COUNTY OF LOS ANGELES

DEPARTMENT OF PUBLIC WORKS

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R E C E I V E D
8-24-11
SWRCB Clerk

August 24, 2011

Mr. Gaylon Lee
Division of Water Quality
State Water Resources Control Board
1001 I Street, 15th Floor
Sacramento, CA 95814

Dear Mr. Lee.

COMMENT RE: USFS SERVICE WAIVER

Thank you for the opportunity to comment on the Draft Statewide Conditional Waiver of Waste Discharge Requirements for nonpoint source discharges related to certain activities on National Forest System Lands in California. We hereby submit the enclosed comments on behalf of the Los Angeles County Flood Control District.

We look forward to your consideration of these comments. If you have any questions, please contact me at (626) 458-4300 or ghildeb@dpw.lacounty.gov or your staff may contact Ms. Angela George at (626) 458-4325 or ageorge@dpw.lacounty.gov

Very truly yours,

GAIL FARBER
Director of Public Works

GARY HILDEBRAND
Assistant Deputy Director
Watershed Management Division

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Enc.

COMMENTS OF THE LOS ANGELES COUNTY FLOOD CONTROL DISTRICT ON THE DRAFT STATEWIDE CONDITIONAL WAIVER OF WASTE DISCHARGE REQUIREMENTS FOR NONPOINT SOURCE DISCHARGES RELATED TO CERTAIN ACTIVITIES ON NATIONAL FOREST SYSTEM LANDS IN CALIFORNIA

The Los Angeles County Flood Control District ("LACFCD") appreciates the opportunity to comment on the Draft Statewide Conditional Waiver ("Conditional Waiver") of Waste Discharge Requirements for Nonpoint Source Discharges related to certain activities in National Forest System (NFS) lands in California. This is an issue of particular significance in Los Angeles County, as NFS lands administered by the United States Department of Agriculture Forest Service ("USFS") are located in three major watersheds in the urbanized area of the County Runoff from the national forests flows directly into the Los Angeles, San Gabriel and Santa Clara Rivers and their tributaries, and in many cases, into improved channels operated by the LACFCD as part of the municipal separate storm sewer system ("MS4"). The waters into which discharges from NFS land flow are subject to the Los Angeles Region Water Quality Control Plan ("Basin Plan").

NFS land contributes a significant amount of runoff into the downstream network of flood control channels and receiving waterbodies. Within Los Angeles County alone, the Angeles National Forest comprises 664,815 acres,[1] which accounts for approximately 25% of the entire land area of the County In the Los Angeles River watershed, NFS land in the Angeles National Forest constitutes 28% of the total watershed area In the San Gabriel and Santa Clara River watersheds, NFS land comprises 38% and 42%, respectively, of the watershed areas.

Additionally, various studies[2,3,4,5] have shown that NFS land contributes a significant portion of pollutants, including bacteria, metals, nutrients, pesticides, sediments, and trash, that ultimately are discharged into the Los Angeles, San Gabriel, and Santa Clara Rivers. All studies cited in these comments are being submitted separately for inclusion in the administrative record, and a copy of the studies will be provided in a Compact Disc.

We note that either the USFS or the Angeles National Forest has been named as a responsible party and has been assigned load allocations in the following Total Maximum Daily Loads ("TMDL"): Los Angeles River Bacteria; Elizabeth Lake and Lake Hughes Trash; and East Fork San Gabriel River Trash The Angeles National Forest has been named as a responsible party and assigned wasteload allocations in the

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[1] http://planning.lacounty.gov/assets/upl/project/gp_web-ch06.pdf
[2] Eric D Stein and Vada K. Yoon (2007): Assessment of Water Quality Concentrations and Loads from Natural Landscapes. Southern California Coastal Research Project, Technical Report 500
[3] T Meixner and P Wohlgemuth (2004): Wildfire Impacts on Water Quality Southwest Hydrology
[4] Bitner et al. (2001): Review of Wildfire Effects on Chemical Water Quality. Los Alamos National Laboratory, New Mexico.
[5] Smith et al. (2011): Wildfire Effects on Water Quality in Forest Catchments: A Review with Implications for Water Supply Journal of Hydrology 396:170-192

following proposed TMDLs: Peck Road Park Lake Nutrients and Toxic Pollutants and Puddingstone Reservoir Nutrients, Mercury, and Toxic Pollutants. Further, Crystal Lake and Monrovia Creek, both located in NFS land, are listed as impaired waterbodies in the Clean Water Act 303(d) list for the Los Angeles Region.

Thus, it would be incorrect for the State Water Resources Control Board ("State Board") to conclude that discharges from the NFS lands have only a "potentially low or moderate impact on water quality" as State Board staff has proposed in the draft Conditional Waiver.[6] The LACFCD and other permittees under the Los Angeles County MS4 permit ("Permit") must have some assurance that discharges from NFS lands are accounted for, and as necessary, mitigated by Best Management Practices ("BMP") that are the sole responsibility of the USFS, since none of the municipalities regulated under the Permit, including the LACFCD, has jurisdiction over such discharges. In addition, the permittees under the Permit do not have responsibility for addressing these pollutants, as the responsibility to coordinate with federal agencies to implement programs addressing discharges that affect downstream MS4s and water bodies was specifically assumed by the Los Angeles Regional Water Quality Control Board (Regional Board) in the Permit:

> Federal . . . entities within the Permittees' boundaries or in jurisdictions outside the Los Angeles County Flood Control District, and not currently named in this Order, may operate storm drain facilities and/or discharge storm water to storm drains and watercourses covered by this Order. The Permittees may lack legal jurisdiction over these entities under state and federal constitutions. *The Regional Board will coordinate with these entities to implement programs that are consistent with the requirements of this Order*[7]

Because of this specific commitment (which, to the LACFCD's knowledge, has not been met by the Regional Board), it would be inappropriate for the State Board to issue to the NFS a waiver of waste discharge requirements without including conditions sufficient to ensure that the discharge of storm water from NFS land does not cause or contribute to a violation of water quality standards in the downgradient waterbodies covered by the Permit.

In light of these facts, the LACFCD hereby requests that the Conditional Waiver not cover discharges from those NFS lands which discharge into the urban watersheds of Los Angeles County, including into the Los Angeles, San Gabriel and Santa Clara River watersheds. Such discharges should either be covered by a specific WDR issued by the Regional Board or by a WDR waiver issued by the Regional Board, in either case containing conditions that are specific to, and protective of, the beneficial uses of the waters in the County.

If the State Board still believes that a statewide waiver is appropriate and should encompass NFS land in Los Angeles County, the Conditional Waiver as proposed does

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[6] Proposed Conditional Waiver, Finding No. 5
[7] Los Angeles County MS4 Permit, Finding D.2 (emphasis added)

not fully address the potential impact of the covered activities within those lands on the water quality of downstream waterbodies in Los Angeles County Unless properly regulated, these activities may affect the ability of downstream MS4 operators to comply with water quality standards and render the Permit impossible to comply with. Our specific comments, which focus on discharges from NFS land in Los Angeles County, are presented below

1. **Discharges from NFS Land Should Meet Water Quality Standards and Should be Routinely Monitored**

   The Conditional Waiver appears to provide for limited water quality monitoring, such as for bacteria and nutrients from range lands. The LACFCD is concerned that the monitoring requirements in the Conditional Waiver as proposed are deficient, because the activities covered under the Waiver potentially generate a variety of pollutants, including bacteria, nutrients, pesticides, metals, solids, and trash. Such discharges, flowing through streams in the NFS lands, eventually enter the LACFCD's MS4 system and may cause or contribute to violations of water quality standards in the Los Angeles, San Gabriel and Santa Clara Rivers. As noted in our general comments above, the USFS or the Angeles National Forest is a responsible party for TMDLs or proposed TMDLs that cover several categories of pollutants, including trash, nutrients, mercury, bacteria and toxic pollutants.

   The LACFCD believes that the monitoring program proposed by the Conditional Waiver does not require the collection of sufficient information to ascertain whether discharges from NFS land are contributing pollutant loading to downstream MS4 systems or are causing or contributing to exceedances of water quality standards in receiving waters. With respect to Los Angeles County, the Conditional Waiver monitoring program should characterize discharges from NFS land, both to assess the overall contribution of such land to water quality and the effectiveness of BMPs, and because downstream municipal stormwater dischargers are being held responsible for pollutants in their storm drain systems, including pollutants that originate from NFS land

   The Conditional Waiver should therefore be revised to provide that discharges from covered activities on NFS lands must meet applicable water quality standards in downstream receiving waters. Further, the monitoring program should be revised so that sufficient data can be collected to fully characterize the quality of such discharges to ensure that the conditions of the Waiver are being met. The water quality monitoring program should include:

   - Monitoring for the full suite of pollutants, including but not limited, to bacteria, nutrients, pesticides, metals, solids, and trash;
   - Conducting toxicity tests using approved test species for freshwater;
   - Sampling frequency sufficient to characterize pollutant loading during dry and wet weather;

- Sampling at major representative discharge points on NFS land; and
- Annual water quality data analysis and reporting.

For NFS land within Los Angeles County, the LACFCD has attached as Exhibit A a proposed monitoring program, including monitoring locations, frequencies, and pollutant types for USFS to monitor discharges from NFS land into waterbodies in the Los Angeles, San Gabriel and Santa Clara River watersheds. These proposed monitoring locations are identified only for major streams that receive discharge from NFS land. The proposed monitoring program also requires annual reporting to the State Board and the Regional Board, with a copy provided to the LACFCD, so that the information can be evaluated and provided to other MS4 dischargers. The scope of the program proposed in Exhibit A is what we believe is necessary to adequately characterize dry and wet weather runoff from NFS lands.

2. The Conditional Waiver Should Have Specific Requirements for the Attainment of TMDLs

As noted above, the USFS or Angeles National Forest is listed as a responsible party in TMDLs and proposed TMDLs covering a variety of pollutants, including bacteria, nutrients, trash and toxic pollutants (Mercury, PCBs, Chlordane, Dieldrin, and DDT). In some TMDLs, the USFS or the Forest has been assigned load allocations as a nonpoint source generator of these pollutants while in others, the Forest has been assigned wasteload allocations as a point source discharger

The Conditional Waiver requires that nonpoint source activities covered by the waiver be consistent with any Basin Plan. This necessarily includes adopted TMDLs, which are incorporated into such plans. The Initial Study and Proposed Mitigated Negative Declaration states (at p. 15) that the proposed Conditional Waiver "requires compliance with all applicable TMDL implementation plans, while compliance with Waiver conditions would be considered to be compliance with those TMDLs without TMDL implementation plans." Compliance with all applicable adopted TMDLs and TMDL implementation plans is therefore required by the waiver.

A review of the Conditional Waiver itself, however, does not disclose any express reference to TMDL compliance or any language that would suggest that the waiver requires compliance with TMDL implementation plans. The Waiver merely states that it is "structured to ensure" that discharges from certain NPS activities on NFS lands comply with "[r]equirements implementing the CWA, especially section 303(d).[8] Also, the Conditional Waiver does not reference in its findings the specific TMDLs applicable to the urban watersheds of Los Angeles County for which the USFS or the Angeles National Forest is a responsible party

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[8] Conditional Waiver at 12, paragraph 33.

As a consequence, from our review of the Conditional Waiver and associated documents, including the draft Water Quality Management Handbook ("WQMH") prepared by the USFS, there does not appear to be any specific undertaking by the USFS to reach attainment with load allocations or wasteload allocations at any TMDLs applicable to NFS land or to comply with any implementation plans for such TMDLs.

Moreover, Chapter 7 of the proposed WQMH addresses TMDL implementation, but it does not contain specific requirements for the USFS to comply with TMDL implementation plans or otherwise to achieve load allocations or wasteload allocations for specific TMDLs.

We therefore request that the Conditional Waiver be modified to provide specifically for compliance with all applicable TMDL implementation plans, including the attainment of load allocations and wasteload allocations.

Further, because the completion of an adequate WQMH is a condition of the waiver, and because the State Board and the USFS are collaborating on the development of the WQMH, the LACFCD encourages State Board staff to work with the USFS to ensure that the WQMH fully addresses the responsibility of the USFS to implement applicable TMDLs, including the attainment of all applicable load allocations and waste load allocations and any associated monitoring requirements.

EXHIBIT A

Proposed Monitoring and Reporting Program Framework for National Forest System Lands within the County of Los Angeles

This Monitoring and Reporting Program Framework is designed to address the following key questions:

Question #1· Do discharges from National Forest System (NFS) land in Los Angeles County covered by State Water Resources Control Board Order No ___, Waiver of Waste Discharge Requirements for Nonpoint Source Discharges Related to Certain Activities on National Forest System Lands in California ("Conditional Waiver"), contribute pollutant loading to downstream receiving waters such that applicable water quality standards are exceeded?

Question #2: Do discharges from NFS land in Los Angeles County comply with the requirements of the Conditional Waiver, including achieving applicable water quality standards?

