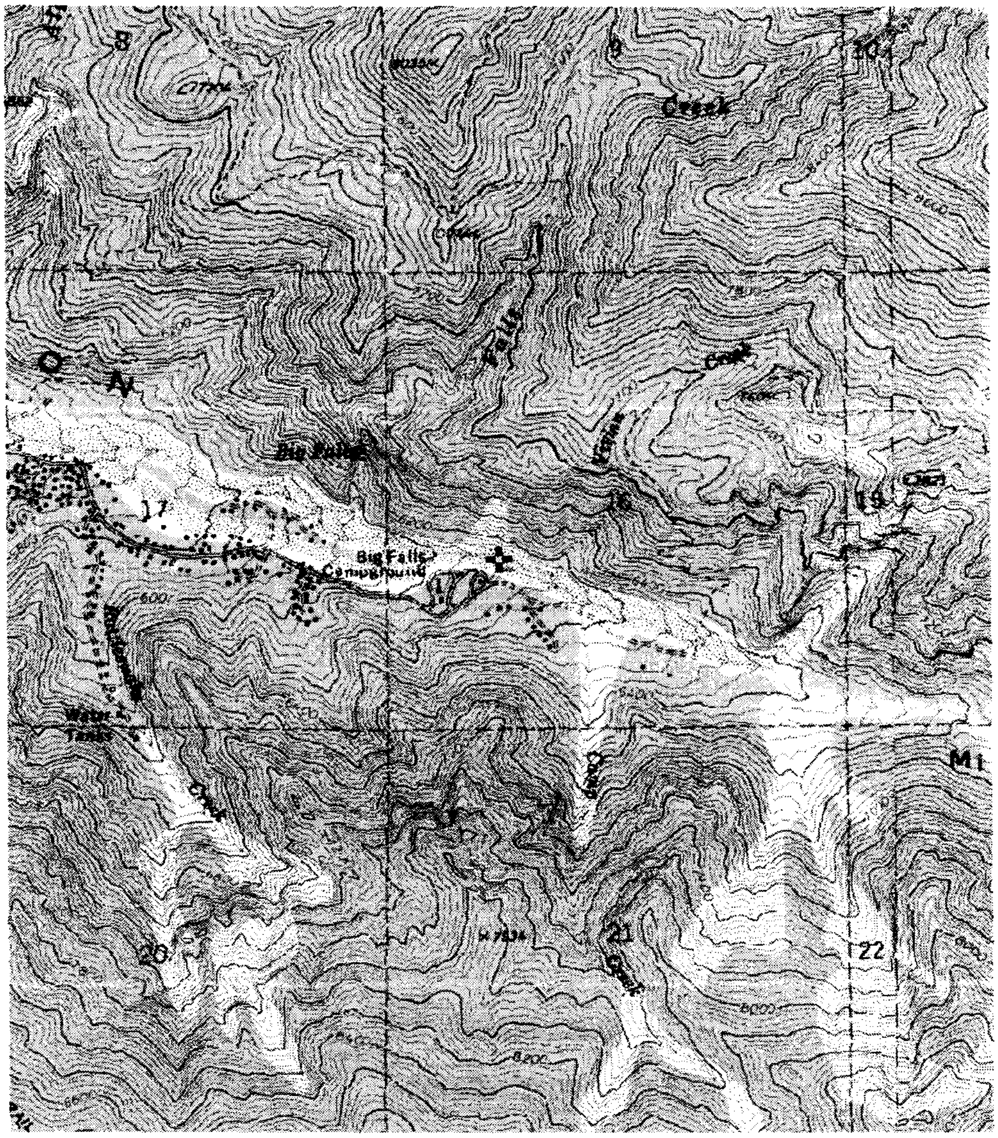
5.3 Mill Creek and Forest Fall

Description:
Site Name: Mill Creek / Forest Fall
Coordinate: 34.087572N 116.88860 (Forest Fall) 34.08214N 116.88968W (Mill Creek)
Watershed: Santa Ana River
Geology: Igneous
Landcover: Shrub/Forest
Sampling Season: Dry/Wet
Previous study done:
Direction: I-215 N -> I-10 E toward REDLANDS
Take the UNIVERSITY STREET exit. 0.2 miles
Turn RIGHT onto N UNIVERSITY ST. <0.1 miles
Turn LEFT onto E CITRUS AVE. 2.5 miles
Turn LEFT onto CRAFTON AVE. 1.0 miles
Turn RIGHT onto MENTONE BLVD/CA-38.
Continue to follow CA-38. 10.4 miles
Turn SLIGHT RIGHT onto VALLEY OF THE FALLS DR. 1.5 miles
Turn RIGHT to stay on VALLEY OF THE FALLS DR. 1.0 miles
End at Forest Falls CA
Big Falls Trailer Parking Lot
Thomas Guide: 4950
Flow: Yes
Cell signal: covered
Note:
Safety Tips: Avalanche and mud slide prone area



Forest Fall and Mill Creek

Mill Creek 34.0821°N, 116.8897°W (NAD27)



APPENDIX IV, Results of ANOVA

1 Results of analysis of variance on dry weather level of metals, nutrients, and solids

1. Effect of geology type

1. Copper

```
Normality Test:        Failed  (P = <0.001)
        Test execution ended by user request, ANOVA on Ranks begun
                Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: DryChem in Notebook
Group N        Missing        Median        25%     75%
Igneous        25      0      0.438  0.2    0.763
Sedimentary    26      0      0.758  0.625  0.9
H = 7.370 with 1 degrees of freedom.  (P = 0.007)

        The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically significant
difference  (P = 0.007)
        To isolate the group or groups that differ from the others use a multiple
comparison procedure.
        All Pairwise Multiple Comparison Procedures (Dunn's Method) :

        Comparison    Diff of Ranks  Q        P<0.05
        Sedimentary vs. Igneous      11.298 2.713   Yes
        Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

2. Iron

```
Normality Test:        Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks

Data source: DryChem in Notebook
One way ANOVA
Group N        Missing        Median        25%     75%
Igneous        25      0      50.75  24.563 128.375
```

```
Sedimentary  26      0        113.5  86.175 196.75
H = 10.020 with 1 degrees of freedom.  (P = 0.002)
```

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.002)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

```
Comparison    Diff of Ranks  Q        P<0.05
Sedimentary vs. Igneous      13.182 3.165   Yes
```

Note: The multiple comparisons on ranks do not include an adjustment for ties.

3. Nickel

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem in Notebook
Group  N        Missing         Median         25%     75%
Igneous         25      0        0.115  0.05    0.314
Sedimentary  26      0        0.579  0.4     0.8
H = 19.451 with 1 degrees of freedom.  (P = <0.001)
```

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

```
Comparison    Diff of Ranks  Q        P<0.05
Sedimentary vs. Igneous      18.36   4.409   Yes
```

Note: The multiple comparisons on ranks do not include an adjustment for ties.

4. Selenium

```
Normality Test:          Failed  (P = <0.001)
```

```
Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem in Notebook
Group  N       Missing         Median        25%    75%
Igneous        25      0       0.257  0.16   0.465
Sedimentary    26      0       1.059  0.702  1.85
H = 19.699 with 1 degrees of freedom.  (P = <0.001)

        The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically significant
difference  (P = <0.001)                To isolate the group or groups that differ
from the others use a multiple comparison procedure.

        All Pairwise Multiple Comparison Procedures (Dunn's Method) :

        Comparison    Diff of Ranks  Q        P<0.05
        Sedimentary vs. Igneous      18.478 4.437   Yes
        Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

5. Orthophosphate

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem in Notebook
Group  N       Missing         Median        25%    75%
Igneous        24      0       0.00375       0.00375         0.0235
Sedimentary    25      0       0.0225 0.00834        0.0545
H = 5.815 with 1 degrees of freedom.  (P = 0.016)

        The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically significant
difference  (P = 0.016)
        To isolate the group or groups that differ from the others use a multiple
comparison procedure.
        All Pairwise Multiple Comparison Procedures (Dunn's Method) :
        Comparison    Diff of Ranks  Q        P<0.05
        Sedimentary vs. Igneous      9.555   2.34     Yes
```

Note: The multiple comparisons on ranks do not include an adjustment for ties.

6. Total dissolved solids

```
Normality Test:        Failed  (P = 0.001)
Test execution ended by user request, ANOVA on Ranks begun

Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem in Notebook
Group  N       Missing        Median        25%    75%
Igneous        25      0      185     123.583         280.75
Sedimentary    25      0      525     406.5   793.5
H = 28.991 with 1 degrees of freedom.  (P = <0.001)
```

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)

To isolate the group or groups that differ from the others use a multiple comparison procedure.

All Pairwise Multiple Comparison Procedures (Dunn's Method) :

```
Comparison    Diff of Ranks  Q        P<0.05
Sedimentary vs. Igneous        22.2     5.384   Yes
```

Note: The multiple comparisons on ranks do not include an adjustment for ties.

2. Natural catchments vs. developed catchments

2.1. Concentration

1. Arsenic

```
Normality Test:       Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.828)
Group Name   N        Missing          Mean   Std Dev          SEM
NL      51       0        -0.177  0.550   0.0770
Dev     4        0        0.887   0.794   0.397
Source of Variation    DF      SS       MS       F        P
Between Groups         1       4.201    4.201    13.094 <0.001
Residual         53       17.003  0.321
Total    54       21.204
```

```
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 0.944
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 2
Comparison    Diff of Means p        q        P        P<0.050
Dev vs. NL    1.064   2         5.117   <0.001 Yes
```

2. Cadmium

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group  N        Missing            Median           25%              75%
NL       51       0          -1.000  -1.301  -0.718
Dev     12       0          0.901   -0.264  2.533
H = 23.940 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Dev vs. NL    28.515 4.848   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

3. Copper

```
Normality Test:          Passed (P = 0.032)
Equal Variance Test:  Failed  (P = 0.003)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group  N        Missing            Median           25%              75%
NL       51       0          -0.171  -0.438  -0.0879
Dev     11       0          2.254   1.425   2.470
H = 26.731 with 1 degrees of freedom.  (P = <0.001)
```

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
Dev vs. NL 31.000 5.169 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

4. Iron
Normality Test: Passed (P > 0.200)
Equal Variance Test: Passed (P = 0.042)
Group Name N Missing Mean Std Dev SEM
NL 51 0 1.924 0.426 0.0597
Dev 8 0 3.059 0.214 0.0758
Source of Variation DF SS MS F P
Between Groups 1 8.909 8.909 54.013 <0.001
Residual 57 9.401 0.165
Total 58 18.310
The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 20
Comparison Diff of Means p q P P<0.050
Dev vs. NL 1.135 2 10.394 <0.001 Yes

5. Lead
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group N Missing Median 25% 75%
NL 51 0 -1.602 -1.602 -1.149
Dev 10 0 1.528 0.854 1.741
H = 25.048 with 1 degrees of freedom. (P = <0.001)

```
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Dev vs. NL    30.500 4.968   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

6. Nickel

```
Normality Test:          Passed (P = 0.017)
Equal Variance Test:  Passed (P = 0.062)
Group Name   N           Missing           Mean   Std Dev           SEM
NL       51        0           -0.524  0.481   0.0673
Dev     8          0           1.965   0.658   0.233
Source of Variation     DF        SS         MS          F          P
Between Groups          1          42.859 42.859 167.540             <0.001
Residual            57         14.581 0.256
Total   58         57.441
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 31
Comparison    Diff of Means p          q          P          P<0.050
Dev vs. NL    2.490   2          18.305 <0.001 Yes
```

7. Selenium

```
Normality Test:          Passed (P = 0.146)
Equal Variance Test:  Passed (P = 0.103)
Group Name   N           Missing           Mean   Std Dev           SEM
NL       51        0           -0.233  0.577   0.0808
Dev     8          0           0.536   0.252   0.0892
Source of Variation     DF        SS         MS          F          P
Between Groups          1          4.097    4.097    13.654 <0.001
Residual            57         17.101 0.300
Total   58         21.198
```

The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).
Power of performed test with alpha = 0.050: 0.954
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 37
Comparison Diff of Means p q P P<0.050
Dev vs. NL 0.770 2 5.226 <0.001 Yes

8. Zinc
Normality Test: Passed (P = 0.077)
Equal Variance Test: Passed (P = 0.448)
Group Name N Missing Mean Std Dev SEM
NL 51 0 -0.249 0.599 0.0839
Dev 11 0 2.528 0.753 0.227
Source of Variation DF SS MS F P
Between Groups 1 69.780 69.780 177.189 <0.001
Residual 60 23.629 0.394
Total 61 93.409
The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 43
Comparison Diff of Means p q P P<0.050
Dev vs. NL 2.777 2 18.825 <0.001 Yes

9. Ammonia
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group N Missing Median 25% 75%
NL 51 0 -2.301 -2.301 -2.138
Dev 10 0 0.219 0.201 0.539
H = 27.159 with 1 degrees of freedom. (P = <0.001)
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)

```
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Dev vs. NL    30.500 4.968   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