Question #3: Are additional best management practices (BMPs) and/or other controls required on NFS land in Los Angeles County so that discharges meet applicable water quality standards?

The requirements of this Monitoring and Reporting Program are to be met by the United States Department of Agriculture Forest Service (USFS) or its authorized representatives.

I. MONITORING LOCATIONS

A. Thirteen (13) monitoring locations are required to characterize the major discharge points from NFS land to downstream waterbodies, including municipal separate storm sewer system (MS4) channels (see locations on attached Figure 1).

B. Monitoring can be done on a rotating basis (i.e. 3-4 stations per year for a 4-year cycle or 6-7 stations over a 2 year cycle).

C. In addition to any required sampling frequency, following a forest fire, all monitoring locations in watersheds affected by the fire shall be sampled for a

minimum of one year following the fire event to evaluate any changes in post-fire water quality.

II. SAMPLING AND ANALYSIS

A. Samples shall be collected from the receiving water during two storm events and two dry weather events every year The first storm event during each year's storm season should be sampled.

B. At a minimum, samples shall be analyzed for the pollutants listed in the attached Table 1 If, after five years of monitoring, one or more of the pollutants has not been detected in the sampling, such pollutants may no longer be monitored.

C. Toxicity testing shall be conducted using test species appropriate for evaluating freshwater chronic toxicity (e.g., *Ceriodaphnia dubia* survival/reproduction).

D. Samples shall be collected and analyzed using approved sampling and laboratory analysis methods.

III. REPORTING REQUIREMENTS

A. USFS shall prepare a report (Monitoring Report) summarizing the results of all monitoring conducted hereunder, including all analytical data, results, methods of evaluating the data, graphical summaries of the data, and an explanation/discussion of the data for each component of the monitoring program.

B. The Monitoring Report shall analyze and discuss any water quality problems disclosed by the monitoring, including discharges which cause or contribute to the exceedance of applicable water quality standards, the potential sources of such exceedances and recommending, if applicable, future monitoring and BMPs to identify and address the sources of the exceedances.

C. No later than August 15, 2013, and annually on August 15 thereafter, USFS shall submit the Monitoring Report to the State Water Resources Control Board and the Los Angeles Regional Water Quality Control Board, with a copy to the Los Angeles County Flood Control District. Each annual report shall emphasize on activities and data collected during the previous fiscal year (July 1 to June 30) as well as evaluation of long-term trends. The Monitoring Reports may be submitted in either paper or electronic format.

Table 1: Minimum list of constituents to be analyzed for National Forest System Lands within the County of Los Angeles.

Pollutant Class	Constituent/ Parameter	Units	EPA's Analytical Method	Sampling Method	Minimum Sampling Frequency
Conventional	Temperature pH SpConductance Dissolved Oxygen	°C Number µmhos/cm mg/L	SM4500H B SM2130B SM4500O G	Grab	2 dry weather events and 2 storm events (first storm of the season and another storm)
Bacteria	E. coli Enterococcus	MPN MPN	SM9230B	Grab	
Nutrients	Ammonia (NH3-N) Nitrate-N Nitrite-N Kjeldahl-N Total Phosphorus	mg/L mg/L mg/L mg/L mg/L	SM4500-NH3 SM4110B SM4110B SM4500NHorg SM4500-PE	Grab/ Composite[1]	
Solids	TSS TDS Turbidity Hardness	mg/L mg/L NTU mg/L	SM2540D SM2540C SM2510B SM2340C	Grab/ Composite[1]	
Metals (Dissolved and Total)	Aluminum Cadmium Copper Chromium Iron Lead Mercury Selenium Zinc	µg/L µg/L µg/L µg/L µg/L µg/L µg/L µg/L µg/L	EPA200.8	Grab/ Composite[1]	
Organics	Total DDTs Chlordane Dieldrin Total PCBs Total PAHs Pyrethroids	µg/L µg/L µg/L µg/L µg/L	EPA608 EPA608 EPA608 EPA608 EPA625	Grab/ Composite[1]	
Others	Cyanide Sulfate	mg/L mg/L	SM4500-CNE SM4110B	Grab/ Composite[1]	
Toxicity	Chronic Toxicity	Pass/fail		Grab/ Composite[1]	
Trash	Trash/Debris	NA	NA	Visual observation and pictures	Every sampling event

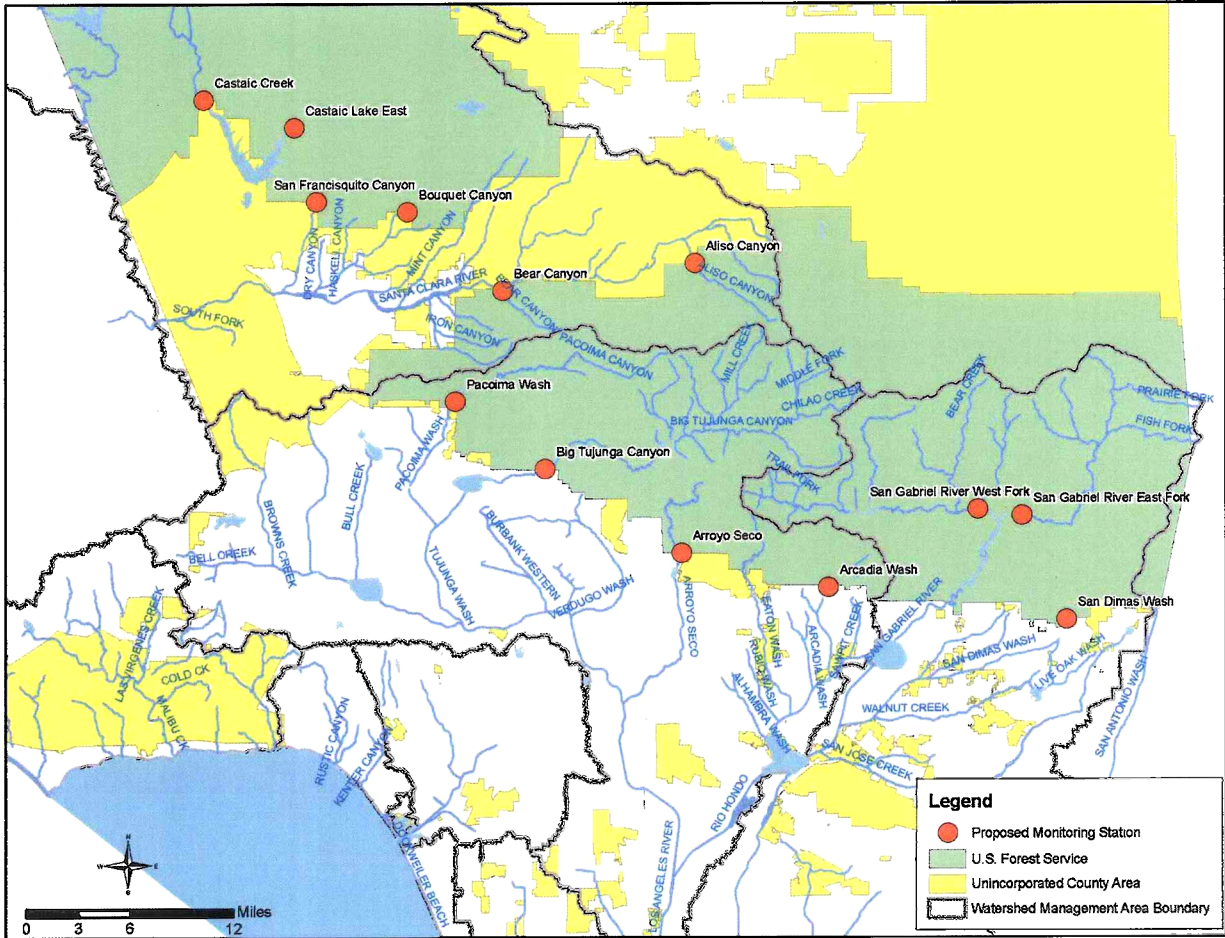[1] Grab sampling for dry weather, composite sampling for wet weather events.

Figure 1: Proposed Water Quality Monitoring Locations for National Forest System Land in County of Los Angeles.

Wildfire Impacts on Water Quality

Tom Meixner, Ph.D. – *University of California, Riverside Department of Environmental Sciences and* **Pete Wohlgemuth** – *United States Forest Service, Pacific Southwest Research Station, Riverside Fire Laboratory*

Much of the attention paid to wildfire and its impacts on the hydrologic cycle focuses on increased danger from flooding and mudslides during the immediate post-fire period. While threats to human health and safety posed by floods, debris flows, and mudslides certainly cause the greatest concern, water quality impacts and their associated risks are nonetheless critical for water utilities and regulatory agencies to address. Important questions are:

- What impact does wildfire have on surface water quality?
- How long does the impact last?
- How far away from burned areas can water quality impacts be felt?
- What beneficial uses can be affected by the changes in water quality induced by wildfire?
- How can adverse impacts of wildfire on water quality be prevented, mitigated, or otherwise minimized?

The quality of surface waters can be examined in terms of physical, chemical, and biological characteristics. Here we consider only the impacts of fire on physical and chemical water properties, based on research in the coniferous forests and chaparral watersheds of California. Biological impacts are inferred from the changes in the physical and chemical properties of surface waters.

Physical Impacts on Water Quality

Most impacts on the physical characteristics of fire-impacted streams are evidenced by changes in sediment load. Increased sediment flows following a fire can impact both ecological health and drinking water operations. The large quantities of post-fire sediment can overwhelm the biological habitat available for aquatic organisms such as fish, as well as organisms that depend on water for some life stage, such as amphibians and insects. This problem of habitat disturbance after a fire has motivated the U.S. Fish and Wildlife Service, the Forest Service, and the Park Service to focus on habitat protection and removal of threatened and endangered species from riparian systems following severe wildfires in Arizona and California.

Large post-fire sediment fluxes impact drinking water systems two ways. First and perhaps foremost is the danger that reservoirs, infiltration basins, and treatment works will be filled, damaged, or otherwise disrupted by sediment. Second, high sediment load is likely to increase pre-treatment processing needs (and costs) for suspended sediment removal. These impacts are highest in areas immediately adjacent to fires. However, as recently
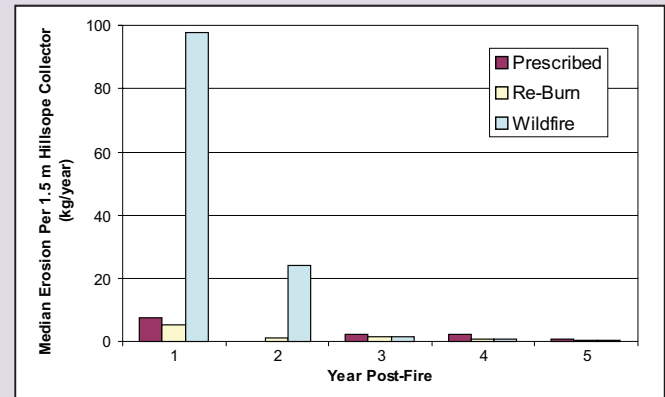
Post-fire sediment load data from the Santa Monica Mountains of Southern California. The prescribed fire occurred in 1988 and data for that fire represent the five years following that fire. The re-burn data are for the same locations as the prescribed fire data except following a wildfire that burned the entire watershed in 1993. The wildfire data are for sites that did not burn in 1988 but did burn in 1993 (from Wohlgemuth et al., 1999).

documented by the Santa Ana Watershed Project Authority (www.sawpa.org), after the fall 2003 wildfires in Southern California, treatment works and reservoirs as far as 100 miles from the fire can be affected by increased sediment loads, particularly in the suspended fraction.

Management techniques can mitigate damages from post-fire sediment export. Permanent and temporary debris basins can be constructed to catch sediment, and earth-moving operations can be performed periodically to clean out basins and maintain their capacity. These methods are expensive in terms of both capital construction costs and maintenance costs. Increasing the fire frequency in a given area through prescribed fires has also been found to reduce post-fire sediment export (see chart above). Loomis et al. (2003) showed that since frequent fire reduces overall sediment loads, Los Angles County could save more than $24 million in annual debris basin cleanout costs through the use of prescribed fires.
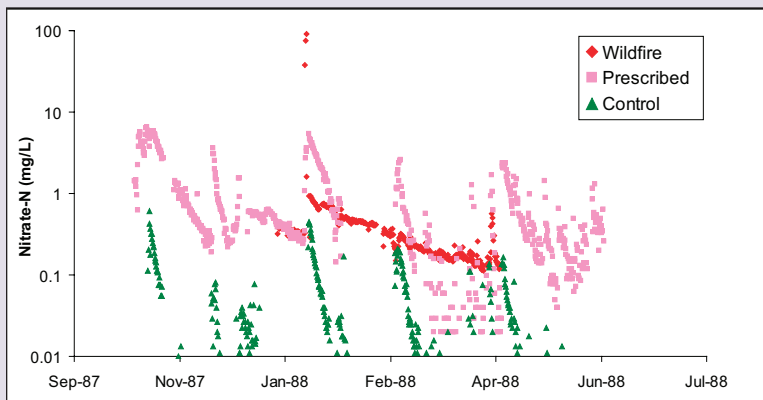
Chemical Water Quality

The impacts of wildfire and prescribed burns on chemical composition of streams are not well-documented, but studies suggest that nutrient loads, particularly phosphorus and nitrogen, increase after fires, and that the effect may be greater

Seasonal variation in nitrate-N concentrations for two burned watersheds (wildfire and prescribed) and one control watershed. The fires both occurred in fall 1984; these data represent the fourth wet season after that fire. The two burned watersheds still have significantly elevated Nitrate-N concentrations compared to the control watershed.
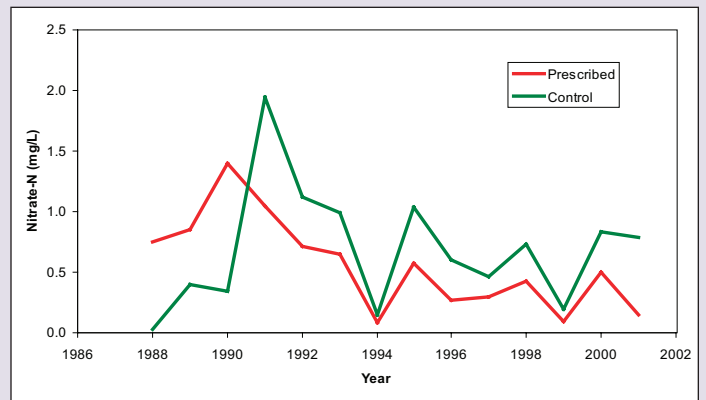
Long-term nitrate-N concentrations from the San Dimas Experimental Forest burn study of Riggan et al. (1994) and continuing data, following a prescribed fire in fall 1984. For the first seven years, concentrations were higher in the burned watershed; the trend reversed in 1991.

from wildfires than from prescribed burns. Phosphorus export increases after wildfires, and to a lesser extent after prescribed fires. Since phosphorus is carried primarily in the sediment load, most of the increase is due to higher post-fire erosion rates, although some phosphorus is concentrated in ash as well.

Nitrogen is exported primarily as nitrate, and post-fire concentrations can exceed the federal drinking water standard of 10 milligrams per liter. A key study on the impact of fire on nitrate export in chaparral ecosystems was conducted at the San Dimas Experimental Forest (SDEF) in Glendora, California by Riggan and others (1994). The study involved six watersheds: two were kept unburned as control watersheds, two were burned under typical prescribed conditions, and two were burned under simulated wildfire conditions. The initial data following the fire in the winter of 1985 showed an increase in nitrate export with an increase in fire severity. Results three years after the fire indicated that fire increased nitrate concentrations in streams during the post-fire period, to concentrations as much as 10 times the federal drinking water standard (see chart above left) and that severity was not as critical in the longer term. Long-term data from SDEF also show that elevated nitrate concentrations can persist for up to 10 years after a fire; however, nitrate concentrations in previously burned watersheds were lower than their unburned counterparts (see chart above right). Note that all watersheds at the San Dimas experimental forest have

elevated nitrate concentrations due to their proximity to the city of Los Angeles.

The effects of high nitrate concentrations on drinking water can spread beyond an area's immediate resources. Mountain areas of Southern California and elsewhere in the West provide what is generally considered the highest quality drinking water, which is often used to dilute drinking water resources impacted by industrial, urban, or agricultural activities. High nitrate concentrations in these "cleaner" waters can compromise the ability of water managers to control drinking water quality.

The results of the SDEF research suggest that wildfires may have a greater impact on water quality than prescribed fire; other studies have demonstrated the relatively benign effects of prescribed fire on water quality (Stephens et al., 2004; Richter et al., 1982). Taken together, these findings indicate that more frequent use of prescribed fire may have a beneficial impact on long-term water quality management in the western United States.

References . . . .

Loomis, J., P.W. Wohlgemuth, A. Gonzales-Caban, and D. Engligh, 2003. *Economic benefits of reducing fire-related sediment in southwestern fire-prone ecosystems, Water. Resour. Res., 39(9):WES 3-1-WES 3-8.*

Richter, D.D., C.W. Ralston, and W.R. Harms, 1982. *Prescribed fire: effects on water quality and forest nutrient cycling, Science, 215(4533): 661-663.*

Riggan, P.J., R.N. Lockwood, P.J. Jacks, C.G. Colver, F. Weirich, L.F. DeBano, and J.A. Brass, 1994. *Effects of fire severity on nitrate mobilization in watersheds subject to chronic atmospheric deposition, Environmental Science and Technology, 28: 369-375.*

Stephens, S.L., T. Meixner, M.A. Poth, B.J. McGurk, and D. Payne, 2004. *Prescribed fire, soils, and stream water chemistry in a watershed in the Lake Tahoe basin, California, International Journal of Wildland Fire, 13(1): 27-35.*

Wohlgemuth , P., J. Beyers, and S. Conard, 1999. *Postfire hillslope erosion in southern California chaparral: A case study of prescribed fire as a sediment management tool, in Proceedings of the Symposium on Fire Economics, Planning and Policy: Bottom Lines. April 5-9, 1999. San Diego, ed. by A. Gonzalez-Caban and P. N. Omi, pp. 269-276, Gen. Technical Report PSW-GTR-173 Pacific Southwest Research Station USDA- Forest Service, Riverside, CA.*

Review Paper

Wildfire effects on water quality in forest catchments: A review with implications for water supply

Hugh G. Smith [a,*], Gary J. Sheridan [a], Patrick N.J. Lane [a], Petter Nyman [a], Shane Haydon [b]

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ARTICLE INFO

SUMMARY

Wildfires burn extensive forest areas around the world each year. In many locations, fire-prone forest catchments are utilised for the supply of potable water to small communities up to large cities. Following wildfire, increased erosion rates and changes to runoff generation and pollutant sources may greatly increase fluxes of sediment, nutrients and other water quality constituents, potentially contaminating water supplies. Most research to date has focused on suspended sediment exports and concentrations after wildfire. Reported first year post-fire suspended sediment exports varied from 0.017 to 50 t ha^{-1} year^{-1} across a large range of catchment sizes (0.021–1655 km^2). This represented an estimated increase of 1–1459 times unburned exports. Maximum reported concentrations of total suspended solids in streams for the first year after fire ranged from 11 to $\sim$500,000 mg L^{-1}. Similarly, there was a large range in first year post-fire stream exports of total N (1.1–27 kg ha^{-1} year^{-1}) and total P (0.03–3.2 kg ha^{-1} year^{-1}), representing a multiple change of 0.3–431 times unburned, while NO$_3^-$ exports of 0.04–13.0 kg ha^{-1} year^{-1} (3–250 times unburned) have been reported. NO$_3^-$, NO$_2^-$, and NH$_3$/NH$_4^+$ concentrations in streams and lakes or reservoirs may increase after wildfire but appear to present a generally low risk of exceeding drinking water guidelines. Few studies have examined post-fire exports of trace elements. The limited observations of trace element concentrations in streams after wildfire found high levels (well over guidelines) of Fe, Mn, As, Cr, Al, Ba, and Pb, which were associated with highly elevated sediment concentrations. In contrast, Cu, Zn, and Hg were below or only slightly above guideline values. Elevated Na$^+$, Cl$^-$ and SO$_4^{2-}$ solute yields have been recorded soon after fire, while reports of concentrations of these constituents were mostly confined to coniferous forest areas in North America, where maximum sampled values were well below recommended limits. Likewise, reported wildfire effects on dissolved organic carbon were generally minor and elevated concentrations largely reflected background conditions. Available cyanide concentrations in small streams may approach levels of concern soon after fire, but increases are likely to be of short duration. Post-fire concentrations of polycyclic aromatic hydrocarbons in streams have been found to increase but remained within the recommended limit. Large increases in exports and concentrations of some constituents after wildfire indicate the potential for impacts on water supply from forest catchments. In response, various water treatment measures may be required and in the absence of adequate treatment facilities or alternative sources, water supplies may be vulnerable to disruption.

Contents

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1. Introduction

Wildfire poses an important threat to life, property, infrastructure, and natural resources in fire-prone forest areas. Each year wildfires burn large areas of forest land around the world, particularly in western North America, south-eastern Australia, and the Mediterranean (FAO, 2001). For example, in Canada the annual area of forest burned ranged between 0.29 and 7.56 million hectares from 1975 to 2005 (Canadian Council of Forest Ministers, 2006). Similarly, in recent years there have been extensive forest areas burned by wildfire in the United States. Between 1997 and 2008, 65 wildfires greater than 100,000 acres (40,469 ha) occurred, many of which included forest areas (National Interagency Fire Centre, 2009). Notably, in the western United States there has been a significant increase in the number, size and severity of wildfires since 1990 (Joint Fire Science Program, 2004).

In south-eastern Australia, wildfire events in 2003, 2006/2007 and 2009 burned a combined area of over 3 million hectares across largely forested upland regions (Victorian Department of Sustainability and Environment, 2009). In response to recent fires there has been an increased focus on all aspects of fire and forest management in Australia, from which the potential impact of wildfire on the quality of water supplies has emerged as one area of concern (Ellis et al., 2004; Parliament of Victoria, 2008; Victorian Bushfires Royal Commission, 2009). Similarly, wildfire events elsewhere have drawn attention to the risk to water supplies in burned forest regions (Scott et al., 1998; Moody and Martin, 2001, 2004; Ice et al., 2004; Rhoads et al., 2006).

Forest catchments are an important source of potable water to communities around the world and in many cases are managed specifically for this purpose (Dudley and Stolton, 2003). It has been reported that for the world's 105 largest cities (top 25 from the Americas, Africa, Asia, Europe and five from Australia) approximately one third (33 cities) obtained a significant proportion of their drinking water from protected forest areas, with a further five cities obtaining water from distant catchment areas which also contained protected forest (Dudley and Stolton, 2003). Furthermore, forest areas are estimated to contribute two-thirds of the freshwater supply in the United States (Committee on Hydrologic Impacts of Forest Management, 2008). Although a number of these forested water supply catchments (such as wet tropical rainforest areas) may be less fire-prone, other catchment areas are particularly susceptible to wildfire events, such as in south-eastern Australia and the western United States. For example, in south-eastern Australia wildfires have burned forested reservoir catchments which supply potable water to Sydney (2001 wildfire), Canberra (2003), Adelaide (2007), Melbourne (2009), as well as various regional towns.

An advantage of using largely undisturbed forest catchments for potable water supply is the generally high quality of water flowing from such regions (Neary et al., 2009). However, following wildfire, increased erosion rates and changes to runoff generation and sources of pollutants can greatly increase the amounts of sediment,

nutrients and other constituents delivered to streams and reservoirs (e.g. Moody and Martin, 2001, 2009; Reneau et al., 2007; Sheridan et al., 2007b; Lane et al., 2008; Wilkinson et al., 2009), potentially resulting in water supplies that are unfit for consumption (White et al., 2006).

In this paper, we review changes to exports and concentrations of key physical and chemical constituents in water that may occur after wildfire in forest catchments. Wildfire effects on the generation and transfer of different constituents are considered in relation to post-fire rainfall and streamflow, erosion processes, and catchment controls reported in the literature. The review takes a particular focus on burned forest environments in south-eastern Australia, given the impact of recent wildfires on water supply catchments and the authors' access to reports and data for this region. The purpose of this review is not to outline the extent of published literature on the geomorphological and hydrological effects of wildfire, as this has been done previously (Shakesby and Doerr, 2006). Instead, we assemble information to provide an indication of the potential for water supply contamination by different constituents following wildfires. Compared to the expanding global research output on the hydrological and geomorphological effects of wildfire, published studies explicitly examining post-fire water quality in relation to drinking water supply, storage or treatment are limited (Moody and Martin, 2004; White et al., 2006).

The review is comprised of an initial section identifying key water quality constituents in forest catchments from a drinking water perspective. The next section examines post-fire exports and concentrations of individual constituents, with reference to hydrological and erosion processes contributing to observed changes after wildfire. The final section provides a summary of review findings and considers implications for water supply before outlining directions for future research.

2. Water quality constituents in forest catchments

This review focuses on a range of physical and chemical constituents that may be derived from forest environments and impact upon drinking water quality. These constituents are readily measurable and may be linked to catchment sources and delivery processes. Consideration of water-borne pathogens such as *Cryptosporidium*, *Giardia* and cyanobacteria is not included and routine monitoring for these specific pathogens is generally not recommended due to the difficulty and expense in their measurement (NHMRC, 2004). Sources of constituents in natural forest catchments include hillslopes, channels and floodplains, with additional inputs from disturbances such as access roads, forestry activities, prescribed burns, and wildfire. Major industrial or agricultural pollutant sources are excluded, with the exception of atmospheric inputs of mercury that have been recorded in forest areas. Forest fires may contribute additional pollutants (e.g. polycyclic aromatic hydrocarbons) that occur in otherwise negligible amounts or increase the store of pre-existing contaminants (such

as via ash deposits) which may be mobilised and delivered to streams. Ash is not identified as an individual water quality pollutant because it may contain various constituents but its contribution to post-fire water quality is considered in Section 3.2.