10. Nitrate+Nitrite

```
Normality Test:        Failed  (P = 0.003)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group  N      Missing          Median          25%              75%
NL     50     0         -1.350  -2.000  -0.854
Dev    8      0         0.458   0.243   0.649
H = 19.550 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Dev vs. NL    28.130 4.375   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

11. Total Phosphorus

```
Normality Test:        Passed (P = 0.183)
Equal Variance Test:   Passed (P = 0.028)
Group Name  N        Missing          Mean   Std Dev          SEM
NL      51      0        -1.321  0.386   0.0540
Dev     8       0        -0.419  0.122   0.0431
Source of Variation    DF       SS       MS       F        P
Between Groups         1        5.619    5.619    42.432 <0.001
Residual         57    7.548    0.132
Total   58      13.166
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
```

```
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 61
Comparison   Diff of Means p      q       P       P<0.050
Dev vs. NL   0.901   2         9.212  <0.001 Yes
```

12. Total suspended solids

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group  N       Missing          Median            25%                75%
NL      51      0         -0.323  -0.602  0.354
Dev     8       0          1.257   1.156  1.414
H = 17.504 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Dev vs. NL    26.608 4.074   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

2.2. Flux

1. Arsenic

```
Normality Test:          Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.111)
Group Name   N        Missing           Mean   Std Dev          SEM
NL       51       0        -0.485  0.700   0.0980
Dev      4        0         0.482   1.460   0.730
Source of Variation    DF       SS        MS        F         P
Between Groups         1        3.464    3.464   5.946   0.018
Residual          53        30.876  0.583
Total   54       34.340
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.018).
Power of performed test with alpha = 0.050: 0.585
```

The power of the performed test (0.585) is below the desired power of 0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 2
Comparison Diff of Means p q P P<0.050
Dev vs. NL 0.966 2 3.448 0.018 Yes

2. Cadmium
   Normality Test: Passed (P > 0.200)
   Equal Variance Test: Failed (P = 0.001)
   Test execution ended by user request, ANOVA on Ranks begun
   Kruskal-Wallis One Way Analysis of Variance on Ranks
   Data source: DryChem Dev Vs NL in Notebook
   Group N Missing Median 25% 75%
   NL 51 0 -1.252 -1.728 -0.571
   Dev 12 0 1.154 -0.907 1.886
   H = 11.060 with 1 degrees of freedom. (P = <0.001)
   The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
   To isolate the group or groups that differ from the others use a multiple comparison procedure.
   All Pairwise Multiple Comparison Procedures (Dunn's Method) :
   Comparison Diff of Ranks Q P<0.05
   Dev vs. NL 19.559 3.326 Yes
   Note: The multiple comparisons on ranks do not include an adjustment for ties.

3. Copper
   Normality Test: Passed (P = 0.024)
   Equal Variance Test: Passed (P = 0.027)
   Group Name N Missing Mean Std Dev SEM
   NL 51 0 -0.560 0.702 0.0983
   Dev 11 0 1.157 1.014 0.306
   Source of Variation DF SS MS F P
   Between Groups 1 26.672 26.672 45.844 <0.001
   Residual 60 34.908 0.582
   Total 61 61.581

```
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 14
Comparison   Diff of Means p      q       P       P<0.050
Dev vs. NL   1.717  2        9.575  <0.001 Yes
```

4. Iron

```
Normality Test:         Passed (P = 0.050)
Equal Variance Test:  Passed (P = 0.459)
Group Name  N        Missing          Mean   Std Dev          SEM
NL      51      0        1.617  0.814  0.114
Dev     8       0        2.721  0.802  0.284
Source of Variation     DF       SS       MS       F        P
Between Groups          1        8.440  8.440  12.786 <0.001
Residual          57        37.628 0.660
Total   58      46.068
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 0.939
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 20
Comparison   Diff of Means p      q       P       P<0.050
Dev vs. NL   1.105  2        5.057  <0.001 Yes
```

5. Lead

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.255)
Group Name  N        Missing          Mean   Std Dev          SEM
NL      51      0        -1.645 0.810  0.113
Dev     10      0        0.611  0.991  0.313
Source of Variation     DF       SS       MS       F        P
Between Groups          1        42.554 42.554 60.302 <0.001
Residual          59        41.635 0.706
Total   60      84.190
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
```

```
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 25
Comparison   Diff of Means p        q         P        P<0.050
Dev vs. NL   2.256  2         10.982 <0.001 Yes
```

6. Nickel

```
Normality Test:         Failed  (P = 0.003)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: DryChem Dev Vs NL in Notebook
Group  N       Missing          Median           25%              75%
NL     51      0          -0.745  -1.139  -0.364
Dev    8       0          1.696   0.792   2.409
H = 18.449 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison   Diff of Ranks  Q        P<0.05
Dev vs. NL   28.054 4.295   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

7. Selenium

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:    Passed (P = 0.884)
Group Name  N           Missing           Mean  Std Dev          SEM
NL      51     0        -0.541  0.846   0.119
Dev     8      0        0.199   0.778   0.275
Source of Variation     DF      SS      MS      F       P
Between Groups          1       3.781   3.781   5.381   0.024
Residual         57     40.050  0.703
Total   58       43.831
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.024).
Power of performed test with alpha = 0.050: 0.531
```

```
The power of the performed test (0.531) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 37
Comparison    Diff of Means p        q        P        P<0.050
Dev vs. NL    0.739   2        3.281   0.024   Yes
```

8. Zinc

```
Normality Test:          Passed (P = 0.190)
Equal Variance Test:  Passed (P = 0.696)
Group Name  N          Missing            Mean   Std Dev          SEM
NL       51        0          -0.556  0.918   0.129
Dev     11        0          1.562   0.932   0.281
Source of Variation    DF       SS         MS        F          P
Between Groups          1          40.626 40.626 47.974 <0.001
Residual           60         50.810 0.847
Total   61        91.437
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 43
Comparison    Diff of Means p        q        P        P<0.050
Dev vs. NL    2.119   2        9.795   <0.001 Yes
```

9. Ammonia

```
Normality Test:          Passed (P = 0.025)
Equal Variance Test:  Passed (P = 0.640)
Group Name  N          Missing            Mean   Std Dev          SEM
NL       51        0          -2.524  0.744   0.104
Dev     10        0          -0.0476             0.806   0.255
Source of Variation    DF       SS         MS        F          P
Between Groups          1          51.276 51.276 90.229 <0.001
Residual           59         33.529 0.568
Total   60        84.805
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 1.000
```

```
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: DataSet
Comparison    Diff of Means p        q        P        P<0.050
Dev vs. NL    2.476   2         13.433 <0.001 Yes
```

10. Nitrate+Nitrite

```
Normality Test:         Passed (P = 0.013)
Equal Variance Test:  Passed (P = 0.777)
Group Name  N           Missing           Mean  Std Dev          SEM
NL      50      0           -1.610  0.959  0.136
Dev     8       0           0.216  0.956  0.338
Source of Variation    DF       SS        MS        F         P
Between Groups         1          22.995 22.995 25.003 <0.001
Residual            56         51.503 0.920
Total   57       74.498
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 0.999
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 55
Comparison    Diff of Means p        q        P        P<0.050
Dev vs. NL    1.826   2         7.072   <0.001 Yes
```

11. Total Phosphorus

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.648)
Group Name  N           Missing           Mean  Std Dev          SEM
NL      51      0           -1.628  0.764  0.107
Dev     8       0           -0.757  0.776  0.274
Source of Variation    DF       SS        MS        F         P
Between Groups         1          5.248   5.248   8.953   0.004
Residual            57         33.410 0.586
Total   58       38.658
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.004).
Power of performed test with alpha = 0.050: 0.806
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 61
Comparison    Diff of Means p        q        P        P<0.050
```

```
Dev vs. NL     0.871  2        4.232  0.004  Yes
```

12. Total suspended solids

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:    Passed (P = 0.407)
Group Name   N          Missing         Mean   Std Dev        SEM
NL      51      0       -0.377  0.984   0.138
Dev     8       0       0.927   0.654   0.231
Source of Variation     DF      SS      MS      F       P
Between Groups          1       11.762  11.762  13.029  <0.001
Residual        57      51.458  0.903
Total   58      63.221
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = <0.001).
Power of performed test with alpha = 0.050: 0.943
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 67
Comparison    Diff of Means p      q       P       P<0.050
Dev vs. NL    1.304   2       5.105   <0.001  Yes
```

2 Results of analysis of variance on wet weather level of metals, nutrients, and solids

1. Effect of geology type

1. Copper

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:    Passed (P = 0.544)
Group Name   N          Missing         Mean   Std Dev        SEM
Igneous         12      0       -0.210  0.768   0.222
Sedimentary     17      0       0.467   0.833   0.202
Source of Variation     DF      SS      MS      F       P
Between Groups          1       3.223   3.223   4.944   0.035
Residual        27      17.601  0.652
Total   28      20.824
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.035).
Power of performed test with alpha = 0.050: 0.472
```

```
The power of the performed test (0.472) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Bonferroni t-test):
Comparisons for factor: Geology
Comparison    Diff of Means t       P       P<0.050
Sedimentary vs. Igneous     0.677  2.224  0.035   Yes
```

2. Nickel

```
Normality Test:        Passed (P > 0.200)
Equal Variance Test:   Passed (P = 0.579)
Group Name  N          Missing         Mean  Std Dev        SEM
Igneous          12    0         -0.592 0.883  0.255
Sedimentary   17       0          0.441  0.936  0.227
Source of Variation     DF        SS        MS        F        P
Between Groups          1         7.511  7.511  8.974  0.006
Residual          27         22.598 0.837
Total   28        30.108
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.006).
Power of performed test with alpha = 0.050: 0.789
The power of the performed test (0.789) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Bonferroni t-test):
Comparisons for factor: Col 35
Comparison    Diff of Means t       P       P<0.050
Sedimentary vs. Igneous      1.033  2.996  0.006   Yes
```

3. Selenium

```
Normality Test:        Passed (P = 0.184)
Equal Variance Test:   Passed (P = 0.915)
Group Name  N          Missing         Mean  Std Dev        SEM
Igneous          12    0         -0.823 0.663  0.191
Sedimentary   17       0         -0.234 0.653  0.158
Source of Variation     DF        SS        MS        F        P
Between Groups          1         2.440  2.440  5.653  0.025
Residual          27         11.653 0.432
Total   28        14.093
```

```
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.025).
Power of performed test with alpha = 0.050: 0.542
The power of the performed test (0.542) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Bonferroni t-test):
Comparisons for factor: Col 107
Comparison    Diff of Means t        P        P<0.050
Sedimentary vs. Igneous        0.589  2.378  0.025   Yes
```

4. Ammonia

```
Normality Test:         Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.121)
Group Name  N         Missing          Mean  Std Dev          SEM
Igneous          12       0         -1.745  0.488  0.141
Sedimentary   17       0         -1.106  0.821  0.199
Source of Variation     DF       SS        MS        F          P
Between Groups          1         2.871  2.871  5.783  0.023
Residual           27         13.404 0.496
Total   28        16.276
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.023).
Power of performed test with alpha = 0.050: 0.554
The power of the performed test (0.554) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Bonferroni t-test):
Comparisons for factor: Col 43
Comparison    Diff of Means t        P        P<0.050
Sedimentary vs. Igneous        0.639  2.405  0.023   Yes
```

2. Natural catchments vs. developed catchments

2.1. Concentration

1. Arsenic

```
Normality Test:         Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
```

```
Data source: Wet_Dev Vs NL in Notebook
Group  N      Missing        Median         25%             75%
NL      29      0          0.473  0.120  1.097
Developed     45      0          2.557  1.790  4.650
H = 31.329 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q         P<0.05
Developed vs. NL       28.664 5.597   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

2. Cadmium

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group  N      Missing        Median         25%             75%
NL      29      0          0.146  0.0374 0.559
Developed     45      0          0.654  0.318  1.868
H = 20.465 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q         P<0.05
Developed vs. NL       23.164 4.523   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

3. Chromium

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
```

```
Group N      Missing        Median        25%              75%
NL     29    0        1.025  0.301  9.651
Developed     45      0       6.572  4.120  22.108
H = 12.204 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Developed vs. NL      17.890 3.493   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

4. Copper

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group N      Missing        Median        25%              75%
NL     29    0        1.641  0.510  5.535
Developed     45      0       21.900 13.573 42.070
H = 34.896 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Developed vs. NL      30.252 5.907   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

5. Iron

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group N      Missing        Median        25%              75%
```

NL 29 0 1008.985 139.196 6439.514
Developed 35 0 3.234 2.091 13.423
H = 28.739 with 1 degrees of freedom. (P = <0.001)
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
NL vs. Developed 25.064 5.361 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

6. Lead
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group N Missing Median 25% 75%
NL 29 0 0.469 0.131 1.995
Developed 45 0 13.002 7.863 36.596
H = 35.421 with 1 degrees of freedom. (P = <0.001)
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
Developed vs. NL 30.479 5.952 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

7. Nickel
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group N Missing Median 25% 75%
NL 29 0 0.722 0.194 5.459

Developed 45 0 11.359 4.716 28.574
H = 20.260 with 1 degrees of freedom. (P = <0.001)
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
Developed vs. NL 23.051 4.501 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

8. Selenium
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook

Group N Missing Median 25% 75%
NL 29 0 0.382 0.0791 0.769
Developed 26 0 1.250 0.405 3.260
H = 6.653 with 1 degrees of freedom. (P = 0.010)
The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.010)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
Developed vs. NL 11.160 2.579 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

9. Zinc
Normality Test: Failed (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group N Missing Median 25% 75%
Developed 45 0 123.266 67.368 260.518