Key water quality constituents, the potential risks associated with each, and associated guideline values are outlined in Table 1. Guideline values were taken from the World Health Organisation (WHO) Guidelines for Drinking Water Quality (2008), and the Australian Drinking Water Guidelines (NHMRC, 2004) were used when a WHO guideline value was not given. Unless otherwise stated, guideline values are for the total amount of a constituent present, regardless of form (i.e. in solution or particle-associated). Total phosphorous (TP) and total nitrogen (TN) do not have drinking water guideline values and instead the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines for freshwater aquatic ecosystems in south-eastern Australia were used for comparison with available post-fire data from this region (ANZECC, 2000). Although the ANZECC guidelines are not related to drinking water, they do provide a reference point for aquatic ecosystem health, with implications for eutrophication and algal blooms which may compromise drinking water quality.

The risks associated with different constituents range from aesthetic concerns (taste or appearance) to potential toxicity or carcinogenicity with prolonged exposure to elevated concentrations. For chemical constituents that present a health risk, calculation of guideline values is based on a Tolerable Daily Intake (TDI), which refers to the amount of substance in water and food per kilogram of body weight that may be ingested over a lifetime without appreciable health risk (WHO, 2008). In addition, body weight (default value of 60 kg; Australian guidelines use 70 kg), the proportion of TDI from drinking water (20% in the absence of exposure data), and a daily value for drinking water consumed (default value for an adult of 2 L) are also included (WHO, 2008). Uncertainty (safety) factors are used to account for interspecies (when transferring from animal studies to humans) and inter-individual variability in humans (both a factor of 10), with additional factors that may be applied covering inadequate databases as well as the nature and severity of effect (WHO, 2008).

Information on the health effects of short duration exposure to elevated chemical constituent concentrations is generally unavailable (NHMRC, 2004; WHO, 2008). Short-term consumption of water with concentrations exceeding guideline values may not necessarily present a health risk (depending on the chemical) assuming longer-term consumption does not exceed set levels (WHO, 2008). Generally, very high constituent concentrations following wildfires are short-lived, although elevated concentrations may persist for some time after post-fire rainfall events. Nonetheless, even exceeding guideline values in the short-term may be problematic for water authorities charged with responsibility for the provision of drinking water that conforms to set standards, particularly where treatment capacity may be insufficient to process polluted water, unaffected reserve supplies are inadequate, or the population is dependent upon a single water source that has been contaminated.

3. Wildfire effects on water quality

Research into wildfire impacts on water quality has tended to focus on suspended sediment and nutrients, with other constituents receiving less attention. Post-fire data for many of the constituents outlined in Table 1 is limited. For this reason, the focus on particular water quality constituents and their associated post-fire sources and delivery processes reflects the extent of available information on those constituents after wildfire. Furthermore, the likelihood of detecting periods when constituent concentrations

exceed guideline values depends upon the sampling regime in relation to the rate and variability of constituent generation and the hydrological variability of the catchment system. In particular, the inclusion of storm event sampling may be critical to quantifying the magnitude and frequency of guideline exceedance for constituents in some systems, particularly in regions prone to high intensity rainfall events that generate rapid stormflow response. This can limit direct comparability between some studies and reported maximum concentration values should be considered in the context of both the sampling regime and the study environment.

3.1. Suspended sediment

Suspended sediment inputs to streams and reservoirs affect the colour and turbidity of water and may also transport various particle-associated contaminants (Horowitz and Elrick, 1987; Horowitz, 1991; Ongley et al., 1992). From a drinking water quality and treatment perspective, elevated suspended sediment concentrations may hinder detection of bacteria and viruses, promote bacterial growth from elevated levels of adsorbed nutrients, and limit effective disinfection (NHMRC, 2004). The strong tendency for many water quality constituents, particularly trace elements and P, to be bound to fine particles with low settling velocities necessitates a focus on fine sediment (Horowitz, 1991; Ongley et al., 1992). Furthermore, coarse material (>1 mm) flux has been shown to transport only a small fraction of TP exports after fire (Noske et al., 2010). As a result, consideration of post-fire bedload or coarse sediment flux is not included in this review.

Importantly, the transport of fine cohesive sediments through the fluvial system may be dominated by composite suspended sediment particles (flocs or aggregates) rather than primary particles (Droppo, 2001; Woodward and Walling, 2007). The structure of these composite particles incorporates microbial communities, organic and inorganic particles, and chemical constituents (Droppo, 2001), which may adversely affect water quality. Findings from burned forest environments indicate that soil aggregates exhibit significantly higher settling velocities than unburned particles of similar diameter, which has been attributed to an increase in burned aggregate density due to reduced organic content and pore space (Blake et al., 2007, 2009a). Furthermore, aggregation of clay particles into coarser composite particles has been attributed to the effect of soil heating (Dyrness and Youngberg, 1957; Giovannini et al., 1988; Giovannini and Lucchesi, 1997), thereby potentially increasing the concentration of contaminants bound to composite particles relative to primary particles of similar size (Blake et al., 2005). Potential consequences resulting from these fire effects on soil particles may include an increase in fine sediment storage and possibly the delayed release of contaminants after fire from degrading aggregates (Blake et al., 2009a).

Studies of wildfire effects on catchment suspended sediment exports and concentrations in streams and reservoirs have revealed a wide divergence of post-fire responses. This reflects the range of factors influencing post-fire erosion and sediment delivery (Shakesby and Doerr, 2006). However, much of the research to date into wildfire effects on sediment flux has focussed on plot to hillslope scales (e.g. Shakesby et al., 1993; Lavee et al., 1995; Prosser and Williams, 1998; Benavides-Solorio and MacDonald, 2001; Coelho et al., 2004; Dragovich and Morris, 2002; Cerdà and Lasanta, 2005; Campo et al., 2006; Sheridan et al., 2007a; Spigel and Robichaud, 2007; Smith and Dragovich, 2008; Blake et al., 2010), with fewer studies linking post-fire erosion response at this scale to downstream sediment delivery, sediment contributions from other sources, and catchment outputs (White and Wells, 1979; Moody and Martin, 2001; Blake et al., 2009b; Wilkinson et al., 2009). In this section, we present post-fire suspended sediment loads/yields

Table 1
Summary of water quality constituents from natural forest catchment sources that may occur in streams and reservoirs after wildfire[a].

Water quality constituent	Reason for risk	Sources	Concentration guideline value[b] (mg L^{-1} unless otherwise stated)	Treatment options	Examples of studies reporting concentrations/exports after wildfire
Aluminium (Al)	Neurotoxic	Leaching from soil and rock, aluminosilicates (insoluble)	No health-based value (0.2 for acid soluble Al for aesthetic reasons)	Flocculation and filtration. Note: Aluminium sulfate is used in water treatment as a coagulant	Gallaher et al. (2002)
Ammonia (NH$_3$)/ ammonium (NH$_4^+$)	Corrosion of copper pipes and fittings; food source for some microorganisms	Microbial metabolism, fertilisers and animal waste	0.5 (aesthetic limit)	Oxidation of ammonia to nitrate	Chessman (1986), Spencer and Hauer (1991), Bayley et al. (1992), Earl and Blinn (2003), and Bladon et al. (2008)
Arsenic (As)	Carcinogenic	Dissolution of minerals, industrial and mining effluent	0.01	Coagulation	Gallaher et al. (2002) and Leak et al. (2003)
Barium (Ba)	Vasoconstriction and peristalsis, convulsions and temporary paralysis	Soil and rock	0.7	Lime softening can remove more than 90%	Gallaher et al. (2002)
Chloride (Cl$^-$)	Aesthetic (taste and corrosion of pipes and fittings)	Dissolution of salt deposits	250 (aesthetic limit)	Removal not possible by conventional treatment processes, require distillation or reverse osmosis	Carignan et al. (2000), Ferreira et al. (2005), and Mast and Clow (2008)
Chromium (Cr)	Hexavalent chromium is carcinogenic, no evidence for carcinogenicity of trivalent chromium	Soils and rock; weathering and oxidation convert insoluble chromium oxide to soluble trivalent chromium	0.05 (for total chromium)	Coagulation/filtration	Gallaher et al. (2002) and Leak et al. (2003)
Copper (Cu)	Poisoning may occur at high concentrations, gastrointestinal symptoms at lower concentrations (3–5 mg L^{-1})	Soils and rock in the form of carbonate and sulphide minerals	2	Increase pH followed by coagulation and filtration	Gallaher et al. (2002)
Cyanide	Highly toxic, affects the thyroid and nervous system	Biomass burning is a major source of free cyanide (HCN and CN$^-$), as well as natural decomposition of some plants, and production by some microorganisms	0.07	No standard methods for the removal of cyanide from drinking water	Gallaher et al. (2002), Barber et al. (2003), and Crouch et al. (2006)
Iron (Fe)	Aesthetic issues (taste and colour) and staining of pipes and fittings	Soils and rock as oxide, sulphide, and carbonate minerals	0.3 (aesthetic limit)	Coagulation and filtration	Wasson et al. (2003), Townsend and Douglas (2004), and White et al. (2006)
Lead (Pb)	Toxic (affects the central nervous system)	Dissolution from natural sources	0.01	Coagulation or lime softening	Gallaher et al. (2002) and Leak et al. (2003)
Manganese (Mn)	Aesthetic (taste and staining of plumbing fixtures)	Soils and rock, exists as both soluble and insoluble compounds in divalent, tetravalent and heptavalent states	0.4	Convert soluble forms of Mn to insoluble precipitates and filter	Wasson et al. (2003), Townsend and Douglas (2004), and White et al. (2006)
Mercury (Hg)	Toxicity (kidneys). Methyl mercury may cause neurological disorders and mental disability	Atmospheric deposition from natural (e.g. volcanoes) and anthropogenic (e.g. coal-fired power plants) sources	WHO: 0.006 (inorganic Hg) Australian: 0.001 (total Hg)	Coagulation moderately effective for inorganic Hg; granular activated carbon effective for removing inorganic and organic Hg	Gallaher et al. (2002)
Nitrate (NO$_3^-$)/ nitrite (NO$_2^-$)	Toxicity associated with reduction of nitrate to nitrite, which affects the transport of oxygen to tissues	Nitrate: formation by oxidation of organic waste, nitrogen-fixing bacteria in soils, or lighting strikes. Nitrite (unstable): formation by reduction of nitrate in low oxygen water	NO$_3^-$: 50 (infants under 3 months) and 100 (adults and infants over 3 months) NO$_2^-$: 3	Conventional water treatment is not effective for nitrate removal	Chessman (1986), Spencer and Hauer (1991), Bayley et al. (1992), Hauer and Spencer (1998), Carignan et al. (2000), Ferreira et al. (2005), Bladon et al. (2008), Lane et al. (2008), and Mast and Clow (2008)
Total nitrogen (TN) [c]	Excessive algal growth and cyanobacterial blooms (eutrophication)	Soil and sediment associated N, organic material.	Not available for drinking water. Aquatic health trigger values for SE Australian freshwaters[c]: Upland river: 0.25 Lowland river: 0.5 Freshwater lake/reservoir: 0.35	Coagulation and filtration would remove most suspended solids and particle associated N	Spencer and Hauer (1991), Bayley et al. (1992), Townsend and Douglas (2004), Sheridan et al. (2007b), Bladon et al. (2008), Lane et al. (2008), and Mast and Clow (2008)

Table 1 (continued)