```
NL      29      0       5.187   1.496   21.491
H = 35.686 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Developed vs. NL       30.592 5.974   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

10. Ammonium

```
Normality Test:          Failed  (P = <0.001)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group  N        Missing           Median            25%                75%
Developed       10      0         0.317   0.202   0.604
NL      29      0       0.0347 0.0150 0.0821
H = 10.764 with 1 degrees of freedom.  (P = 0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = 0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Developed vs. NL       13.717 3.281   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

11. Total Kjeldahl nitrogen

```
Normality Test:          Failed  (P = 0.004)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL in Notebook
Group  N        Missing           Median            25%                75%
Developed       7       0         2.768   2.263   6.780
NL      15      0       1.263   0.898   1.662
```

```
H = 9.840 with 1 degrees of freedom.  (P = 0.002)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = 0.002)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q       P<0.05
Developed vs. NL      9.324  3.137   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

12. Total Phosphorus

```
Normality Test:        Passed (P = 0.070)
Equal Variance Test:   Passed (P = 0.119)
Group Name  N          Missing        Mean   Std Dev        SEM
NL     21      0       -1.467  0.622  0.136
Dev    13      0       -0.506  1.017  0.282
Source of Variation     DF     SS      MS      F       P
Between Groups          1      7.406   7.406   11.768 0.002
Residual        32      20.138 0.629
Total   33      27.544
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.002).
Power of performed test with alpha = 0.050: 0.906
All Pairwise Multiple Comparison Procedures (Bonferroni t-test):
Comparisons for factor: Col 54
Comparison    Diff of Means t       P       P<0.050
Dev vs. NL    0.960   3.430   0.002   Yes
```

13. Nitrate+nitrite

```
Normality Test:         Failed  (P = 0.007)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL_LogTransformed in Notebook
Group  N       Missing         Median          25%             75%
NL      29     0        -0.520 -0.665  -0.170
Developed      27      0       0.141   -0.203  0.469
H = 11.577 with 1 degrees of freedom.  (P = <0.001)
```

The differences in the median values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = <0.001)
To isolate the group or groups that differ from the others use a multiple comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison Diff of Ranks Q P<0.05
Developed vs. NL 14.840 3.402 Yes
Note: The multiple comparisons on ranks do not include an adjustment for ties.

2.2. Flux

1. Arsenic
Normality Test: Passed (P = 0.041)
Equal Variance Test: Passed (P = 0.487)
Group Name N Missing Mean Std Dev SEM
NL 29 0 -0.0599 0.938 0.174
Developed 45 0 0.583 1.201 0.179
Source of Variation DF SS MS F P
Between Groups 1 7.285 7.285 5.952 0.017
Residual 72 88.126 1.224
Total 73 95.411
The differences in the mean values among the treatment groups are greater than would be expected by chance; there is a statistically significant difference (P = 0.017).
Power of performed test with alpha = 0.050: 0.590
The power of the performed test (0.590) is below the desired power of 0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 1
Comparison Diff of Means p q P P<0.050
Developed vs. NL 0.643 2 3.450 0.017 Yes

2. Copper
Normality Test: Passed (P = 0.012)
Equal Variance Test: Passed (P = 0.623)
Group Name N Missing Mean Std Dev SEM
NL 29 0 0.537 1.102 0.205
Developed 45 0 1.546 1.337 0.199
Source of Variation DF SS MS F P

```
Between Groups    1    17.942 17.942 11.468 0.001
Residual    72    112.649    1.565
Total  73    130.590
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.001).
Power of performed test with alpha = 0.050: 0.909
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 13
Comparison   Diff of Means p      q      P      P<0.050
Developed vs. NL    1.009  2      4.789  0.001  Yes
```

3. Iron

```
Normality Test:         Passed (P = 0.046)
Equal Variance Test:  Failed  (P = 0.003)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL_LogTransformed in Notebook
Group  N     Missing        Median        25%          75%
NL     29    0       3.631  2.535  4.069
Developed    35     0       6.032  3.781  7.516
H = 17.536 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q      P<0.05
Developed vs. NL      19.578 4.188   Yes
```

4. Lead

```
Normality Test:         Failed  (P = 0.002)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks    Data source:
Wet_Dev Vs NL_LogTransformed in Notebook
Group  N     Missing        Median        25%          75%
NL     29    0       0.185  -0.719 0.674
Developed    45     0       1.407  0.787  2.264
H = 15.934 with 1 degrees of freedom.  (P = <0.001)
```

```
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q        P<0.05
Developed vs. NL      20.442 3.992   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

5. Nickel

```
Normality Test:          Passed (P > 0.200)
Equal Variance Test:  Passed (P = 0.760)
Group Name  N          Missing           Mean  Std Dev          SEM
NL      29        0          0.365   1.205   0.224
Developed      45        0           1.208   1.280   0.191
Source of Variation      DF        SS        MS        F          P
Between Groups           1         12.541 12.541 8.011    0.006
Residual          72        112.717          1.566
Total   73        125.259
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant
difference  (P = 0.006).
Power of performed test with alpha = 0.050: 0.753
The power of the performed test (0.753) is below the desired power of
0.800.
You should interpret the negative findings cautiously.
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 25
Comparison    Diff of Means p         q        P        P<0.050
Developed vs. NL       0.843   2         4.003   0.006   Yes
```

6. Zinc

```
Normality Test:           Failed  (P = 0.002)
Test execution ended by user request, ANOVA on Ranks begun
Kruskal-Wallis One Way Analysis of Variance on Ranks
Data source: Wet_Dev Vs NL_LogTransformed in Notebook
Group  N        Missing             Median            25%                75%
Developed      45        0        2.380   1.740   3.181
NL      29        0          1.267   0.459   1.702
```

```
H = 15.408 with 1 degrees of freedom.  (P = <0.001)
The differences in the median values among the treatment groups are
greater than would be expected by chance; there is a statistically
significant difference  (P = <0.001)
To isolate the group or groups that differ from the others use a multiple
comparison procedure.
All Pairwise Multiple Comparison Procedures (Dunn's Method) :
Comparison    Diff of Ranks  Q       P<0.05
Developed vs. NL      20.102 3.925   Yes
Note: The multiple comparisons on ranks do not include an adjustment for
ties.
```

7. Ammonium

```
Normality Test:    Passed (P > 0.200)
Equal Variance Test:        Passed (P = 0.259)
Group Name        N         Missing          Mean   Std Dev          SEM
Developed 10      0         0.420   0.732   0.232
NL 29      0      -1.019 0.926   0.172
Source of Variation          DF        SS        MS        F         P
Between Groups  1           15.404 15.404 19.775 <0.001
Residual    37       28.821 0.779
Total        38       44.225
The differences in the mean values among the treatment groups are greater
than would be expected by chance; there is a statistically significant difference
(P = <0.001).
Power of performed test with alpha = 0.050: 0.994
All Pairwise Multiple Comparison Procedures (Tukey Test):
Comparisons for factor: Col 41
Comparison         Diff of Means  p         q         P          P<0.050
Developed vs. NL 1.439  2          6.289   <0.001 Yes
```

APPENDIX V, Seasonal pattern

Table 1. Seasonal pattern in % coefficients of variations (% CV)

Parameter	% CV	
	Winter 2004/2005	Winter 2005/2006
Ammonia	0.91	0.78
Arsenic	37.14	3.70
Cadmium	16.41	1.81
Chromium	69.66	7.93
Copper	107.96	9.66
Dissolved Organic Carbon	206.19	282.90
Iron	41085.77	3568.96
Lead	19.36	4.16
Nickel	33.51	5.21
Nitrate+Nitrite	14.33	0.73
Orthophosphate	2.73	3.79
Selenium	17.33	14622.13
Total Dissolved Solids	9510.37	74.91
Total Organic Carbon	147.49	295.15
Total Phosphorus	0.52	5.29
Total Suspended Solids	1154.68	392.60
Zinc	509.31	29.01

Table 2. Seasonal pattern in geometric means of flow-weighted mean concentrations

Parameter	GeomeanFWMC	
	Winter 2004/2005	Winter 2005/2006
Ammonia	0.08	0.02
Arsenic	1.23	0.13
Cadmium	0.43	0.05
Chromium	4.98	0.43
Copper	5.27	0.49
Dissolved Organic Carbon	3.30	7.42
Iron	3335.74	301.42
Lead	1.42	0.19
Mercury	0.01	0.33
Nickel	3.53	0.18
Nitrate+Nitrite	0.66	0.02
Orthophosphate	0.08	0.15
Selenium	0.77	318.33
Total Dissolved Solids	191.56	1.21
Total Organic Carbon	2.61	7.93
Total Phosphorus	0.02	0.12
Total Suspended Solids	135.30	77.52
Zinc	21.50	1.45

APPENDIX VI, Dry-weather concentrations, loads, and fluxes for each study site

Table 1. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	Site Name	Concentration	Unit	Load	Unit	Flux	Unit
Ammonia	Arroyo Seco	0.006	mg/L	0.106	kg/day	0.002	kg/daykm2
Ammonia	Bear Creek WFSGR	0.006	mg/L	0.360	kg/day	0.005	kg/daykm2
Ammonia	Cattle Creek EFSGR	0.007	mg/L	0.506	kg/day	0.010	kg/daykm2
Ammonia	Coldbrook NFSGR	0.009	mg/L	0.321	kg/day	0.021	kg/daykm2
Ammonia	Chesebro Creek	0.005	mg/L	0.082	kg/day	0.011	kg/daykm2
Ammonia	Cold Creek	0.005	mg/L	0.012	kg/day	0.008	kg/daykm2
Ammonia	Cristianitos Creek	0.005	mg/L	0.006	kg/day	0.000	kg/daykm2
Ammonia	San Juan Creek	0.007	mg/L	0.262	kg/day	0.003	kg/daykm2
Ammonia	Santiago Creek	0.005	mg/L	0.095	kg/day	0.006	kg/daykm2
Ammonia	Bell Creek	0.005	mg/L	0.055	kg/day	0.003	kg/daykm2
Ammonia	Silverado Creek	0.007	mg/L	0.077	kg/day	0.005	kg/daykm2
Ammonia	Seven Oaks Dam	0.006	mg/L	0.136	kg/day	0.014	kg/daykm2
Ammonia	Cajon Creek	0.008	mg/L	0.157	kg/day	0.002	kg/daykm2
Ammonia	Mill Creek	0.005	mg/L	0.288	kg/day	0.018	kg/daykm2
Ammonia	Fry Creek	0.005	mg/L	0.005	kg/day	0.046	kg/daykm2
Ammonia	Piru Creek	0.011	mg/L	0.738	kg/day	0.002	kg/daykm2
Ammonia	Sespe Creek	0.008	mg/L	0.357	kg/day	0.003	kg/daykm2
Ammonia	Bear Creek Matilija	0.007	mg/L	0.071	kg/day	0.007	kg/daykm2
Ammonia	Tenaja Creek	0.005	mg/L	0.022	kg/day	0.000	kg/daykm2
Arsenic	Arroyo Seco	2.208	µg/L	24.846	g/day	0.572	g/daykm2
Arsenic	Bear Creek WFSGR	0.517	µg/L	33.801	g/day	0.464	g/daykm2
Arsenic	Cattle Creek EFSGR	5.374	µg/L	371.140	g/day	7.585	g/daykm2
Arsenic	Coldbrook NFSGR	0.088	µg/L	3.573	g/day	0.238	g/daykm2
Arsenic	Chesebro Creek	5.420	µg/L	88.890	g/day	11.805	g/daykm2
Arsenic	Cold Creek	0.908	µg/L	2.269	g/day	1.473	g/daykm2
Arsenic	Cristianitos Creek	1.525	µg/L	1.883	g/day	0.039	g/daykm2
Arsenic	San Juan Creek	2.760	µg/L	91.497	g/day	0.898	g/daykm2
Arsenic	Santiago Creek	0.554	µg/L	9.889	g/day	0.577	g/daykm2
Arsenic	Bell Creek	0.944	µg/L	11.743	g/day	0.644	g/daykm2
Arsenic	Silverado Creek	1.180	µg/L	14.943	g/day	0.886	g/daykm2
Arsenic	Seven Oaks Dam	0.197	µg/L	4.458	g/day	0.455	g/daykm2
Arsenic	Cajon Creek	0.951	µg/L	14.710	g/day	0.179	g/daykm2
Arsenic	Mill Creek	0.123	µg/L	9.320	g/day	0.590	g/daykm2
Arsenic	Fry Creek	0.110	µg/L	0.062	g/day	0.623	g/daykm2
Arsenic	Piru Creek	2.119	µg/L	94.016	g/day	0.197	g/daykm2
Arsenic	Sespe Creek	0.452	µg/L	16.475	g/day	0.128	g/daykm2
Arsenic	Bear Creek Matilija	0.289	µg/L	3.036	g/day	0.313	g/daykm2
Arsenic	Tenaja Creek	1.380	µg/L	5.067	g/day	0.096	g/daykm2

Table 2. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Cadmium	Arroyo Seco	0.213	µg/L	4.145	g/day	0.095	g/daykm2
Cadmium	Bear Creek WFSGR	0.189	µg/L	10.536	g/day	0.145	g/daykm2
Cadmium	Cattle Creek EFSGR	0.193	µg/L	12.938	g/day	0.264	g/daykm2
Cadmium	Coldbrook NFSGR	0.189	µg/L	6.655	g/day	0.443	g/daykm2
Cadmium	Chesebro Creek	1.148	µg/L	18.820	g/day	2.499	g/daykm2
Cadmium	Cold Creek	0.241	µg/L	0.465	g/day	0.302	g/daykm2
Cadmium	Cristianitos Creek	0.050	µg/L	0.062	g/day	0.001	g/daykm2
Cadmium	San Juan Creek	0.356	µg/L	16.464	g/day	0.162	g/daykm2
Cadmium	Santiago Creek	0.067	µg/L	1.014	g/day	0.059	g/daykm2
Cadmium	Bell Creek	0.243	µg/L	2.459	g/day	0.135	g/daykm2
Cadmium	Silverado Creek	0.173	µg/L	2.720	g/day	0.161	g/daykm2
Cadmium	Seven Oaks Dam	0.075	µg/L	1.795	g/day	0.183	g/daykm2
Cadmium	Cajon Creek	0.150	µg/L	1.689	g/day	0.021	g/daykm2
Cadmium	Mill Creek	0.100	µg/L	4.943	g/day	0.313	g/daykm2
Cadmium	Fry Creek	0.075	µg/L	0.053	g/day	0.526	g/daykm2
Cadmium	Piru Creek	0.067	µg/L	4.286	g/day	0.009	g/daykm2
Cadmium	Sespe Creek	0.192	µg/L	9.144	g/day	0.071	g/daykm2
Cadmium	Bear Creek Matilija	0.192	µg/L	1.294	g/day	0.133	g/daykm2
Cadmium	Tenaja Creek	0.075	µg/L	0.270	g/day	0.005	g/daykm2
Chromium	Arroyo Seco	0.122	µg/L	1.484	g/day	0.034	g/daykm2
Chromium	Bear Creek WFSGR	0.067	µg/L	3.045	g/day	0.042	g/daykm2
Chromium	Cattle Creek EFSGR	0.316	µg/L	19.796	g/day	0.405	g/daykm2
Chromium	Coldbrook NFSGR	0.316	µg/L	12.290	g/day	0.818	g/daykm2
Chromium	Chesebro Creek	0.465	µg/L	7.626	g/day	1.013	g/daykm2
Chromium	Cold Creek	0.754	µg/L	2.378	g/day	1.544	g/daykm2
Chromium	Cristianitos Creek	0.050	µg/L	0.062	g/day	0.001	g/daykm2
Chromium	San Juan Creek	0.263	µg/L	7.898	g/day	0.078	g/daykm2
Chromium	Santiago Creek	0.210	µg/L	5.240	g/day	0.306	g/daykm2
Chromium	Bell Creek	0.198	µg/L	2.431	g/day	0.133	g/daykm2
Chromium	Silverado Creek	0.223	µg/L	3.353	g/day	0.199	g/daykm2
Chromium	Seven Oaks Dam	0.050	µg/L	1.147	g/day	0.117	g/daykm2
Chromium	Cajon Creek	0.459	µg/L	7.568	g/day	0.092	g/daykm2
Chromium	Mill Creek	0.260	µg/L	21.669	g/day	1.371	g/daykm2
Chromium	Fry Creek	0.103	µg/L	0.060	g/day	0.602	g/daykm2
Chromium	Piru Creek	0.250	µg/L	10.446	g/day	0.022	g/daykm2
Chromium	Sespe Creek	0.067	µg/L	2.708	g/day	0.021	g/daykm2
Chromium	Bear Creek Matilija	0.128	µg/L	1.052	g/day	0.108	g/daykm2
Chromium	Tenaja Creek	0.305	µg/L	0.950	g/day	0.018	g/daykm2

Table 3. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Copper	Arroyo Seco	0.508	µg/L	7.134	g/day	0.164	g/daykm2
Copper	Bear Creek WFSGR	1.409	µg/L	33.777	g/day	0.463	g/daykm2
Copper	Cattle Creek EFSGR	1.256	µg/L	19.324	g/day	0.395	g/daykm2
Copper	Coldbrook NFSGR	1.064	µg/L	10.150	g/day	0.675	g/daykm2
Copper	Chesebro Creek	5.058	µg/L	82.945	g/day	11.015	g/daykm2
Copper	Cold Creek	0.814	µg/L	2.007	g/day	1.303	g/daykm2
Copper	Cristianitos Creek	0.794	µg/L	0.980	g/day	0.020	g/daykm2
Copper	San Juan Creek	0.638	µg/L	24.044	g/day	0.236	g/daykm2
Copper	Santiago Creek	0.493	µg/L	11.360	g/day	0.663	g/daykm2
Copper	Bell Creek	0.557	µg/L	6.038	g/day	0.331	g/daykm2
Copper	Silverado Creek	1.328	µg/L	16.802	g/day	0.997	g/daykm2
Copper	Seven Oaks Dam	0.262	µg/L	6.156	g/day	0.628	g/daykm2
Copper	Cajon Creek	0.924	µg/L	15.240	g/day	0.186	g/daykm2
Copper	Mill Creek	0.476	µg/L	29.450	g/day	1.864	g/daykm2
Copper	Fry Creek	0.125	µg/L	0.066	g/day	0.665	g/daykm2
Copper	Piru Creek	0.746	µg/L	39.310	g/day	0.082	g/daykm2
Copper	Sespe Creek	0.916	µg/L	34.192	g/day	0.266	g/daykm2
Copper	Bear Creek Matilija	0.656	µg/L	7.841	g/day	0.808	g/daykm2
Copper	Tenaja Creek	0.125	µg/L	0.378	g/day	0.007	g/daykm2
DOC	Arroyo Seco	2.819	mg/L	56.396	kg/day	1.297	kg/daykm2
DOC	Bear Creek WFSGR	2.600	mg/L	158.044	kg/day	2.168	kg/daykm2
DOC	Cattle Creek EFSGR	2.003	mg/L	130.597	kg/day	2.669	kg/daykm2
DOC	Coldbrook NFSGR	2.450	mg/L	82.599	kg/day	5.496	kg/daykm2
DOC	Chesebro Creek	9.800	mg/L	160.724	kg/day	21.345	kg/daykm2
DOC	Cold Creek	3.883	mg/L	10.188	kg/day	6.615	kg/daykm2
DOC	Cristianitos Creek	5.550	mg/L	6.854	kg/day	0.140	kg/daykm2
DOC	San Juan Creek	3.667	mg/L	135.017	kg/day	1.325	kg/daykm2