Water quality constituent	Reason for risk	Sources	Concentration guideline value[b] (mg L^{-1} unless otherwise stated)	Treatment options	Examples of studies reporting concentrations/exports after wildfire
Organic carbon (organic C)	Dissolved organic C (DOC) may contribute to the formation of disinfection by-products	Soils and sediment, organic material and ash	No WHO or Australian drinking water guideline available. 5 mg L^{-1} for DOC used in Ontario, Canada	Coagulation and filtration to remove particle-associated organic C	Carignan et al. (2000), McEachern et al. (2000), Minshall et al. (2001), Wasson et al. (2003), Petticrew et al. (2006), and Mast and Clow (2008)
Total phosphorous (TP)[c]	Excessive algal growth and cyanobacterial blooms (eutrophication)	Soil and sediment associated P, organic material, release of P from benthic sediments due to change in redox conditions	Not available for drinking water. TP aquatic health trigger values for SE Australian freshwaters[c]: Upland river: 0.02 Lowland river: 0.05 Freshwater lake/reservoir: 0.01	Coagulation and filtration would remove most suspended solids and particle associated P	Spencer and Hauer (1991), Bayley et al. (1992), Prepas et al. (2003), Townsend and Douglas (2004), Sheridan et al. (2007b), Bladon et al. (2008), Lane et al. (2008), Mast and Clow (2008), Blake et al. (2009b), and Gabos et al., (2001)
Polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs)[d]	Toxic, carcinogenic, undergo bioaccumulation, accumulate in soils and sediments	May be produced during forest fires. Estimated emissions of PCDD/Fs from wildfires of 0.5–28 µg per tonne of fuel burned[e]	Not available	Not available	
Polycyclic aromatic hydrocarbons (PAH)	Most toxicological studies examine benzo(a)pyrene (BaP), one type of PAH. PAHs are carcinogenic and mutagenic	Formed during incomplete combustion of organic matter, such as during forest fires or volcanic eruptions	0.0007 (for BaP); threshold values unavailable for other PAHs	Conventional treatment of coagulation, settling, and filtration are capable of reducing BaP concentrations and probably also for other PAHs	Olivella et al. (2006) and Vila-Escalé et al. (2007)
Sodium (Na$^+$)	Aesthetic (taste)	Dissolution of salt deposits	200 (aesthetic limit)	Removal not possible by conventional treatment processes, requires distillation or reverse osmosis	Carignan et al. (2000), Gallaher et al. (2002), and Ferreira et al. (2005)
Sulfate (SO$_4^{2-}$)	Aesthetic (taste), purgative effects may occur at high concentrations. It may contribute to increased corrosion of pipes.	Occurs naturally in various minerals. Aluminium sulfate is used as a flocculant in water treatment and copper sulfate is used as a control of blue-green algae in water storages	500 (250 for aesthetic reasons)	Most sulfate salts are highly soluble and cannot be removed from drinking water by conventional treatment processes, desalination methods are required	Carignan et al. (2000), Earl and Blinn (2003), Ferreira et al. (2005), and Mast and Clow (2008)
Total dissolved solids (TDS)	Aesthetic (taste). High TDS may also result in excessive corrosion of pipes and fittings.	TDS may comprise of inorganic salts, small amounts of organic material, clay particles, colloidal iron and manganese oxides and silica <0.45 µm (filter membrane)	500 (aesthetic limit)	TDS are difficult to remove, requires high energy/expensive reverse osmosis or distillation techniques	Chessman (1986), Lathrop (1994), and Gerla and Galloway (1998)
Turbidity/total suspended solids (TSS)	Health risk is associated with suspended material that may carry disease-causing microorganisms or particles that have adsorbed toxic organic or inorganic compounds	Turbidity in water results from the presence of suspended material, such as clay particles, plankton or other microrganisms	5 NTU (aesthetic limit)	Coagulation followed by filtration through granular media	Chessman (1986), Gerla and Galloway (1998), Gallaher et al. (2002), Lane et al. (2006), White et al. (2006), Wilkinson et al. (2006), Sheridan et al. (2007b) and Mast and Clow (2008)
Zinc (Zn)	Aesthetic (taste). Zn is an essential element for humans. Consumption of very high amounts may have gastrointestinal effects	Widely distributed in rocks	3 (aesthetic limit)	Coagulation using aluminium sulfate at pH 6.5–7 (30% removal) or lime softening at pH 9.5–10 (60% removal)	Gallaher et al. (2002)

[a] Table 1 was compiled from information provided by the World Health Organisation (WHO)'s Guidelines for Drinking-Water Quality (2008) and the Australian Drinking Water Guidelines (NHMRC, 2004).

[b] Concentration guideline values (as well as recommended values based on aesthetic concerns) are from WHO (2008), with NHMRC (2004) guidelines used in the absence of WHO guidelines (drinking water values for TP, TN and PCDD/Fs are not contained in these guidelines). Note that, unless otherwise stated, guideline values refer to the total amount of a substance present in a sample regardless of form (in solution or attached to suspended material).

[c] Information on TP and TN is from the Australian and New Zealand Environment and Conservation Council (ANZECC) guidelines (2000) for aquatic ecosystems in south-eastern Australia (chapter 3). The reported guidelines are for south-eastern Australian freshwater bodies and represent trigger values for adverse effects to aquatic ecosystems and not for human health or aesthetic effects.

[d] Information on PCDD/Fs is from the Australian Commonwealth Government's National Pollution Inventory (NPI) Fact sheet on PCDD/Fs: (http://www.npi.gov.au/substances/polychlorinated-dioxins/index.html).

[e] Sources of PCDD/Fs are from Environment Australia (2002).

Table 2

Summary of post-fire annual suspended sediment yields from catchment-scale studies in forest environments burned by wildfire.

References	Location	Catchment area (km^2)	Method[a]	Annual suspended sediment yield in $t\ ha^{-1}\ year^{-1}$ (and load in t)		Multiple increase relative to unburned yields (first year after fire)
				First year after fire	Subsequent years after fire	
Mayor et al. (2007)	Xortà Mountains, Eastern Spain	0.021	VS	0.65 (9.58); average sediment yield over 7 years		n/a
Blake et al. (2009b)	Blue Mountains, near Sydney, Australia	0.89	TB	0.58 (51.6)[b]	n/a	n/a
Scott (1993)	Southwestern Cape, South Africa	(a) 1.32 (b) 2.01	CM	(a) 5.2 (686) (b) 6.0 (1206)	n/a	n/a
Lane et al. (2006)	East Kiewa River, NE Victoria, Australia	(a) 1.36 (b) 2.44	CM	(a) 2.05 (280) (b) 0.88 (216)	2nd year: (a) 0.39 (56) (b) 0.35 (84)	8–9
Kunze and Stednick (2006)	Colorado Front Range, USA	(a) 2.2 (b) 3.9	RC	n/a	2nd year (summer): (a) 0.38 (84) b) 1.44 (562)	n/a
Reneau et al. (2007)	New Mexico, USA	16.6	VS[c]	9.0 (14,913)	2nd year: 5.2 (8637) 3rd year: 2.1 (3472) 4th year: 0.74 (1232) 5th year: 0.67 (1120)	106[b]
Moody and Martin (2001, 2004)	Colorado Front Range, USA	46.9[d]	VS[e]	50 (233,750)[e]	n/a	560
Lane et al. (2006)	West Kiewa River, NE Victoria, Australia	100.5	CM	0.29 (2890)	n/a	n/a
Petticrew et al. (2006)	Central British Columbia, Canada	135	CM	0.009 (115)[f]	n/a	1.7
Wilkinson et al. (2009)	Little River, Blue Mountains, Australia	183	RC	0.21 (3843)	2nd year: 1.02 (18,666)	104–250
Tomkins et al. (2007)	Nattai River, Blue Mountains, Australia	446	RC	1st year: 1968 wildfire: 0.74 (33,004) 2001/2002 wildfire: 0.017 (763)	2nd year: 1968 wildfire: 0.011 (508) 2001/2002 wildfire: 0.011 (486)	3rd year: 1968 wildfire: 0.106 (4741) 2001/2002 wildfire: 0.003 (120) — n/a
Sheridan et al. (2007b)	Victoria, Australia: (a) Ovens River (b) Tambo River-1 (c) Dargo River (d) Tambo River-2 (e) Mitta Mitta River (f) Kiewa River	(a) 495 (b) 523 (c) 676 (d) 895 (e) 1533 (f) 1655	OLE	1st year: (a) 0.83 (41,260) (b) 0.46 (24,147)[g] (c) 0.22 (14,854) (d) 0.37 (32,967) (e) 3.3 (511,559) (f) 0.11 (17,880)	2nd year: (a) 0.26 (12,678) (b) n/a (c) 0.30 (20,131) (d) 0.35 (31,386) (e) 0.54 (83,374) (f) n/a	3rd year: (a) 0.05 (2588) (b) n/a (c) 0.40 (27,188) (d) 0.07 (6101) (e) 0.68 (104,170) (f) n/a — (a) 24 (b) 1459 (c) 21 (d) 171 (e) 168 (f) 1.3

[a] Method of sediment yield estimation: continuous monitoring of discharge and turbidity/TSS (CM); rating curve derived from measurements of discharge and TSS (RC); other load estimation techniques based on flow and TSS data (OLE); volumetric surveys of reservoirs converted to mass of sediment (VS); and sediment tracer budgeting (TB).

[b] Sediment yield estimate was based on ^7Be sediment budget (<63 μm fraction) for the first 3 months after wildfire (Blake et al., 2009b).

[c] The estimate of suspended sediment yield was based on the density of fine sediment (excluding ash) deposited in the reservoir (1.12 $g\ cm^{-3}$), with the multiple increase value relative to the average annual unburned fine sediment input to the reservoir.

[d] The burn area of 46.9 km^2 (in two sub-catchments within a larger unburned river basin) was used to calculate the suspended sediment yield (determined by reservoir survey) based on the assessment that the burn dominated the post-fire sediment yield (Moody and Martin, 2001, 2004).

[e] Sediment volume was converted to mass using a density of 1.7 $g\ cm^{-3}$ provided by the authors and the suspended sediment load was calculated from the difference between total load and bed load (Moody and Martin, 2001, 2004).

[f] Post-fire monitoring was for a 7 month period (covering the spring snowmelt) only (Petticrew et al., 2006).

[g] Suspended sediment yield data for the Tambo River (site 1) was for a 6 month period only (Sheridan et al., 2007b).

and suspended sediment concentration or turbidity data, with reference to reported erosion processes and hydrological drivers contributing to observed wildfire effects. Post-fire suspended sediment load, concentration and turbidity data inevitably incorporate an ash component (particularly in the first year after fire). Ash and its contribution to post-fire water quality are considered separately in the next section.

A summary of annual suspended sediment yields from catchment-scale studies in forest environments burned by wildfire is provided in Table 2. The yield data is presented in order of increasing catchment size (ranging from 0.021 to 1655 km^2) and, where available, for multiple years after the burn. The magnitude of suspended sediment yields in the first year after fire vary substantially, ranging from 0.017 to 50 t ha^{-1} year^{-1}, with an approximate peak in yields for catchments ranging in area from 1 to 50 km^2. Likewise, estimates of multiple increases (i.e. post-fire yield increases as multiples of reported pre-fire or unburned control catchment yields) for the first year after fire reveal large variation, ranging from 1 to 1459 times estimates of unburned annual suspended sediment yields.

The uncertainties associated with the estimation of suspended sediment yields (and multiple increase values) can be large and have been reported by some authors (Sheridan et al., 2007b; Wilkinson et al., 2009). Measurement of sediment yields using different techniques may also hinder comparability (Table 2). To address this, we limited the comparison to catchment-scale studies that report suspended sediment (using flow-based estimation techniques) or fine sediment (generally <63 μm for studies using volumetric surveys or tracer techniques) yields for the first year after fire (except where otherwise stated). This excluded studies that only reported total sediment loads after fire because the suspended or fine sediment fraction of the total load was unknown. For the purpose of comparison, suspended sediment yields are presented in t ha^{-1} year^{-1}. However, it should be noted that such a measure can be misleading, given that sediment supply may be dominated by localised sources (e.g. channels) rather than distributed uniformly across a catchment (Smith, 2008; Moody and Martin, 2009).

The range in suspended sediment yields after fire reflects various factors, including rainfall patterns, catchment burn extent and severity, erosion processes, sediment sources (location and connectivity to major tributary streams), and scale effects (such as increased opportunities for sediment storage with increasing catchment size). Suspended sediment yields following the first year after fire generally decline as vegetation cover is re-established and fire impacts on soil and hillslope hydrological properties (e.g. changes to soil water repellency and hillslope surface roughness) decline to pre-fire levels (Prosser and Williams, 1998; Lane et al., 2006; Sheridan et al., 2007a; Reneau et al., 2007). Increases in annual suspended sediment yields in subsequent years may reflect large rainfall events impacting on partially-recovered catchments and/or stormflows in tributary streams remobilising sediment deposits from previous post-fire flow events (Moody and Martin, 2001; Mayor et al., 2007; Wilkinson et al., 2009).

The magnitude, intensity and frequency of post-fire rainfall and associated flow events are key drivers of erosion and sediment delivery in many burned catchments (Robichaud et al., 2007; Malmon et al., 2007; Cannon et al., 2008; Moody and Martin, 2009). The importance of rainfall patterns for explaining the large variation in post-fire suspended sediment yields is apparent from a number of the studies shown in Table 2. For example, the large sediment yield (50 t ha^{-1}; 560 times unburned) reported by Moody and Martin (2004) for the first year after fire was mostly attributed (estimated 80%) to channel erosion and incision of unchannelised drainage lines in response to flash floods generated by short duration, high intensity summer storms (peak storm

intensity 90 mm h^{-1}) (Moody and Martin, 2001). Short, intense storm events were also important for generating the large post-fire suspended sediment yields (9.0 t ha^{-1}; 106 times unburned) reported by Reneau et al. (2007) and have been identified as triggers of post-fire runoff-generated debris flows which produce high sediment yields (Cannon et al., 2008). In south-eastern Australia, a single summer storm (>2 h; 43 mm; peak 15-min intensity of 80 mm h^{-1}) accounted for 45% (127 t) and 47% (101 t) of the total suspended sediment yield in the first year after fire from two small wet *Eucalyptus* forest mountain catchments (Lane et al., 2006). The impact of a longer duration rainfall event (3 days; 243 mm) was also captured by Lane et al. (2006) and accounted for a further 34% and 29% of total first year suspended sediment yields from the two burned study catchments.