DOC	Santiago Creek	3.133	mg/L	76.249	kg/day	4.449	kg/daykm2
DOC	Bell Creek	1.639	mg/L	10.751	kg/day	0.590	kg/daykm2
DOC	Silverado Creek	3.017	mg/L	38.577	kg/day	2.288	kg/daykm2
DOC	Seven Oaks Dam	2.333	mg/L	53.056	kg/day	5.414	kg/daykm2
DOC	Cajon Creek	4.300	mg/L	68.691	kg/day	0.837	kg/daykm2
DOC	Mill Creek	2.200	mg/L	126.470	kg/day	8.004	kg/daykm2
DOC	Fry Creek	4.375	mg/L	4.049	kg/day	40.486	kg/daykm2
DOC	Piru Creek	3.067	mg/L	146.395	kg/day	0.306	kg/daykm2
DOC	Sespe Creek	3.500	mg/L	120.906	kg/day	0.941	kg/daykm2
DOC	Bear Creek Matilija	2.567	mg/L	33.486	kg/day	3.452	kg/daykm2
DOC	Tenaja Creek	5.225	mg/L	23.738	kg/day	0.450	kg/daykm2

Table 4. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Iron	Arroyo Seco	33.558	µg/L	633.004	g/day	14.562	g/dayKm2
Iron	Bear Creek WFSGR	14.537	µg/L	981.877	g/day	13.469	g/dayKm2
Iron	Cattle Creek EFSGR	26.964	µg/L	1941.240	g/day	39.674	g/dayKm2
Iron	Coldbrook NFSGR	43.639	µg/L	2008.966	g/day	133.664	g/dayKm2
Iron	Chesebro Creek	466.000	µg/L	7642.609	g/day	1014.955	g/dayKm2
Iron	Cold Creek	145.333	µg/L	459.146	g/day	298.147	g/dayKm2
Iron	Cristianitos Creek	109.750	µg/L	135.531	g/day	2.772	g/dayKm2
Iron	San Juan Creek	137.642	µg/L	4436.441	g/day	43.550	g/dayKm2
Iron	Santiago Creek	110.183	µg/L	1236.523	g/day	72.143	g/dayKm2
Iron	Bell Creek	132.133	µg/L	818.963	g/day	44.924	g/dayKm2
Iron	Silverado Creek	247.750	µg/L	2676.658	g/day	158.758	g/dayKm2
Iron	Seven Oaks Dam	87.567	µg/L	2008.137	g/day	204.912	g/dayKm2
Iron	Cajon Creek	258.417	µg/L	4454.806	g/day	54.294	g/dayKm2
Iron	Mill Creek	99.283	µg/L	9524.469	g/day	602.814	g/dayKm2
Iron	Fry Creek	60.763	µg/L	25.843	g/day	258.429	g/dayKm2
Iron	Piru Creek	172.333	µg/L	7712.794	g/day	16.145	g/dayKm2
Iron	Sespe Creek	102.142	µg/L	3511.662	g/day	27.337	g/dayKm2
Iron	Bear Creek Matilija	166.342	µg/L	1517.782	g/day	156.472	g/dayKm2
Iron	Tenaja Creek	200.500	µg/L	759.927	g/day	14.398	g/dayKm2
Lead	Arroyo Seco	0.025	µg/L	0.443	g/day	0.010	g/dayKm2
Lead	Bear Creek WFSGR	0.025	µg/L	1.514	g/day	0.021	g/dayKm2
Lead	Cattle Creek EFSGR	0.025	µg/L	1.459	g/day	0.030	g/dayKm2
Lead	Coldbrook NFSGR	0.025	µg/L	0.943	g/day	0.063	g/dayKm2
Lead	Chesebro Creek	0.043	µg/L	0.697	g/day	0.093	g/dayKm2
Lead	Cold Creek	0.037	µg/L	0.107	g/day	0.070	g/dayKm2
Lead	Cristianitos Creek	0.025	µg/L	0.031	g/day	0.001	g/dayKm2
Lead	San Juan Creek	0.076	µg/L	3.427	g/day	0.034	g/dayKm2
Lead	Santiago Creek	0.025	µg/L	0.474	g/day	0.028	g/dayKm2
Lead	Bell Creek	0.043	µg/L	0.430	g/day	0.024	g/dayKm2
Lead	Silverado Creek	0.025	µg/L	0.308	g/day	0.018	g/dayKm2
Lead	Seven Oaks Dam	0.099	µg/L	2.123	g/day	0.217	g/dayKm2
Lead	Cajon Creek	1.255	µg/L	27.967	g/day	0.341	g/dayKm2
Lead	Mill Creek	0.063	µg/L	5.808	g/day	0.368	g/dayKm2
Lead	Fry Creek	0.145	µg/L	0.056	g/day	0.560	g/dayKm2
Lead	Piru Creek	0.089	µg/L	2.334	g/day	0.005	g/dayKm2
Lead	Sespe Creek	0.025	µg/L	0.925	g/day	0.007	g/dayKm2
Lead	Bear Creek Matilija	0.129	µg/L	0.687	g/day	0.071	g/dayKm2
Lead	Tenaja Creek	0.120	µg/L	0.453	g/day	0.009	g/dayKm2

Table 5. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Nickel	Arroyo Seco	0.140	µg/L	2.857	g/day	0.066	g/dayKm2
Nickel	Bear Creek WFSGR	0.067	µg/L	4.178	g/day	0.057	g/dayKm2
Nickel	Cattle Creek EFSGR	0.122	µg/L	9.128	g/day	0.187	g/dayKm2
Nickel	Coldbrook NFSGR	0.110	µg/L	5.017	g/day	0.334	g/dayKm2
Nickel	Chesebro Creek	5.110	µg/L	83.806	g/day	11.130	g/dayKm2
Nickel	Cold Creek	0.448	µg/L	1.325	g/day	0.860	g/dayKm2
Nickel	Cristianitos Creek	0.665	µg/L	0.821	g/day	0.017	g/dayKm2
Nickel	San Juan Creek	0.375	µg/L	13.731	g/day	0.135	g/dayKm2
Nickel	Santiago Creek	0.632	µg/L	6.306	g/day	0.368	g/dayKm2
Nickel	Bell Creek	0.553	µg/L	4.689	g/day	0.257	g/dayKm2
Nickel	Silverado Creek	1.170	µg/L	13.637	g/day	0.809	g/dayKm2
Nickel	Seven Oaks Dam	0.100	µg/L	2.443	g/day	0.249	g/dayKm2
Nickel	Cajon Creek	0.665	µg/L	10.793	g/day	0.132	g/dayKm2
Nickel	Mill Creek	0.301	µg/L	17.538	g/day	1.110	g/dayKm2
Nickel	Fry Creek	0.063	µg/L	0.033	g/day	0.332	g/dayKm2
Nickel	Piru Creek	0.544	µg/L	26.216	g/day	0.055	g/dayKm2
Nickel	Sespe Creek	0.703	µg/L	25.942	g/day	0.202	g/dayKm2
Nickel	Bear Creek Matilija	0.583	µg/L	7.112	g/day	0.733	g/dayKm2
Nickel	Tenaja Creek	0.616	µg/L	2.465	g/day	0.047	g/dayKm2
Nitrate+Nitrite	Arroyo Seco	0.128	mg/L	1.805	kg/day	0.042	kg/dayKm2
Nitrate+Nitrite	Bear Creek WFSGR	0.105	mg/L	7.298	kg/day	0.100	kg/dayKm2
Nitrate+Nitrite	Cattle Creek EFSGR	0.166	mg/L	9.112	kg/day	0.186	kg/dayKm2
Nitrate+Nitrite	Coldbrook NFSGR	0.466	mg/L	12.699	kg/day	0.845	kg/dayKm2
Nitrate+Nitrite	Chesebro Creek	0.060	mg/L	0.984	kg/day	0.131	kg/dayKm2
Nitrate+Nitrite	Cold Creek	0.043	mg/L	0.107	kg/day	0.069	kg/dayKm2
Nitrate+Nitrite	Cristianitos Creek	0.075	mg/L	0.093	kg/day	0.002	kg/dayKm2
Nitrate+Nitrite	San Juan Creek	0.080	mg/L	2.518	kg/day	0.025	kg/dayKm2
Nitrate+Nitrite	Santiago Creek	0.123	mg/L	4.488	kg/day	0.262	kg/dayKm2
Nitrate+Nitrite	Bell Creek	0.113	mg/L	1.644	kg/day	0.090	kg/dayKm2
Nitrate+Nitrite	Silverado Creek	0.097	mg/L	1.198	kg/day	0.071	kg/dayKm2
Nitrate+Nitrite	Seven Oaks Dam	0.042	mg/L	0.888	kg/day	0.091	kg/dayKm2
Nitrate+Nitrite	Cajon Creek	1.399	mg/L	28.416	kg/day	0.346	kg/dayKm2
Nitrate+Nitrite	Mill Creek	0.067	mg/L	3.445	kg/day	0.218	kg/dayKm2
Nitrate+Nitrite	Fry Creek	0.010	mg/L	0.009	kg/day	0.091	kg/dayKm2
Nitrate+Nitrite	Piru Creek	0.020	mg/L	1.028	kg/day	0.002	kg/dayKm2
Nitrate+Nitrite	Sespe Creek	0.024	mg/L	0.856	kg/day	0.007	kg/dayKm2
Nitrate+Nitrite	Bear Creek Matilija	0.017	mg/L	0.335	kg/day	0.035	kg/dayKm2
Nitrate+Nitrite	Tenaja Creek	0.010	mg/L	0.043	kg/day	0.001	kg/dayKm2

Table 6. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Orthophosphate	Arroyo Seco	0.017	mg/L	0.170	kg/day	0.004	kg/dayKm2
Orthophosphate	Bear Creek WFSGR	0.416	mg/L	0.629	kg/day	0.009	kg/dayKm2
Orthophosphate	Cattle Creek EFSGR	0.004	mg/L	0.219	kg/day	0.004	kg/dayKm2
Orthophosphate	Coldbrook NFSGR	0.009	mg/L	0.153	kg/day	0.010	kg/dayKm2
Orthophosphate	Chesebro Creek	0.135	mg/L	2.214	kg/day	0.294	kg/dayKm2
Orthophosphate	Cold Creek	0.025	mg/L	0.055	kg/day	0.036	kg/dayKm2
Orthophosphate	Cristianitos Creek	0.074	mg/L	0.091	kg/day	0.002	kg/dayKm2
Orthophosphate	San Juan Creek	0.013	mg/L	0.297	kg/day	0.003	kg/dayKm2
Orthophosphate	Santiago Creek	0.037	mg/L	0.568	kg/day	0.033	kg/dayKm2
Orthophosphate	Bell Creek	0.070	mg/L	0.696	kg/day	0.038	kg/dayKm2
Orthophosphate	Silverado Creek	0.068	mg/L	0.694	kg/day	0.041	kg/dayKm2
Orthophosphate	Seven Oaks Dam	0.019	mg/L	0.408	kg/day	0.042	kg/dayKm2
Orthophosphate	Cajon Creek	0.033	mg/L	0.606	kg/day	0.007	kg/dayKm2
Orthophosphate	Mill Creek	0.009	mg/L	0.287	kg/day	0.018	kg/dayKm2
Orthophosphate	Fry Creek	0.082	mg/L	0.127	kg/day	1.265	kg/dayKm2
Orthophosphate	Piru Creek	0.032	mg/L	1.451	kg/day	0.003	kg/dayKm2
Orthophosphate	Sespe Creek	0.048	mg/L	1.964	kg/day	0.015	kg/dayKm2
Orthophosphate	Bear Creek Matilija	0.030	mg/L	0.419	kg/day	0.043	kg/dayKm2
Orthophosphate	Tenaja Creek	0.004	mg/L	0.016	kg/day	0.000	kg/dayKm2
Selenium	Arroyo Seco	0.948	µg/L	22.130	g/day	0.509	g/dayKm2
Selenium	Bear Creek WFSGR	0.185	µg/L	12.084	g/day	0.166	g/dayKm2
Selenium	Cattle Creek EFSGR	0.319	µg/L	19.063	g/day	0.390	g/dayKm2
Selenium	Coldbrook NFSGR	0.148	µg/L	5.076	g/day	0.338	g/dayKm2
Selenium	Chesebro Creek	67.925	µg/L	1114.000	g/day	147.942	g/dayKm2
Selenium	Cold Creek	0.761	µg/L	1.884	g/day	1.223	g/dayKm2
Selenium	Cristianitos Creek	0.990	µg/L	1.223	g/day	0.025	g/dayKm2
Selenium	San Juan Creek	0.331	µg/L	9.194	g/day	0.090	g/dayKm2
Selenium	Santiago Creek	1.045	µg/L	16.185	g/day	0.944	g/dayKm2
Selenium	Bell Creek	2.267	µg/L	19.370	g/day	1.063	g/dayKm2
Selenium	Silverado Creek	3.911	µg/L	49.144	g/day	2.915	g/dayKm2
Selenium	Seven Oaks Dam	0.102	µg/L	2.336	g/day	0.238	g/dayKm2
Selenium	Cajon Creek	1.019	µg/L	15.384	g/day	0.187	g/dayKm2
Selenium	Mill Creek	0.288	µg/L	17.866	g/day	1.131	g/dayKm2
Selenium	Fry Creek	0.110	µg/L	0.062	g/day	0.623	g/dayKm2
Selenium	Piru Creek	0.640	µg/L	37.464	g/day	0.078	g/dayKm2
Selenium	Sespe Creek	1.317	µg/L	49.776	g/day	0.387	g/dayKm2
Selenium	Bear Creek Matilija	1.392	µg/L	15.322	g/day	1.580	g/dayKm2
Selenium	Tenaja Creek	0.716	µg/L	2.740	g/day	0.052	g/dayKm2

Table 7. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Total Dissolved Solids	Arroyo Seco	269.833	mg/L	4850.611	kg/day	111.585	kg/daykm2
Total Dissolved Solids	Bear Creek WFSGR	168.000	mg/L	9803.143	kg/day	134.474	kg/daykm2
Total Dissolved Solids	Cattle Creek EFSGR	189.667	mg/L	10269.183	kg/day	209.875	kg/daykm2
Total Dissolved Solids	Coldbrook NFSGR	120.683	mg/L	6641.223	kg/day	441.864	kg/daykm2
Total Dissolved Solids	Chesebro Creek	2270.000	mg/L	37229.017	kg/day	4944.093	kg/daykm2
Total Dissolved Solids	Cold Creek	422.333	mg/L	974.686	kg/day	632.913	kg/daykm2
Total Dissolved Solids	Cristianitos Creek	730.000	mg/L	901.479	kg/day	18.439	kg/daykm2
Total Dissolved Solids	San Juan Creek	340.333	mg/L	11864.870	kg/day	116.471	kg/daykm2
Total Dissolved Solids	Santiago Creek	439.722	mg/L	8716.326	kg/day	508.537	kg/daykm2
Total Dissolved Solids	Bell Creek	505.500	mg/L	5978.294	kg/day	327.937	kg/daykm2
Total Dissolved Solids	Silverado Creek	810.833	mg/L	10081.785	kg/day	597.971	kg/daykm2
Total Dissolved Solids	Seven Oaks Dam	138.833	mg/L	3200.895	kg/day	326.622	kg/daykm2
Total Dissolved Solids	Cajon Creek	419.667	mg/L	6418.690	kg/day	78.229	kg/daykm2
Total Dissolved Solids	Mill Creek	117.611	mg/L	6656.172	kg/day	421.277	kg/daykm2
Total Dissolved Solids	Fry Creek	57.500	mg/L	66.936	kg/day	669.358	kg/daykm2
Total Dissolved Solids	Piru Creek	343.250	mg/L	9533.166	kg/day	19.955	kg/daykm2
Total Dissolved Solids	Sespe Creek	869.667	mg/L	30233.263	kg/day	235.352	kg/daykm2
Total Dissolved Solids	Bear Creek Matilija	710.389	mg/L	9877.821	kg/day	1018.332	kg/daykm2
Total Dissolved Solids	Tenaja Creek	399.500	mg/L	1657.807	kg/day	31.410	kg/daykm2
Total Kjeldahl Nitrogen	Arroyo Seco	0.307	mg/L	5.341	kg/day	0.123	kg/daykm2
Total Kjeldahl Nitrogen	Bear Creek WFSGR	0.308	mg/L	14.005	kg/day	0.192	kg/daykm2
Total Kjeldahl Nitrogen	Cattle Creek EFSGR	0.230	mg/L	13.425	kg/day	0.274	kg/daykm2
Total Kjeldahl Nitrogen	Coldbrook NFSGR	0.230	mg/L	8.673	kg/day	0.577	kg/daykm2
Total Kjeldahl Nitrogen	Chesebro Creek	0.655	mg/L	10.742	kg/day	1.427	kg/daykm2
Total Kjeldahl Nitrogen	Cold Creek	0.305	mg/L	0.851	kg/day	0.553	kg/daykm2
Total Kjeldahl Nitrogen	Cristianitos Creek	0.350	mg/L	0.432	kg/day	0.009	kg/daykm2
Total Kjeldahl Nitrogen	San Juan Creek	0.230	mg/L	8.020	kg/day	0.079	kg/daykm2
Total Kjeldahl Nitrogen	Santiago Creek	0.285	mg/L	4.579	kg/day	0.267	kg/daykm2
Total Kjeldahl Nitrogen	Bell Creek	0.230	mg/L	2.515	kg/day	0.138	kg/daykm2
Total Kjeldahl Nitrogen	Silverado Creek	0.230	mg/L	2.835	kg/day	0.168	kg/daykm2
Total Kjeldahl Nitrogen	Seven Oaks Dam	0.230	mg/L	5.277	kg/day	0.538	kg/daykm2
Total Kjeldahl Nitrogen	Cajon Creek	0.363	mg/L	4.844	kg/day	0.059	kg/daykm2
Total Kjeldahl Nitrogen	Mill Creek	0.230	mg/L	13.227	kg/day	0.837	kg/daykm2
Total Kjeldahl Nitrogen	Fry Creek	0.230	mg/L	0.210	kg/day	2.103	kg/daykm2
Total Kjeldahl Nitrogen	Piru Creek	0.520	mg/L	39.366	kg/day	0.082	kg/daykm2
Total Kjeldahl Nitrogen	Sespe Creek	0.523	mg/L	23.572	kg/day	0.183	kg/daykm2
Total Kjeldahl Nitrogen	Bear Creek Matilija	0.387	mg/L	3.619	kg/day	0.373	kg/daykm2
Total Kjeldahl Nitrogen	Tenaja Creek	0.230	mg/L	0.991	kg/day	0.019	kg/daykm2

Table 8. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Total Organic Carbon	Arroyo Seco	3.183	mg/L	53.971	kg/day	1.242	kg/daykm2
Total Organic Carbon	Bear Creek WFSGR	1.950	mg/L	103.905	kg/day	1.425	kg/daykm2
Total Organic Carbon	Cattle Creek EFSGR	2.317	mg/L	103.054	kg/day	2.106	kg/daykm2
Total Organic Carbon	Coldbrook NFSGR	1.850	mg/L	60.606	kg/day	4.032	kg/daykm2
Total Organic Carbon	Chesebro Creek	7.950	mg/L	130.384	kg/day	17.315	kg/daykm2
Total Organic Carbon	Cold Creek	3.117	mg/L	8.283	kg/day	5.378	kg/daykm2
Total Organic Carbon	Cristianitos Creek	3.800	mg/L	4.693	kg/day	0.096	kg/daykm2
Total Organic Carbon	San Juan Creek	3.500	mg/L	121.215	kg/day	1.190	kg/daykm2
Total Organic Carbon	Santiago Creek	3.650	mg/L	117.620	kg/day	6.862	kg/daykm2
Total Organic Carbon	Bell Creek	2.400	mg/L	33.897	kg/day	1.859	kg/daykm2
Total Organic Carbon	Silverado Creek	2.750	mg/L	37.435	kg/day	2.220	kg/daykm2
Total Organic Carbon	Seven Oaks Dam	2.350	mg/L	53.533	kg/day	5.463	kg/daykm2
Total Organic Carbon	Cajon Creek	3.483	mg/L	59.558	kg/day	0.726	kg/daykm2
Total Organic Carbon	Mill Creek	1.600	mg/L	90.514	kg/day	5.729	kg/daykm2
Total Organic Carbon	Fry Creek	3.975	mg/L	3.364	kg/day	33.638	kg/daykm2
Total Organic Carbon	Piru Creek	9.967	mg/L	152.443	kg/day	0.319	kg/daykm2
Total Organic Carbon	Sespe Creek	6.917	mg/L	139.072	kg/day	1.083	kg/daykm2
Total Organic Carbon	Bear Creek Matilija	3.233	mg/L	70.643	kg/day	7.283	kg/daykm2
Total Organic Carbon	Tenaja Creek	4.425	mg/L	17.831	kg/day	0.338	kg/daykm2
Total Phosphorus	Arroyo Seco	0.042	mg/L	0.760	kg/day	0.017	kg/daykm2
Total Phosphorus	Bear Creek WFSGR	0.075	mg/L	5.545	kg/day	0.076	kg/daykm2
Total Phosphorus	Cattle Creek EFSGR	0.068	mg/L	5.558	kg/day	0.114	kg/daykm2
Total Phosphorus	Coldbrook NFSGR	0.069	mg/L	3.715	kg/day	0.247	kg/daykm2
Total Phosphorus	Chesebro Creek	0.215	mg/L	3.526	kg/day	0.468	kg/daykm2
Total Phosphorus	Cold Creek	0.051	mg/L	0.109	kg/day	0.071	kg/daykm2
Total Phosphorus	Cristianitos Creek	0.100	mg/L	0.123	kg/day	0.003	kg/daykm2
Total Phosphorus	San Juan Creek	0.063	mg/L	2.012	kg/day	0.020	kg/daykm2
Total Phosphorus	Santiago Creek	0.045	mg/L	0.397	kg/day	0.023	kg/daykm2
Total Phosphorus	Bell Creek	0.063	mg/L	0.610	kg/day	0.033	kg/daykm2
Total Phosphorus	Silverado Creek	0.058	mg/L	0.614	kg/day	0.036	kg/daykm2
Total Phosphorus	Seven Oaks Dam	0.056	mg/L	1.282	kg/day	0.131	kg/daykm2
Total Phosphorus	Cajon Creek	0.088	mg/L	1.495	kg/day	0.018	kg/daykm2
Total Phosphorus	Mill Creek	0.017	mg/L	0.846	kg/day	0.054	kg/daykm2
Total Phosphorus	Fry Creek	0.110	mg/L	0.066	kg/day	0.655	kg/daykm2
Total Phosphorus	Piru Creek	0.060	mg/L	1.944	kg/day	0.004	kg/daykm2
Total Phosphorus	Sespe Creek	0.041	mg/L	1.281	kg/day	0.010	kg/daykm2
Total Phosphorus	Bear Creek Matilija	0.030	mg/L	0.195	kg/day	0.020	kg/daykm2
Total Phosphorus	Tenaja Creek	0.176	mg/L	0.637	kg/day	0.012	kg/daykm2

Table 9. Dry-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	Concentration	Unit	Load	Unit	Flux	Unit
Total Suspended Solids	Arroyo Seco	0.292	mg/L	5.316	kg/day	0.122	kg/daykm2
Total Suspended Solids	Bear Creek WFSGR	0.883	mg/L	83.735	kg/day	1.149	kg/daykm2
Total Suspended Solids	Cattle Creek EFSGR	0.367	mg/L	21.049	kg/day	0.430	kg/daykm2
Total Suspended Solids	Coldbrook NFSGR	0.750	mg/L	34.325	kg/day	2.284	kg/daykm2
Total Suspended Solids	Chesebro Creek	4.000	mg/L	65.602	kg/day	8.712	kg/daykm2
Total Suspended Solids	Cold Creek	1.833	mg/L	7.167	kg/day	4.654	kg/daykm2
Total Suspended Solids	Cristianitos Creek	0.250	mg/L	0.309	kg/day	0.006	kg/daykm2
Total Suspended Solids	San Juan Creek	8.167	mg/L	426.634	kg/day	4.188	kg/daykm2
Total Suspended Solids	Santiago Creek	0.958	mg/L	9.505	kg/day	0.555	kg/daykm2
Total Suspended Solids	Bell Creek	0.792	mg/L	4.240	kg/day	0.233	kg/daykm2
Total Suspended Solids	Silverado Creek	0.250	mg/L	3.082	kg/day	0.183	kg/daykm2
Total Suspended Solids	Seven Oaks Dam	2.283	mg/L	53.084	kg/day	5.417	kg/daykm2
Total Suspended Solids	Cajon Creek	20.350	mg/L	405.293	kg/day	4.940	kg/daykm2
Total Suspended Solids	Mill Creek	0.500	mg/L	43.514	kg/day	2.754	kg/daykm2
Total Suspended Solids	Fry Creek	4.150	mg/L	3.380	kg/day	33.803	kg/daykm2
Total Suspended Solids	Piru Creek	2.550	mg/L	52.396	kg/day	0.110	kg/daykm2
Total Suspended Solids	Sespe Creek	0.375	mg/L	15.688	kg/day	0.122	kg/daykm2
Total Suspended Solids	Bear Creek Matilija	6.167	mg/L	24.371	kg/day	2.512	kg/daykm2
Total Suspended Solids	Tenaja Creek	2.375	mg/L	14.777	kg/day	0.280	kg/daykm2
Zinc	Arroyo Seco	0.737	µg/L	16.150	g/day	0.372	kg/daykm2
Zinc	Bear Creek WFSGR	0.402	µg/L	12.445	g/day	0.171	kg/daykm2
Zinc	Cattle Creek EFSGR	0.541	µg/L	13.162	g/day	0.269	kg/daykm2
Zinc	Coldbrook NFSGR	0.551	µg/L	14.489	g/day	0.964	kg/daykm2
Zinc	Chesebro Creek	10.210	µg/L	167.449	g/day	22.238	kg/daykm2
Zinc	Cold Creek	1.737	µg/L	4.493	g/day	2.918	kg/daykm2
Zinc	Cristianitos Creek	0.298	µg/L	0.367	g/day	0.008	kg/daykm2
Zinc	San Juan Creek	0.560	µg/L	19.986	g/day	0.196	kg/daykm2
Zinc	Santiago Creek	0.763	µg/L	23.449	g/day	1.368	kg/daykm2
Zinc	Bell Creek	0.705	µg/L	7.599	g/day	0.417	kg/daykm2
Zinc	Silverado Creek	6.834	µg/L	79.689	g/day	4.727	kg/daykm2
Zinc	Seven Oaks Dam	0.353	µg/L	7.843	g/day	0.800	kg/daykm2
Zinc	Cajon Creek	1.789	µg/L	34.670	g/day	0.423	kg/daykm2
Zinc	Mill Creek	0.223	µg/L	17.340	g/day	1.097	kg/daykm2
Zinc	Fry Creek	1.207	µg/L	1.275	g/day	12.749	kg/daykm2
Zinc	Piru Creek	0.415	µg/L	8.507	g/day	0.018	kg/daykm2
Zinc	Sespe Creek	0.472	µg/L	8.828	g/day	0.069	kg/daykm2
Zinc	Bear Creek Matilija	0.989	µg/L	13.650	g/day	1.407	kg/daykm2
Zinc	Tenaja Creek	0.936	µg/L	4.838	g/day	0.092	kg/daykm2

APPENDIX VII, Wet-weather concentrations, loads, and fluxes for each study site

Table 1. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Ammonia	Arroyo Seco	0.03	mg/L	3.46	kg	0.08	kg/km2
Ammonia	Bear Creek WFSGR	0.01	mg/L	10.23	kg	0.09	kg/km2
Ammonia	Cattle Creek EFSGR	0.05	mg/L	0.40	kg	0.01	kg/km2
Ammonia	Coldbrook NFSGR	0.03	mg/L	1.05	kg	0.07	kg/km2
Ammonia	Chesebro Creek	1.32	mg/L	12.19	kg	1.62	kg/km2