In contrast, Tomkins et al. (2007) observed a first year suspended sediment yield of only 0.017 t ha^{-1} from the Nattai River catchment (446 km^2; >50% burned), part of the Lake Burragorang reservoir catchment (the main water supply of Sydney, Australia), during a period of below average rainfall following wildfire in 2001/2002. Reservoir sedimentation in the first 12 months after that fire was estimated to account for only 1–1.6% of total sedimentation since the reservoir was completed in 1960 (Wilkinson et al., 2007). Despite this, erosion estimates for burned hillslopes within the Nattai catchment ranged from 50 to 100 t ha^{-1} 5 months after the fire for areas of low to extreme fire severities (Shakesby and Doerr, 2006), revealing the extent to which colluvial and in-channel storage attenuated downstream suspended sediment delivery to the reservoir (Wilkinson et al., 2009). Transport limitation can be an important restriction on sediment delivery to streams and catchment outlets (Moody and Martin, 2001; Petticrew et al., 2006). In-channel storage of post-fire sediment deposits may result in lagged suspended sediment yield responses which are dependent upon the timing and magnitude of subsequent discharge events to remobilise these stores (Wilkinson et al., 2009). The increased stormflow response to rainfall events that may occur after fire also declines with post-fire recovery, thereby potentially reducing the capacity of subsequent flows to remove stored sediment and increasing residence times (Moody and Martin, 2001).

Reporting of post-fire suspended sediment concentrations (measured by the concentration of total suspended solids; TSS) or turbidity in streams and reservoirs is limited. Most studies included in Table 3 are from south-eastern Australia, which reflects both patterns in data reporting and the impact of multiple large wildfire events in this region. We focus on maximum values in order to quantify the effect of wildfire on TSS/turbidity (relative to pre-fire or unburned control maximums) and identify instances of guideline exceedance. This approach requires consideration of stream sampling regimes to assess the likelihood that sampling will have captured the brief periods of elevated TSS/turbidity, particularly during stormflows. Failure to reasonably characterise TSS/turbidity across a range of flows may result in underestimation of the risk to water quality, which is likely when routine weekly to monthly sampling is the only source of TSS/turbidity information for streams that respond rapidly to rainfall (Richards and Holloway, 1987; Walling et al., 1992; Robertson and Roerish, 1999). Such streams require additional storm-based sampling across event hydrographs to improve both load estimation and to characterise the magnitude of TSS/turbidity change (Robertson and Roerish, 1999).

Post-fire turbidity values for streams were less frequently reported than TSS but were more readily available for reservoirs. This presents a challenge, given that turbidity is the primary measure of the particulate content of water samples in drinking water guidelines (NHMRC, 2004; WHO, 2008), yet TSS is more commonly reported in the literature. This focus on TSS probably reflects the greater level of comparability and precision of TSS measurements

Table 3
Maximum total suspended solids (TSS) concentration and turbidity data from streams and reservoirs in forest environments burned by wildfire.

References	Location	Catchment area (km²) (B: burned and UB: unburned)	Post-fire sampling regime and duration of sampling	Pre-fire maximum TSS concentration (mg L⁻¹)	Post-fire maximums		
					TSS concentration (mg L⁻¹)		Turbidity (NTU)
Streams							
Gallaher et al., 2002	Jemez Mountains and Pajarito Plateau, New Mexico, USA	n/a (40 sites)	Storm events; 5 months	43,140	76,000 (12 out of 272 samples exceeded the pre-fire maximum)		n/a
Lane et al., 2006	East Kiewa River, NE Victoria, Australia	1.36, 2.44	Weekly to fortnightly and storm events; 3 years	n/a	47,152		n/a
Malmon et al., 2007[a]	Pueblo Canyon, Jemez Mountains and Pajarito Plateau, New Mexico, USA	22	Storm events during summer over 3 years	<15,000	~500,000		n/a
Gerla and Galloway, 1998	Yellowstone National Park, Wyoming, USA	B: 64 UB: 49	Weekly to monthly during spring to autumn; 5 years	n/a	n/a		B: 90 UB: 85
Mast and Clow, 2008	Glacier National Park, NW Montana	B: 96.4 UB: 47.3	2× weekly (snowmelt) to monthly; 4 years	n/a	B: 147 UB: 1497		n/a
Brown, 1972	Snowy Mountains, NSW, Australia	(a) 27 (b) 141	Low flow with some storm events; 5 years	(a) 7052 (b) 334	(a) 143,000 (b) 112,000		n/a
Wilkinson et al., 2006	Little River, Blue Mountains, Australia	183	Low flow and storm events; 12 months	82	2646		n/a
Chessman, 1986	Victoria, SE Australia	B: 40–750 (11 sites) UB: 110	Low flow and storm events; 3 months	n/a	B: 11–2300 UB: 163		130
Leak et al., 2003	Buckland River, Victoria, SE Australia	322	Single flow event	n/a	59,000		129,000
Sheridan et al., 2007b	Victoria, Australia		Low flow and storm events; 3 years	Event flow:	1st year	2nd year / 3rd year	n/a
	(a) Ovens River	(a) 495		(a) 280	(a) 1700	(a) 330 / (a) 83	
	(b) Tambo River-1	(b) 523		(b) 9	(b) 59,000	(b) n/a / (b) n/a	
	(c) Dargo River	(c) 676		(c) 34	(c) 1600	(c) 990 / (c) 930	
	(d) Tambo River-2	(d) 895		(d) 90	(d) 15,000	(d) 9100 / (d) 2000	
	(e) Mitta Mitta River	(e) 1533		(e) 260	(e) 43,000	(e) 2200 / (e) 2000	
	(f) Kiewa River	(f) 1655		(f) 63	(F) 140	(f) n/a / (f) n/a	

(*continued on next page*)

Table 3 (continued)

References	Location	Catchment area (km²)/reservoir capacity (GL)	Post-fire sampling regime and duration of sampling	Pre-fire maximum turbidity (NTU)	Post-fire maximums	
					TSS concentration (mg L⁻¹)	Turbidity (NTU)
Reservoirs						
White et al., 2006	Bendora Reservoir, Cotter River, ACT, Australia	91.5/11.5	Not reported; 3 years	Previous maximums: −118 at bottom (>30 m depth) after 1983 wildfire and −18 at 15 m (above thermocline) after a 190 mm rain event in January 1995	n/a	3000 at bottom after January 2003 wildfire and 2 storm events (each approx. 60 mm) 1 month after fires
Goulburn-Murray Water/ Victorian Water Resources Data Warehouse[b,c]	(a) Lake William Hovel (b) Lake Buffalo (c) Lake Glenmaggie (d) Lake Eildon Victoria, Australia	(a) 332/13.7 (b) 1150/23.9 (c) 1891/178 (d) 3885/3334	Fortnightly to monthly; 2 years	(a) 4 (0%)[d] (b) 18 (16%)[d] (c) 130 (74%)[d] (d) 7 (2%)[d] (maximums prior to wildfire in 2006/2007)	n/a	(a) 5.7 (3.4%)[d] (b) 20 (22%)[d] (c) 1398 (100%)[d] (d) 16 (11%)[d]
Alexander et al., 2004	Dartmouth Reservoir, NE Victoria, Australia	3611/3900	5 sampling intervals; 7 months	1 (surface)	<4 (all depths to 100 m)[e]	5 (surface)

[a] Maximum pre and post-fire TSS concentrations were interpreted from figures presented by Malmon et al. (2007). The actual maximum values were not stated.

[b] Data was provided by Goulburn-Murray Water (L. Mattner, pers. comm., 18 May 2009) for Lakes William Hovel (LWH), Buffalo (LB) and Eildon (LE), while the Victorian Water Resources Data Warehouse (http://www.vicwaterdata.net/vicwaterdata/home.aspx) was accessed to obtain data for Lake Glenmaggie (LG).

[c] Turbidity data prior to the 2006/2007 wildfire was available for 2003–2006 for LWH, LB and LE, whereas a longer record (1978–2006) was available for LG which included the effect of a wildfire that burned 17% of the catchment in 1998. Note that the catchment of LB was burned by wildfire in 2003 (35% of the catchment area) and again in 2006/2007 (near complete burn). Reservoir sampling was at off-take points or outflows.

[d] Percentages indicate the proportion of turbidity values exceeding 5 NTU (guideline value) relative to the total number of pre and post-2006/2007 wildfire measurements.

[e] Data from depth-stratified sampling located near the dam wall (Alexander et al., 2004).

and the limited transferability of turbidity–TSS relationships between different catchments. Durations of elevated TSS/turbidity levels in streams after wildfire were also generally not reported. While periods of maximum TSS/turbidity may occur briefly during stormflow events, elevated levels may persist beyond initial event timescales, particularly where there are large post-fire inputs of sediment to streams leading to in-channel storage and remobilisation by subsequent flow events (e.g. Lyon and O'Connor, 2008). Large storage reservoirs are more likely to reduce the magnitude and rate of change of TSS/turbidity inputs from tributary streams, resulting in generally lower peak TSS/turbidities that may persist for longer, with potential implications for recovery times and water supply restrictions (White et al., 2006). In contrast to stream sampling, fixed-interval measurements in large reservoirs may better capture the more gradual changes in TSS/turbidity resulting from the attenuating effect of these large water bodies on variable turbid inflows.

Maximum reported TSS concentrations measured during stormflows in the first year after fire range from 11 to ~500,000 mg L^{-1} for streams with catchments varying in size from 1.36 to 1655 km^2 (Table 3). The highest reported maximum TSS values after fire occurred during flash floods in a semi-arid ephemeral stream located in New Mexico (Malmon et al., 2007). In all studies, with the exception of that by Mast and Clow (2008), TSS maximums after fire exceeded unburned (or pre-fire) maximums. Mast and Clow (2008) found that wildfire did not affect TSS concentrations in a subalpine conifer forest catchment in Montana, USA, suggesting that sediment yields from subalpine streams may be less affected by fire than lower elevation streams because of a slower rate of water release during spring snowmelt (the main sediment transport period).

The highest TSS concentrations in streams after wildfire generally occurred in response to erosion events triggered by intense summer storms (Gallaher et al., 2002; Leak et al., 2003; Lane et al., 2006; Malmon et al., 2007; Sheridan et al., 2007b). For example, following wildfire in 2003, runoff-generated debris flows that scoured channels to bedrock (Fig. 1) were produced from a cluster of small catchments (<200 ha) by a very high intensity, short duration storm event (estimated at 150 mm in 1 h) in the upper Buckland River, north-eastern Victoria (Lyon and O'Connor, 2008; Tryhorn et al., 2008; Nyman et al., in press). A pulse of highly turbid water, with a peak TSS concentration of 59,000 mg L^{-1} (129,000 NTU) measured 30 km downstream (Leak et al., 2003), travelled down the Buckland and into the Ovens River. Subsequently, turbidity levels in the Ovens River remained well in excess of the guideline value (5 NTU), with the peak turbidity (2370 NTU)

Fig. 1. Debris flow-scoured channel in a tributary of the upper Buckland catchment, eastern Victoria, following wildfire in 2003. Note the person standing in the middle of the channel for scale (photo provided by Gary Sheridan).

at Wangaratta (located over 150 km downstream from the source) recorded 12 days after the event (Leak et al., 2003; Lyon and O'Connor, 2008). Similarly, following wildfire in summer 2006/2007, debris flows occurred in response to high intensity rainfall in small tributary sub-catchments of the upper Macalister River catchment (1891 km^2; 90% burned) in eastern Victoria (Nyman et al., in press). The debris flows delivered large quantities of ash and sediment to the Macalister River, which impacted on water quality in Lake Glenmaggie (located 60 km downstream). The maximum TSS and turbidity recorded at the Glenmaggie Dam outflow after the debris flows was 280 mg L^{-1} and 1398 NTU, respectively. Mean pre-fire monthly turbidity at the outflow for the period 1978–2006 was 10.7 NTU, whereas for the first year after the fire it was 29 times greater at 306 NTU. This included the impact of both the debris flows and large flood events in June (estimated at >100 years recurrence interval) and November 2007 (Parliament of Victoria, 2008).