Ammonia	Cristianitos Creek	0.50	mg/L	74.63	kg	1.53	kg/km2
Ammonia	Santiago Creek	0.02	mg/L	3.59	kg	0.21	kg/km2
Ammonia	Bell Creek	0.02	mg/L	0.50	kg	0.03	kg/km2
Ammonia	Silverado Creek	0.03	mg/L	7.95	kg	0.47	kg/km2
Ammonia	Mill Creek	0.01	mg/L	0.12	kg	0.01	kg/km2
Ammonia	Fry Creek	0.01	mg/L	0.03	kg	0.05	kg/km2
Ammonia	Piru Creek	0.03	mg/L	21.14	kg	0.04	kg/km2
Ammonia	Sespe Creek	0.09	mg/L	119.96	kg	0.93	kg/km2
Ammonia	Bear Creek Matilija	0.08	mg/L	11.61	kg	1.20	kg/km2
Ammonia	Runkle Canyon	0.47	mg/L	5.58	kg	1.64	kg/km2
Ammonia	Tenaja Creek	0.06	mg/L	5.10	kg	0.10	kg/km2
Ammonia	Arroyo Sequit	1.64	mg/L	36.73	kg	1.34	kg/km2
Arsenic	Arroyo Seco	0.89	µg/L	79.63	g	1.83	g/km2
Arsenic	Bear Creek WFSGR	0.02	µg/L	19.38	g	0.17	g/km2
Arsenic	Cattle Creek EFSGR	3.50	µg/L	427.67	g	8.74	g/km2
Arsenic	Coldbrook NFSGR	0.49	µg/L	16.37	g	1.09	g/km2
Arsenic	Chesebro Creek	4.40	µg/L	40.65	g	5.40	g/km2
Arsenic	Cristianitos Creek	0.86	µg/L	127.47	g	2.61	g/km2
Arsenic	Santiago Creek	0.22	µg/L	51.31	g	2.99	g/km2
Arsenic	Bell Creek	0.37	µg/L	11.63	g	0.64	g/km2
Arsenic	Silverado Creek	5.47	µg/L	2282.55	g	135.38	g/km2
Arsenic	Mill Creek	0.01	µg/L	0.25	g	0.02	g/km2
Arsenic	Fry Creek	0.05	µg/L	0.22	g	0.35	g/km2
Arsenic	Piru Creek	0.47	µg/L	386.58	g	0.81	g/km2
Arsenic	Sespe Creek	0.36	µg/L	453.26	g	3.53	g/km2
Arsenic	Bear Creek Matilija	0.08	µg/L	11.50	g	1.19	g/km2
Arsenic	Runkle Canyon	1.30	µg/L	36.18	g	10.61	g/km2
Arsenic	Tenaja Creek	0.73	µg/L	50.46	g	0.96	g/km2
Arsenic	Arroyo Sequit	0.96	µg/L	30.84	g	1.13	g/km2

Table 2. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Cadmium	Arroyo Seco	0.37	µg/L	19.38	g	0.45	g/km2
Cadmium	Bear Creek WFSGR	0.02	µg/L	21.57	g	0.19	g/km2
Cadmium	Cattle Creek EFSGR	0.13	µg/L	16.00	g	0.33	g/km2
Cadmium	Coldbrook NFSGR	0.19	µg/L	5.75	g	0.38	g/km2
Cadmium	Chesebro Creek	2.38	µg/L	22.00	g	2.92	g/km2
Cadmium	Cristianitos Creek	1.08	µg/L	159.95	g	3.27	g/km2
Cadmium	Santiago Creek	0.11	µg/L	33.22	g	1.94	g/km2
Cadmium	Bell Creek	0.32	µg/L	10.42	g	0.57	g/km2
Cadmium	Silverado Creek	0.43	µg/L	155.10	g	9.20	g/km2
Cadmium	Mill Creek	0.05	µg/L	0.96	g	0.06	g/km2
Cadmium	Fry Creek	0.13	µg/L	0.60	g	0.94	g/km2
Cadmium	Piru Creek	0.04	µg/L	28.89	g	0.06	g/km2
Cadmium	Sespe Creek	0.20	µg/L	254.32	g	1.98	g/km2
Cadmium	Bear Creek Matilija	0.04	µg/L	5.67	g	0.58	g/km2
Cadmium	Runkle Canyon	0.44	µg/L	14.15	g	4.15	g/km2
Cadmium	Tenaja Creek	0.34	µg/L	21.19	g	0.40	g/km2
Cadmium	Arroyo Sequit	0.35	µg/L	40.05	g	1.46	g/km2
Chromium	Arroyo Seco	6.97	µg/L	311.63	g	7.17	g/km2
Chromium	Bear Creek WFSGR	0.08	µg/L	85.60	g	0.76	g/km2
Chromium	Cattle Creek EFSGR	0.91	µg/L	68.99	g	1.41	g/km2
Chromium	Coldbrook NFSGR	2.17	µg/L	69.01	g	4.59	g/km2
Chromium	Chesebro Creek	12.25	µg/L	113.16	g	15.03	g/km2
Chromium	Cristianitos Creek	37.02	µg/L	5472.52	g	111.94	g/km2
Chromium	Santiago Creek	0.25	µg/L	51.07	g	2.98	g/km2
Chromium	Bell Creek	2.52	µg/L	84.81	g	4.65	g/km2
Chromium	Silverado Creek	0.64	µg/L	213.93	g	12.69	g/km2
Chromium	Mill Creek	0.06	µg/L	1.15	g	0.07	g/km2
Chromium	Fry Creek	0.06	µg/L	0.22	g	0.35	g/km2
Chromium	Piru Creek	8.94	µg/L	7302.10	g	15.29	g/km2
Chromium	Sespe Creek	5.40	µg/L	6834.62	g	53.20	g/km2
Chromium	Bear Creek Matilija	0.41	µg/L	61.80	g	6.37	g/km2
Chromium	Runkle Canyon	38.32	µg/L	1030.63	g	302.24	g/km2
Chromium	Tenaja Creek	2.82	µg/L	169.41	g	3.21	g/km2
Chromium	Arroyo Sequit	16.31	µg/L	646.11	g	23.59	g/km2

Table 3. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Copper	Arroyo Seco	3.63	µg/L	328.13	g	7.55	g/km2
Copper	Bear Creek WFSGR	0.25	µg/L	267.30	g	2.38	g/km2
Copper	Cattle Creek EFSGR	0.86	µg/L	66.46	g	1.36	g/km2
Copper	Coldbrook NFSGR	3.25	µg/L	105.77	g	7.04	g/km2
Copper	Chesebro Creek	13.32	µg/L	122.98	g	16.33	g/km2
Copper	Cristianitos Creek	44.96	µg/L	6646.80	g	135.95	g/km2
Copper	Santiago Creek	0.38	µg/L	83.59	g	4.88	g/km2
Copper	Bell Creek	2.22	µg/L	74.15	g	4.07	g/km2
Copper	Silverado Creek	2.11	µg/L	612.88	g	36.35	g/km2
Copper	Mill Creek	0.03	µg/L	0.50	g	0.03	g/km2
Copper	Fry Creek	0.12	µg/L	0.51	g	0.80	g/km2
Copper	Piru Creek	5.51	µg/L	4496.95	g	9.41	g/km2
Copper	Sespe Creek	4.83	µg/L	6109.51	g	47.56	g/km2
Copper	Bear Creek Matilija	0.61	µg/L	90.83	g	9.36	g/km2
Copper	Runkle Canyon	41.49	µg/L	1126.50	g	330.35	g/km2
Copper	Tenaja Creek	2.33	µg/L	133.03	g	2.52	g/km2
Copper	Arroyo Sequit	6.88	µg/L	299.38	g	10.93	g/km2
DOC	Arroyo Seco	6.75	mg/L	1755.11	kg	40.38	kg/km2
DOC	Bear Creek WFSGR	8.62	mg/L	9065.74	kg	80.71	kg/km2
DOC	Cattle Creek EFSGR	3.19	mg/L	217.98	kg	4.45	kg/km2
DOC	Coldbrook NFSGR	2.37	mg/L	130.21	kg	8.66	kg/km2
DOC	Santiago Creek	3.28	mg/L	28.18	kg	1.64	kg/km2
DOC	Bell Creek	3.95	mg/L	79.53	kg	4.36	kg/km2
DOC	Silverado Creek	5.69	mg/L	70.30	kg	4.17	kg/km2
DOC	Mill Creek	34.01	mg/L	643.25	kg	40.71	kg/km2
DOC	Fry Creek	76.58	mg/L	243.20	kg	380.00	kg/km2
DOC	Piru Creek	5.80	mg/L	4738.22	kg	9.92	kg/km2
DOC	Sespe Creek	5.53	mg/L	6991.82	kg	54.43	kg/km2
DOC	Bear Creek Matilija	5.61	mg/L	836.25	kg	86.21	kg/km2
DOC	Tenaja Creek	6.24	mg/L	668.08	kg	12.66	kg/km2
DOC	Arroyo Sequit	21.40	mg/L	6831.66	kg	249.42	kg/km2

Table 4. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Iron	Arroyo Seco	2264.78	µg/L	211927.13	g	4875.25	g/km2
Iron	Bear Creek WFSGR	66.78	µg/L	70211.07	g	625.04	g/km2
Iron	Cattle Creek EFSGR	412.30	µg/L	9124.45	g	186.48	g/km2
Iron	Coldbrook NFSGR	3398.36	µg/L	109084.33	g	7257.77	g/km2
Iron	Chesebro Creek	7602.15	µg/L	70201.33	g	9322.89	g/km2
Iron	Cristianitos Creek	36031.01	µg/L	5326835.85	g	108955.53	g/km2
Iron	Santiago Creek	121.22	µg/L	24726.52	g	1442.62	g/km2
Iron	Bell Creek	2023.85	µg/L	68067.45	g	3733.82	g/km2
Iron	Silverado Creek	399.52	µg/L	106492.58	g	6316.29	g/km2
Iron	Mill Creek	7.86	µg/L	148.68	g	9.41	g/km2
Iron	Fry Creek	90.74	µg/L	377.03	g	589.11	g/km2
Iron	Piru Creek	7962.21	µg/L	6501263.70	g	13608.66	g/km2
Iron	Sespe Creek	7253.36	µg/L	9178430.69	g	71449.72	g/km2
Iron	Bear Creek Matilija	443.92	µg/L	66137.21	g	6818.27	g/km2
Iron	Runkle Canyon	59447.58	µg/L	1647673.32	g	483188.66	g/km2
Iron	Tenaja Creek	3322.19	µg/L	202429.68	g	3835.35	g/km2
Iron	Arroyo Sequit	5363.26	µg/L	268287.69	g	9795.10	g/km2
Lead	Arroyo Seco	2.26	µg/L	164.35	g	3.78	g/km2
Lead	Bear Creek WFSGR	0.05	µg/L	50.95	g	0.45	g/km2
Lead	Cattle Creek EFSGR	0.15	µg/L	1.84	g	0.04	g/km2
Lead	Coldbrook NFSGR	0.97	µg/L	31.86	g	2.12	g/km2
Lead	Chesebro Creek	2.49	µg/L	22.96	g	3.05	g/km2
Lead	Cristianitos Creek	27.21	µg/L	4022.73	g	82.28	g/km2
Lead	Santiago Creek	0.11	µg/L	10.15	g	0.59	g/km2
Lead	Bell Creek	1.23	µg/L	41.38	g	2.27	g/km2
Lead	Silverado Creek	1.03	µg/L	313.99	g	18.62	g/km2
Lead	Mill Creek	0.01	µg/L	0.11	g	0.01	g/km2
Lead	Fry Creek	0.13	µg/L	0.55	g	0.86	g/km2
Lead	Piru Creek	1.85	µg/L	1512.67	g	3.17	g/km2
Lead	Sespe Creek	1.54	µg/L	1942.64	g	15.12	g/km2
Lead	Bear Creek Matilija	0.23	µg/L	34.43	g	3.55	g/km2
Lead	Runkle Canyon	14.73	µg/L	379.53	g	111.30	g/km2
Lead	Tenaja Creek	1.44	µg/L	80.98	g	1.53	g/km2
Lead	Arroyo Sequit	0.73	µg/L	59.09	g	2.16	g/km2

Table 5. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWM C	Unit	Load	Unit	Flux	Unit
Nickel	Arroyo Seco	2.20	µg/L	154.40	g	3.55	g/km2
Nickel	Bear Creek WFSGR	0.10	µg/L	107.12	g	0.95	g/km2
Nickel	Cattle Creek EFSGR	0.53	µg/L	23.58	g	0.48	g/km2
Nickel	Coldbrook NFSGR	1.47	µg/L	45.59	g	3.03	g/km2
Nickel	Chesebro Creek	22.71	µg/L	209.75	g	27.86	g/km2
Nickel	Cristianitos Creek	34.37	µg/L	5081.27	g	103.93	g/km2
Nickel	Santiago Creek	0.27	µg/L	66.06	g	3.85	g/km2
Nickel	Bell Creek	1.66	µg/L	55.73	g	3.06	g/km2
Nickel	Silverado Creek	1.35	µg/L	444.08	g	26.34	g/km2
Nickel	Mill Creek	0.02	µg/L	0.40	g	0.03	g/km2
Nickel	Fry Creek	0.01	µg/L	0.05	g	0.08	g/km2
Nickel	Piru Creek	5.76	µg/L	4702.39	g	9.84	g/km2
Nickel	Sespe Creek	5.36	µg/L	6781.00	g	52.79	g/km2
Nickel	Bear Creek Matilija	0.49	µg/L	72.32	g	7.46	g/km2
Nickel	Runkle Canyon	35.87	µg/L	999.84	g	293.21	g/km2
Nickel	Tenaja Creek	1.21	µg/L	70.28	g	1.33	g/km2
Nickel	Arroyo Sequit	14.78	µg/L	661.25	g	24.14	g/km2
Nitrate+Nitrite	Arroyo Seco	0.47	mg/L	91.24	kg	2.10	kg/km2
Nitrate+Nitrite	Bear Creek WFSGR	0.13	mg/L	133.65	kg	1.19	kg/km2
Nitrate+Nitrite	Cattle Creek EFSGR	0.52	mg/L	43.21	kg	0.88	kg/km2
Nitrate+Nitrite	Coldbrook NFSGR	0.54	mg/L	24.81	kg	1.65	kg/km2
Nitrate+Nitrite	Chesebro Creek	1.65	mg/L	15.25	kg	2.02	kg/km2
Nitrate+Nitrite	Cristianitos Creek	1.25	mg/L	184.30	kg	3.77	kg/km2
Nitrate+Nitrite	Santiago Creek	0.23	mg/L	33.05	kg	1.93	kg/km2
Nitrate+Nitrite	Bell Creek	0.47	mg/L	14.84	kg	0.81	kg/km2
Nitrate+Nitrite	Silverado Creek	0.23	mg/L	41.44	kg	2.46	kg/km2
Nitrate+Nitrite	Mill Creek	0.26	mg/L	5.00	kg	0.32	kg/km2
Nitrate+Nitrite	Fry Creek	0.01	mg/L	0.05	kg	0.07	kg/km2
Nitrate+Nitrite	Piru Creek	0.17	mg/L	141.63	kg	0.30	kg/km2