Further examples of impacts on TSS and turbidity levels in reservoirs may be identified following the 2003 and 2006/2007 wildfires in south-eastern Australia. White et al. (2006) reported an increase in turbidity in the Bendora reservoir (supplying drinking water to Canberra) on the Cotter River (482 km^2; 98% burned) following the 2003 wildfire. This was 30 times the previously recorded maximum turbidity (after wildfire in 1983 that burned 12% of the upper Cotter catchment). White et al. (2006) also reported that 5 NTU (at 3 m depth) was exceeded 2% of the time during the pre-fire period (1967–2002) and 10% during the post-fire period (2003–2005). Water quality in the reservoir returned to near pre-fire conditions within 2 years of the fire. Examination of data for four reservoirs with catchments burned during the 2006/2007 wildfire in Victoria revealed all experienced a post-fire increase in the proportion of samples exceeding 5 NTU (Table 3). The largest increase occurred in Lake Glenmaggie, rising from 74% of samples before the fire (1978–2006) to 100% (2007–2009) after the fire.

Large water quality impacts in reservoirs do not automatically result from inflows with high TSS/turbidity. This was apparent in the case of the large Dartmouth reservoir (3900 GL capacity) in north-east Victoria, with a 3611 km^2 catchment that was 95% burned in 2003. Only a small change in turbidity was recorded near the dam wall and TSS remained <4 mg L^{-1} at all depths measured up to 12 months after the fire (Alexander et al., 2004). In contrast, the maximum TSS concentration recorded in the Mitta Mitta River (the main tributary of Dartmouth) was 43,000 mg L^{-1}, while an estimated suspended sediment load of 511,559 t (approximately 168 times pre-fire yields) passed the nearest gauging site 35 km upstream of the reservoir (Sheridan et al., 2007b). This contrast between inflows and the reservoir water quality near the dam wall probably reflects the considerable capacity for a reservoir of this size to mitigate impacts on water quality from contaminated inflows.

3.2. Ash

Ash deposits on hillslopes after wildfire may form a large store of particulate carbon (charcoal, black carbon) and contain elevated concentrations of various nutrients, trace elements, as well as other potential contaminants (Amiro et al., 1996; Johansen et al., 2003; Goforth et al., 2005). The ash layer from a severe burn in forest areas with high fuel loads may be 2–10 cm thick and equate to 1–5 kg m^{-2} (Doerr et al., 2008), with depths of up to 20 cm having been reported (Gabet and Sternberg, 2008). The low density ash may be readily entrained by overland flow and result in water quality impacts soon after fire, with the potential for rapid depletion of the hillslope ash store (Reneau et al., 2007). Hillslope ash beds have also been identified as a factor in post-fire changes to hillslope runoff generation and erodibility, which has implications

for the magnitude of water quality impacts. For example, reduced soil infiltration rates have been attributed to ash clogging of soil macropores and the formation of surface crusts (Mallik et al., 1984; Neary et al., 2005; Onda et al., 2008). Following sufficient rainfall and saturation of the ash layer, it has been found that the transport capacity of runoff is enhanced due to increased fluid density with incorporation of ash into the flow. This may lead to a positive feedback mechanism of increased ash entrainment and possibly the generation of progressively bulked debris flows with high erosion rates and the potential for large downstream water quality impacts (Cannon, 2001; Gabet and Sternberg, 2008).

The store of constituents in burned forest ash and the effect of ash on water quality have received only limited attention. A difficulty in assessing the chemical composition of ash is the high level of variability, which reflects the type of vegetation and part of the plant (bark, wood or leaves) burned, climate, soil type, and combustion conditions (Someshwar, 1996; Demeyer et al., 2001). For this reason, examples are presented only to give an indication of the type and range of constituents that may be present in ash. In a review of the properties of wood ash (white ash), Demeyer et al. (2001) reported that calcium carbonate ($CaCO_3$) is the major compound of ash along with other carbonates and oxides of metals and silica. Wood ash is highly alkaline, increasing soil pH by up to 3 pH units immediately after burning compared to unburned soils (Ulery et al., 1993). Someshwar (1996) reported a median concentration of P in bark ash of 1.57% (15,700 mg kg^{-1}), while Ferreira et al. (2005) found 8900 mg kg^{-1} of P in ash under burned *Pinus pinaster* stands in Portugal. Khanna et al. (1994) reported P and N concentrations in ash from *Eucalyptus* litter of 160–12,000 and 300–14,000 mg kg^{-1}, respectively. Concentrations of organic C and N in ash will depend on the extent of combustion, with dark ash formed by incomplete combustion (Demeyer et al., 2001; Goforth et al., 2005). For example, Goforth et al. (2005) reported average organic C and N concentrations in dark ash that were 7–17 and 5.2–10.5 times greater than in white ash, respectively, for burned conifer forest and pine–oak woodland in southern California. The concentrations of organic C and N in white or dark ash were 3900–66,300 mg kg^{-1} and 400–4200 mg kg^{-1}, respectively (Goforth et al., 2005).

Microelement concentrations in ash may also vary greatly. Fe is the most abundantly present and is probably part of the structural framework of ash (Someshwar, 1996; Demeyer et al., 2001). Ferreira et al. (2005) reported concentrations of Fe (1466 mg kg^{-1}), Mn (2570 mg kg^{-1}), Zn (201 mg kg^{-1}), and Cu (57 mg kg^{-1}) for pine ash. Higher maximum concentrations of Fe (600–10,000 mg kg^{-1}), Mn (60–100,000 mg kg^{-1}), Zn (20–370 mg kg^{-1}) and Cu (12–340 mg kg^{-1}), were recorded for ash formed by burning *Eucalyptus* litter (Khanna et al., 1994). These authors also reported Al and Pb concentrations in ash of 1000–18,000 and 4–152 mg kg^{-1}, respectively. Someshwar (1996) measured mean levels of Hg, Cd and As in wood ash and reported concentrations of <0.5, <10, and 23 mg kg^{-1}. The solubility of various constituents was examined by Plumlee et al. (2007), who undertook water leachate tests (1:20 ash to deionized water) on ash samples collected after wildfires in chaparral vegetation in southern California. These authors reported mean solution concentrations (mg L^{-1}) for Cl$^-$ (32), NO$_3^-$ (4.1), and SO$_4^{2-}$ (179), with low (<1 mg L^{-1}) concentrations of P, Al, Ba, Cu and Fe and very low (i.e. <0.005 mg L^{-1}) concentrations of As, Cr, Hg, Mn, Pb, and Zn.

Ash can form a significant component of suspended material flux within the first year after fire, with the rate of removal of ash from hillslopes dependent upon the erosivity of post-fire rainfall and wind events (Reneau et al., 2007; Woods and Balfour, 2008). For example, Cerdà and Doerr (2008) reported that 153 mm of rainfall over a 6 day period removed most of a 36 mm ash layer only 3 weeks after a high severity fire in eastern Spain.

At the catchment-scale, the ash yield in the first year after fire was 2.1 t ha^{-1} (3567 t or 19% of fine sediment exported) for a mixed conifer catchment (16.6 km^2) in New Mexico, which accounted for >90% of total ash exports (Reneau et al., 2007). Even where only a small increase in post-fire mineral sediment delivery occurred, significant increases in the export and in-channel storage of organic material (associated with formation of in-stream biofilms and possible delivery of black carbon from ash washed off hillslopes) were observed in British Columbia in the first 15 months after fire (Petticrew et al., 2006).

The specific effect of ash on stream water quality is difficult to quantify given that the contribution of ash is rarely distinguished from that of mineral sediment delivered to streams. An exception to this is a study by Earl and Blinn (2003) in burned forest within the Gila River catchment, New Mexico. This study involved both an experimental ash input (1140 L ash slurry delivered over a 1.25 h period) to a first-order stream as well as monitoring of streams in burned catchments. The experimental ash input resulted in an immediate change to water quality, with peak concentrations (in mg L^{-1}) exceeding pre-ash concentrations for various ions, including NH$_3$/NH$_4^+$ (1.35 and pre-ash: below detectable limit), NO$_3^-$ (0.08 and pre-ash: below detectable limit), and SO$_4^{2-}$ (50.5 and pre-ash: 15.8). Following the ash experiment, most parameters returned to levels similar to the reference stream within 24 h and concentrations in burned catchment streams returned to pre-fire levels within 4 months (Earl and Blinn, 2003). Atmospheric deposition of ash may also result in short-term impacts on stream water quality (Spencer and Hauer, 1991; Lathrop, 1994; Hauer and Spencer, 1998). Notably, Spencer and Hauer (1991) reported that TP and TN concentrations increased 5–60 times over background levels within two days of a wildfire in north-west Montana. Peak concentrations of 0.21 mg L^{-1} (TP), 0.35 mg L^{-1} (TN), 0.06 mg L^{-1} (NO$_3^-$), and 0.26 mg L^{-1} (NH$_3$/NH$_4^+$) were recorded (below drinking water guideline values for NO$_3^-$ and NH$_3$/NH$_4^+$), with concentrations declining to background levels within several days to weeks after the fire.

3.3. Nitrogen and phosphorous

Increased exports and concentrations of N and P in various forms following wildfire can be problematic for managers of water supply catchments. Elevated concentrations of NO$_3^-$ and NO$_2^-$ present a potential risk to human health primarily through reduction of NO$_3^-$ to NO$_2^-$, which may affect oxygen transport in red blood cells, while high concentrations of NH$_3$/NH$_4^+$ may corrode copper pipes and fittings. N and P are limiting nutrients for growth of aquatic plants, algae and cyanobacteria (blue-green algae) in water bodies. Eutrophication increases the risk of potentially toxic blooms, with implications for human health, aesthetics (taste, odour and colour), and aquatic ecosystem function (NHMRC, 2004; Drewry et al., 2006). Post-fire increases in stream exports and concentrations of N and P may result from atmospheric and runoff inputs of ash, as well as soil erosion and remobilisation of sediment stored in colluvial deposits, channels and floodplains. Studies do not distinguish ash, soil, and remobilised sediment contributions to fluxes of these nutrients, and for this reason we do not partition N and P loads as ash or sediment-derived.

Burning can result in changes to soil N and P, which may affect post-fire exports and concentrations of these constituents in runoff and streams. Wildfire may cause a very substantial reduction of N (92%) and P (76%) stores in forest floor surface organic material (O horizon) due to combustion and volatilization, with smaller reductions (N 31–51%) recorded under lower intensity burns (Murphy et al., 2006a,b). Burning and heating may reduce surface soil TN (Chambers and Attiwill, 1994; Murphy et al., 2006b; Baird et al., 1999), while increasing NH$_4$–N (from combustion), which tends

Table 4

Summary of post-fire exports of phosphorous [total P (TP), particulate P (PP)] and nitrogen [total N (TN), NO_3^-, NH_3/NH_4^+] in various forms from plot and catchment-scale studies in forest environments burned by wildfire.

References	Location	Vegetation	Sampling regime	Burnt plot (m²) or catchment area(s) (km²)	P or N form	First year export (kg ha⁻¹ year⁻¹) after wildfire (multiple increases over pre-fire or unburned control) P	N
Plot-scale							
Thomas et al., 2000	Águeda River, central Portugal	Eucalyptus globulus plantation	Storm events	16	NO_3^-	n/a	0.75–1.4 (3–5×)[a]
Ferreira et al., 2005	Águeda River, central Portugal	Pinus pinaster plantation	Storm events	16	NO_3^-	n/a	0.49 (29×)[b]
Spigel and Robichaud, 2007	Bitterroot National Forest, west-central Montana, USA	Ponderosa pine/Douglas-fire	Storm events	100	TN	n/a	Mean: 48 Range: 1–100[c]
Catchment-scale							
Bayley et al., 1992	North-west Ontario, Canada	Boreal pine forest	Weekly (ice-free period, May–October)	0.12, 0.56, 1.7	TP	TP: 0.03–0.13 (1.4×)[d]	NO_3^-: 0.04–0.42 (5.9×)[d]
					NO_3^-		NH_3/NH_4^+: 0.05–0.11 (1.9×)[d]
					NH_3/NH_4^+ TN		TN: 1.14–2.05 (1.6×)[d]
Ferreira et al., 2005	Águeda River, central Portugal	Pinus pinaster plantation	Weekly and storm events	1.1	NO_3^-	n/a	2.5 (250×)[b]
Lane et al., 2008	East Kiewa River, NE Victoria, Australia	Wet Eucalyptus forest	Weekly–fortnightly and storm events	1.36, 2.44	TP NO_3^- TN	1.67 (4–5×)	NO_3^-: 13.0[e] TN: 15.3 (6×)
Bladon et al., 2008	Rocky Mountain region, SW Alberta, Canada	Montane to subalpine coniferous forests	Snowmelt (10–14 days), winter (1–2 monthly) and storm events	3.6, 7.1, 8.2	NO_3^-	n/a	NO_3^-: 3.4–12.4 (12.7×)[f]
					NH_3/NH_4^+ TN		NH_3/NH_4^+: 0.06–0.15 (1.9×)[f] TN: 8.2–27.1 (8.8×)[f]
Blake et al., 2009b	Blue Mountains, near Sydney, Australia	Dry Eucalyptus forest	n/a	0.89	PP	0.49 [g]	n/a
Prepas et al., 2003	Central Alberta, Canada	Mixed species boreal forest	Pre-fire: 2× daily	248	PP	PP: 0.04 (1.5×)[h]	n/a
			Post-fire: 1–2 times weekly and storm events		TP	TP: 0.06 (1.3×)[h]	
Townsend and Douglas, 2004	Kakadu National Park, Northern Australia	Tropical savannah, open dry *Eucalyptus* forest	Every 3 days and storm events	6.6	TP TN	0.03 (1.8×)	1.2 (1.6×)
Mast and Clow, 2008	Glacier National Park, NW Montana	Subalpine coniferous forest	2× weekly (during snowmelt) to monthly	96.4	TP TN	0.03 (0.3×)	2.95 (2×)
Sheridan et al., 2007b	(a) Ovens River (b) Tambo River-1	Dry and wet Eucalyptus forests, subalpine woodland	Pre-fire: monthly Post-fire: fixed interval and storm events	(a) 495 (b) 523	TP TN	(a) 1.1 (9×) (b) 0.6 (431×)[i]	(a) 8.2 (9×) (b) 2.7 (94×)[i]
	(c) Dargo River (d) Tambo River-2 (e) Mitta Mitta River (f) Kiewa River Victoria, SE Australia			(c) 676 (d) 895 (e) 1533 (f) 1655		(c) 0.41 (10×) (d) 0.26 (30×) (e) 3.2 (37×) (f) 0.13 (1×)	(c) 2.8 (7×) (d) 1.4 (12×) (e) 14.1 (20×) (f) 2.2 (1×)

[a] NO_3^- exports (converted from NO_3–N) were based on two plots for the first year after fire, with the multiple increase relative to the mean annual export from an unburnt control plot (Thomas et al., 2000).