Nitrate+Nitrite	Sespe Creek	0.25	mg/L	321.99	kg	2.51	kg/km2
Nitrate+Nitrite	Bear Creek Matilija	0.27	mg/L	40.71	kg	4.20	kg/km2
Nitrate+Nitrite	Runkle Canyon	3.76	mg/L	78.57	kg	23.04	kg/km2
Nitrate+Nitrite	Tenaja Creek	0.27	mg/L	29.88	kg	0.57	kg/km2
Nitrate+Nitrite	Arroyo Sequit	2.03	mg/L	40.06	kg	1.46	kg/km2

Table 6. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Orthophosphate	Arroyo Seco	0.08	mg/L	4.08	kg	0.09	kg/km2
Orthophosphate	Bear Creek WFSGR	0.00	mg/L	3.94	kg	0.04	kg/km2
Orthophosphate	Cattle Creek EFSGR	0.09	mg/L	9.56	kg	0.20	kg/km2
Orthophosphate	Coldbrook NFSGR	0.00	mg/L	0.27	kg	0.02	kg/km2
Orthophosphate	Chesebro Creek	0.43	mg/L	3.99	kg	0.53	kg/km2
Orthophosphate	Cristianitos Creek	0.11	mg/L	16.51	kg	0.34	kg/km2
Orthophosphate	Santiago Creek	0.01	mg/L	1.84	kg	0.11	kg/km2
Orthophosphate	Bell Creek	0.05	mg/L	1.30	kg	0.07	kg/km2
Orthophosphate	Silverado Creek	0.02	mg/L	4.04	kg	0.24	kg/km2
Orthophosphate	Mill Creek	0.01	mg/L	0.14	kg	0.01	kg/km2
Orthophosphate	Fry Creek	0.04	mg/L	0.13	kg	0.21	kg/km2
Orthophosphate	Piru Creek	0.06	mg/L	45.62	kg	0.10	kg/km2
Orthophosphate	Sespe Creek	0.06	mg/L	69.66	kg	0.54	kg/km2
Orthophosphate	Bear Creek Matilija	0.05	mg/L	7.51	kg	0.77	kg/km2
Orthophosphate	Runkle Canyon	0.16	mg/L	4.90	kg	1.44	kg/km2
Orthophosphate	Tenaja Creek	0.11	mg/L	8.66	kg	0.16	kg/km2
Orthophosphate	Arroyo Sequit	0.09	mg/L	9.49	kg	0.35	kg/km2
Selenium	Arroyo Seco	0.52	µg/L	69.13	g	1.59	g/km2
Selenium	Bear Creek WFSGR	0.02	µg/L	16.13	g	0.14	g/km2
Selenium	Cattle Creek EFSGR	0.33	µg/L	41.66	g	0.85	g/km2
Selenium	Coldbrook NFSGR	0.31	µg/L	9.82	g	0.65	g/km2
Selenium	Chesebro Creek	4.88	µg/L	45.06	g	5.98	g/km2
Selenium	Cristianitos Creek	2.53	µg/L	373.58	g	7.64	g/km2
Selenium	Santiago Creek	1.04	µg/L	282.35	g	16.47	g/km2
Selenium	Bell Creek	1.40	µg/L	45.37	g	2.49	g/km2
Selenium	Silverado Creek	4.01	µg/L	1491.95	g	88.49	g/km2
Selenium	Mill Creek	0.04	µg/L	0.81	g	0.05	g/km2
Selenium	Fry Creek	0.19	µg/L	0.87	g	1.35	g/km2
Selenium	Piru Creek	0.53	µg/L	431.11	g	0.90	g/km2
Selenium	Sespe Creek	0.69	µg/L	874.74	g	6.81	g/km2
Selenium	Bear Creek Matilija	0.19	µg/L	28.45	g	2.93	g/km2
Selenium	Runkle Canyon	0.53	µg/L	17.22	g	5.05	g/km2
Selenium	Tenaja Creek	0.50	µg/L	47.69	g	0.90	g/km2
Selenium	Arroyo Sequit	0.17	µg/L	11.74	g	0.43	g/km2

Table 7. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Total Dissolved Solids	Arroyo Seco	401.52	mg/L	107251.82	kg	2467.26	kg/km2
Total Dissolved Solids	Bear Creek WFSGR	71.81	mg/L	75492.03	kg	672.06	kg/km2
Total Dissolved Solids	Cattle Creek EFSGR	176.54	mg/L	11813.97	kg	241.45	kg/km2
Total Dissolved Solids	Coldbrook NFSGR	1152.48	mg/L	83407.46	kg	5549.40	kg/km2
Total Dissolved Solids	Chesebro Creek	504.78	mg/L	4661.38	kg	619.04	kg/km2
Total Dissolved Solids	Cristianitos Creek	108.60	mg/L	16055.98	kg	328.41	kg/km2
Total Dissolved Solids	Santiago Creek	334.96	mg/L	33064.48	kg	1929.08	kg/km2
Total Dissolved Solids	Bell Creek	338.24	mg/L	8092.33	kg	443.90	kg/km2
Total Dissolved Solids	Silverado Creek	667.83	mg/L	101408.36	kg	6014.73	kg/km2
Total Dissolved Solids	Mill Creek	131.22	mg/L	2481.82	kg	157.08	kg/km2
Total Dissolved Solids	Fry Creek	96.98	mg/L	366.78	kg	573.09	kg/km2
Total Dissolved Solids	Sespe Creek	417.54	mg/L	528357.23	kg	4113.01	kg/km2
Total Dissolved Solids	Bear Creek Matilija	327.80	mg/L	48837.54	kg	5034.80	kg/km2
Total Dissolved Solids	Runkle Canyon	227.03	mg/L	6164.17	kg	1807.67	kg/km2
Total Dissolved Solids	Tenaja Creek	349.11	mg/L	35083.64	kg	664.71	kg/km2
Total Dissolved Solids	Arroyo Sequit	173.77	mg/L	47593.68	kg	1737.63	kg/km2
Total Kjeldahl Nitrogen	Arroyo Seco	1.76	mg/L	597.72	kg	13.75	kg/km2
Total Kjeldahl Nitrogen	Bear Creek WFSGR	0.89	mg/L	938.63	kg	8.36	kg/km2
Total Kjeldahl Nitrogen	Cattle Creek EFSGR	0.88	mg/L	1.10	kg	0.02	kg/km2
Total Kjeldahl Nitrogen	Coldbrook NFSGR	0.73	mg/L	53.11	kg	3.53	kg/km2
Total Kjeldahl Nitrogen	Santiago Creek	0.78	mg/L	9.73	kg	0.57	kg/km2
Total Kjeldahl Nitrogen	Bell Creek	1.31	mg/L	26.36	kg	1.45	kg/km2
Total Kjeldahl Nitrogen	Silverado Creek	0.91	mg/L	11.27	kg	0.67	kg/km2
Total Kjeldahl Nitrogen	Mill Creek	1.26	mg/L	23.88	kg	1.51	kg/km2
Total Kjeldahl Nitrogen	Fry Creek	1.20	mg/L	3.82	kg	5.98	kg/km2
Total Kjeldahl Nitrogen	Piru Creek	2.18	mg/L	1776.08	kg	3.72	kg/km2
Total Kjeldahl Nitrogen	Sespe Creek	3.07	mg/L	3881.31	kg	30.21	kg/km2
Total Kjeldahl Nitrogen	Bear Creek Matilija	1.36	mg/L	202.88	kg	20.92	kg/km2
Total Kjeldahl Nitrogen	Tenaja Creek	1.29	mg/L	214.38	kg	4.06	kg/km2
Total Kjeldahl Nitrogen	Arroyo Sequit	1.80	mg/L	574.96	kg	20.99	kg/km2

Table 8. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Total Organic Carbon	Arroyo Seco	6.53	mg/L	1939.51	kg	44.62	kg/km2
Total Organic Carbon	Bear Creek WFSGR	7.92	mg/L	8322.18	kg	74.09	kg/km2
Total Organic Carbon	Cattle Creek EFSGR	2.45	mg/L	109.39	kg	2.24	kg/km2
Total Organic Carbon	Coldbrook NFSGR	3.08	mg/L	153.80	kg	10.23	kg/km2
Total Organic Carbon	Santiago Creek	3.22	mg/L	26.89	kg	1.57	kg/km2
Total Organic Carbon	Bell Creek	4.18	mg/L	84.25	kg	4.62	kg/km2
Total Organic Carbon	Silverado Creek	6.46	mg/L	79.77	kg	4.73	kg/km2
Total Organic Carbon	Mill Creek	44.49	mg/L	841.56	kg	53.26	kg/km2
Total Organic Carbon	Fry Creek	76.04	mg/L	241.48	kg	377.32	kg/km2
Total Organic Carbon	Piru Creek	6.71	mg/L	5479.83	kg	11.47	kg/km2
Total Organic Carbon	Sespe Creek	6.66	mg/L	8430.79	kg	65.63	kg/km2
Total Organic Carbon	Bear Creek Matilija	6.33	mg/L	943.63	kg	97.28	kg/km2
Total Organic Carbon	Tenaja Creek	6.01	mg/L	659.92	kg	12.50	kg/km2
Total Organic Carbon	Arroyo Sequit	22.05	mg/L	7037.25	kg	256.93	kg/km2
Total Phosphorus	Arroyo Seco	0.01	mg/L	0.14	kg	0.00	kg/km2
Total Phosphorus	Cattle Creek EFSGR	0.02	mg/L	0.56	kg	0.01	kg/km2
Total Phosphorus	Coldbrook NFSGR	0.14	mg/L	8.09	kg	0.54	kg/km2
Total Phosphorus	Chesebro Creek	0.01	mg/L	0.07	kg	0.01	kg/km2
Total Phosphorus	Cristianitos Creek	0.02	mg/L	2.66	kg	0.05	kg/km2
Total Phosphorus	Santiago Creek	0.06	mg/L	1.64	kg	0.10	kg/km2
Total Phosphorus	Bell Creek	0.12	mg/L	2.40	kg	0.13	kg/km2
Total Phosphorus	Silverado Creek	0.14	mg/L	3.40	kg	0.20	kg/km2
Total Phosphorus	Mill Creek	0.05	mg/L	0.87	kg	0.06	kg/km2
Total Phosphorus	Fry Creek	0.12	mg/L	0.45	kg	0.70	kg/km2
Total Phosphorus	Runkle Canyon	0.01	mg/L	0.18	kg	0.05	kg/km2
Total Phosphorus	Tenaja Creek	0.18	mg/L	7.74	kg	0.15	kg/km2
Total Phosphorus	Arroyo Sequit	0.09	mg/L	1.71	kg	0.06	kg/km2

Table 9. Wet-weather concentrations, loads, and fluxes for each study site

Parameter	SiteName	FWMC	Unit	Load	Unit	Flux	Unit
Total Suspended Solids	Arroyo Seco	107.03	mg/L	12054.09	kg	277.30	kg/km2
Total Suspended Solids	Bear Creek WFSGR	6.29	mg/L	6616.49	kg	58.90	kg/km2
Total Suspended Solids	Cattle Creek EFSGR	223.76	mg/L	3728.27	kg	76.20	kg/km2
Total Suspended Solids	Coldbrook NFSGR	54.25	mg/L	3926.55	kg	261.25	kg/km2
Total Suspended Solids	Chesebro Creek	200.85	mg/L	1854.69	kg	246.31	kg/km2
Total Suspended Solids	Cristianitos Creek	4689.18	mg/L	693250.13	kg	14179.79	kg/km2
Total Suspended Solids	Santiago Creek	13.97	mg/L	417.79	kg	24.38	kg/km2
Total Suspended Solids	Bell Creek	95.09	mg/L	3020.85	kg	165.71	kg/km2
Total Suspended Solids	Silverado Creek	38.70	mg/L	3105.45	kg	184.19	kg/km2
Total Suspended Solids	Mill Creek	0.25	mg/L	4.73	kg	0.30	kg/km2
Total Suspended Solids	Fry Creek	11.08	mg/L	39.18	kg	61.22	kg/km2
Total Suspended Solids	Piru Creek	5454.92	mg/L	4454023.04	kg	9323.31	kg/km2
Total Suspended Solids	Sespe Creek	51969.43	mg/L	65762315.29	kg	511928.35	kg/km2
Total Suspended Solids	Bear Creek Matilija	242.25	mg/L	36092.15	kg	3720.84	kg/km2
Total Suspended Solids	Runkle Canyon	2375.17	mg/L	43860.43	kg	12862.30	kg/km2
Total Suspended Solids	Tenaja Creek	184.15	mg/L	16357.92	kg	309.93	kg/km2
Total Suspended Solids	Arroyo Sequit	461.24	mg/L	147232.56	kg	5375.41	kg/km2
Zinc	Arroyo Seco	12.64	µg/L	833.40	g	19.17	g/km2
Zinc	Bear Creek WFSGR	0.25	µg/L	263.01	g	2.34	g/km2
Zinc	Cattle Creek EFSGR	2.05	µg/L	171.23	g	3.50	g/km2
Zinc	Coldbrook NFSGR	13.98	µg/L	450.27	g	29.96	g/km2
Zinc	Chesebro Creek	38.66	µg/L	357.03	g	47.41	g/km2
Zinc	Cristianitos Creek	204.32	µg/L	30206.40	g	617.84	g/km2
Zinc	Santiago Creek	1.46	µg/L	365.47	g	21.32	g/km2
Zinc	Bell Creek	10.03	µg/L	337.20	g	18.50	g/km2
Zinc	Silverado Creek	13.29	µg/L	4272.08	g	253.39	g/km2
Zinc	Mill Creek	0.06	µg/L	1.07	g	0.07	g/km2
Zinc	Fry Creek	1.74	µg/L	7.64	g	11.93	g/km2
Zinc	Piru Creek	16.11	µg/L	13151.22	g	27.53	g/km2
Zinc	Sespe Creek	14.35	µg/L	18163.98	g	141.40	g/km2
Zinc	Bear Creek Matilija	1.34	µg/L	199.69	g	20.59	g/km2
Zinc	Runkle Canyon	182.85	µg/L	5129.84	g	1504.35	g/km2
Zinc	Tenaja Creek	12.50	µg/L	641.19	g	12.15	g/km2
Zinc	Arroyo Sequit	12.10	µg/L	699.22	g	25.53	g/km2