[b] Monitoring undertaken for 14 months after the wildfire (Ferreira et al., 2005).

[c] TN exports from plots were based on the mean and range of data reported from four sites (six plots at each site) (Spigel and Robichaud, 2007).

[d] Reported post-fire values are 3 years averages from three catchments, with pre-fire data collected over 2-years. Multiple increases are based on mean values from the three catchments (Bayley et al., 1992).

[e] Lane et al. (2008) reported NO_3–N exports, which have been converted to NO_3^- for comparison.

[f] Multiple increases are based on mean export values from three burnt and two unburnt control catchments (Bladon et al., 2008).

[g] PP export based on a sediment budget (<63 μm fraction) derived using ^{7}Be for the first 3 months after wildfire (Blake et al., 2009a,b).

[h] Exports were calculated from the sum of baseflow and summer storm period export data (Prepas et al., 2003).

[i] TP and TN data for the Tambo River (site 1) are for a 6 month period only (Sheridan et al., 2007b).

to decline in the months after the fire as NO_3–N increases from nitrification of the additional NH_4–N (Khanna and Raison, 1986; Weston and Attiwill, 1990; Covington and Sackett, 1992). Soil P generally does not decrease after wildfire because the volatilization temperature of P (>550 °C) is much greater than N (200 °C) (Raison, 1979; Hernandez et al., 1997; Murphy et al., 2006b). However, fire may increase soil concentrations of available P (Chambers and Attiwill, 1994; Cade-Menun et al., 2000), while up to 20% of particulate P in burned sediment has been shown to be potentially bioavailable (Blake et al., 2010). This latter point has implications for water quality and potential eutrophication of water bodies with increased post-fire erosion and downstream sediment flux after fire.

The reported effect of wildfire on exports of N and P from different forest environments varies markedly. Fire effects on stream exports of TN and TP range from a small decline or minor increase (multiple change of 0.3–2 times unburned exports) to substantial increases (20–431 times unburned) from large burned catchments in south-eastern Australia (Bayley et al., 1992; Townsend and Douglas, 2004; Sheridan et al., 2007b; Mast and Clow, 2008). TN and TP stream exports in the first year after fire were 1.1–27 and 0.03–3.2 kg ha^{-1} year^{-1}, respectively (Table 4). Higher exports of TN have been reported at the plot-scale than at the catchment-scale, ranging from 1 to 100 kg ha^{-1} year^{-1} for the first year after fire in central-west Montana (Spigel and Robichaud, 2007). NO_3^- exports range from 0.49–1.4 kg ha^{-1} year^{-1} at the plot-scale in Eucalyptus and pine plantations to 0.04–13.0 kg ha^{-1} year^{-1} at the catchment-scale, representing a multiple increase of 3–250 times unburned exports (Table 4). Data on post-fire exports of NH_3/NH_4^+ is limited, with two studies from conifer forest catchments in Canada reporting low exports (0.05–0.15 kg ha^{-1} year^{-1}) and a multiple increase of 1.9 times unburned levels in both cases (Bayley et al., 1992; Bladon et al., 2008). The range in catchment exports of N and P may reflect differences in burn area and severity, erosion processes, the extent of delivery to streams, soil and forest vegetation types, as well as rates of pre-fire atmospheric deposition (Baird et al., 1999; Stephens et al., 2004; Townsend and Douglas, 2004; Mast and Clow, 2008).

The available data suggests that the particle-associated fraction may dominate exports of N (69%) and P (77–94%) during stormflow events in the first year after fire (Prepas et al., 2003; Lane et al., 2008). In contrast, Mast and Clow (2008) reported that 90% of the TN exported from a burned subalpine coniferous forest catchment in north-west Montana was in dissolved form and similar to the unburned control catchment. However, that fire did not change suspended sediment concentrations, thereby minimising the effect of the fire on particulate N export. The contribution of particulate forms of N and P may be expected to decline with time since fire as vegetation recovery reduces erosion rates and runoff generation leading to a decline in sediment delivery (Lane et al., 2008).

Studies reporting concentrations of N and P in various forms in streams and reservoirs after wildfire are more extensive than those estimating exports (e.g. Wright, 1976; Chessman, 1986; Gerla and Galloway, 1998; Hauer and Spencer, 1998; Townsend and Douglas, 2000; Minshall et al., 2001; Gallaher et al., 2002; Malmer, 2004; Wilkinson et al., 2006; Lane et al., 2008). Generally, reported concentrations of NO_3^-, NO_2^-, and NH_3/NH_4^+ do not exceed the concentration guideline values for drinking water (Table 1). No drinking water guidelines exist for TN or TP (or other P forms), and instead the aquatic health guideline values for freshwaters in south-eastern Australia were used for comparison with studies from this region (ANZECC, 2000). Unfortunately, information is rarely provided on the duration over which observed concentrations are sustained, although elevated concentrations during flow events (stormflow or snowmelt events) may be expected to occur over periods in the order of hours to days. An important caveat on this assessment is the sampling regime adopted (Table 4) and the hydrological and constituent variability of the systems examined, which may greatly affect the ability of monitoring to capture the full range of post-fire constituent concentrations.

In subalpine coniferous forest streams, Mast and Clow (2008) observed first year post-fire NO_3^- concentrations 10 times higher than an unburned control catchment, with a maximum concentration of 0.8 mg L^{-1}, which was well below the guideline level of 50 mg L^{-1}. These authors noted that NO_3^- concentrations decreased fourfold during the 4 years study period but still remained elevated compared to the unburned catchment at the end of monitoring. In contrast, TP and NH_3/NH_4^+ concentrations appeared to be unaffected by the fire. Hauer and Spencer (1998), also working in burned conifer forest mountain catchments (1.8–238 km^2) in north-west Montana, reported maximum NO_3^- (1.9 mg L^{-1}) and NH_3/NH_4^+ (0.29 mg L^{-1}) concentrations for a 5 years period after wildfire. Maximum concentrations for both constituents were
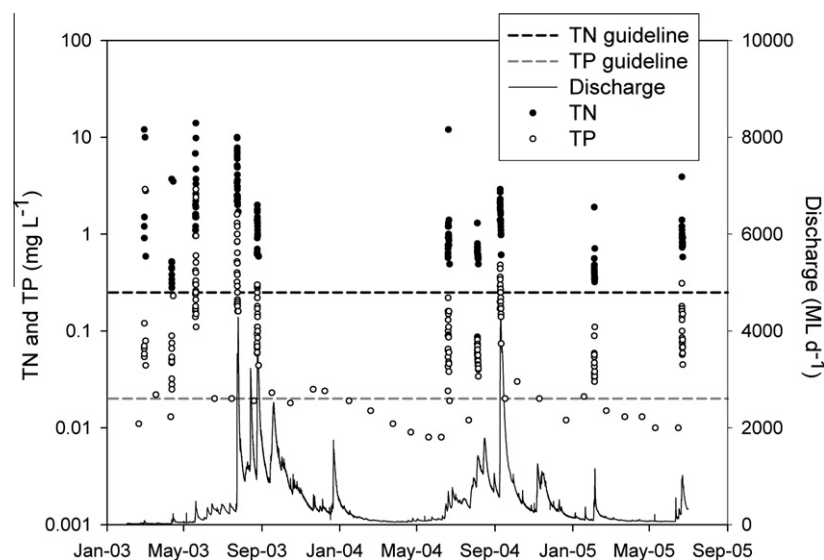

Fig. 2. Discharge, TN and TP concentrations for the Ovens River at Bright, north-east Victoria, for a period of two and a half years after the 2003 wildfires. Data provided by North East Water (T. Smith, pers. comm., 22 May 2009).

below drinking water guidelines. For similar regional settings in Canada, Bladon et al. (2008) observed a peak concentration for NO_3^- of 1.7 mg L^{-1} and Gluns and Toews (1989) reported 0.93 mg L^{-1}, both following high severity wildfire and both well below the drinking water guideline value.

Elevated concentrations of N and P in various forms have been reported after wildfire in south-eastern Australia. Based on storm-flow sampling in *Eucalyptus* forest catchments (40–750 km^2) in eastern Victoria, Chessman (1986) recorded maximum concentrations for NO_3^- (5.3 mg L^{-1}), NO_2^- (0.36 mg L^{-1}), NH_3/NH_4^+ (4.0 mg L^{-1}), and TP (0.82 mg L^{-1}) during a 3 month period after wildfire. The maximum TP and NH_3/NH_4^+ concentrations exceeded guideline thresholds by a factor of 41 times the aquatic health value for upland streams in south-eastern Australia and 8 times the drinking water value, respectively, whereas NO_3^- and NO_2^- concentrations were below the drinking water guideline values. Following the post-fire debris flows in the Buckland River catchment (referred to in Section 3.1), maximum TN and TP concentrations of 410 and 110 mg L^{-1} (1640 and 5500 times the regional aquatic health guideline values, respectively) were recorded at a water supply off-take point 30 km downstream (Leak et al., 2003). In contrast, the Ovens River upstream of the junction with the Buckland River (495 km^2; 55% burned), which was unaffected by the debris flows, recorded much lower maximum TN and TP concentrations. However, during the subsequent 2.5 years after the fire, TN and TP concentrations in the Ovens River exceeded the aquatic health guideline values during all automatically sampled flow events (Fig. 2). Despite declining annual exports of TN and TP in the Ovens (Sheridan et al., 2007b), only a slight reduction in monitored flow event concentrations was apparent. In contrast, Townsend and Douglas (2004), in a very different setting, reported no significant difference between pre and post-fire concentrations of TN and TP in open *Eucalyptus* forest streams in the wet/dry tropics of northern Australia, which they attributed to the low severity of the burn and the low relief in the 6.6 km^2 catchment.

Post-fire N and P concentration changes in lakes and reservoirs have not been widely reported, with published work largely confined to natural lakes in temperate and boreal forest regions of North America. McColl and Grigal (1977) observed that N concentrations in tributary streams and three oligotrophic lakes (area: 29–40 ha; depth: 4–5 m) in north-east Minnesota were unaffected by wildfire, with differences between tributary streams attributed largely to contrasting soil types. For the same lake systems, Wright (1976) recorded a post-fire increase in TP inputs from tributary streams but no increase in TP concentrations in the lakes, which were dominated (95%) by atmospheric inputs of P. In contrast, McEachern et al. (2000) observed a significant increase in mean TN (1.2 times unburned) and TP (2.6 times unburned) concentrations in lakes with burned catchments 2 years after fire compared to unburned boreal subartic lakes of northern Alberta. Likewise, Carignan et al. (2000), reported higher median concentrations of NO_3^- (maximum 60 times) and TP (2–3 times) in lakes with burned catchments compared to similar undisturbed lakes in the boreal forests of Québec, Canada, and noted that impacts were proportional to the catchment area burned divided by the lake volume or area.

In south-eastern Australia, data on post-fire changes to nutrient concentrations in lakes is largely confined to periodic measurements at reservoir off-take points or outflows. For example, nutrient data from water sampling in four reservoirs before and after the 2006/2007 wildfire in eastern Victoria is presented in Fig. 3, with the data for Lakes William Hovell, Buffalo and Eildon provided by Goulburn-Murray Water (L. Mattner, pers. comm., 18 May 2009), while data for Lake Glenmaggie was obtained through the Victorian Water Resources Data Warehouse. These measurements indicated that post-fire increases in mean NO_x, TN, and
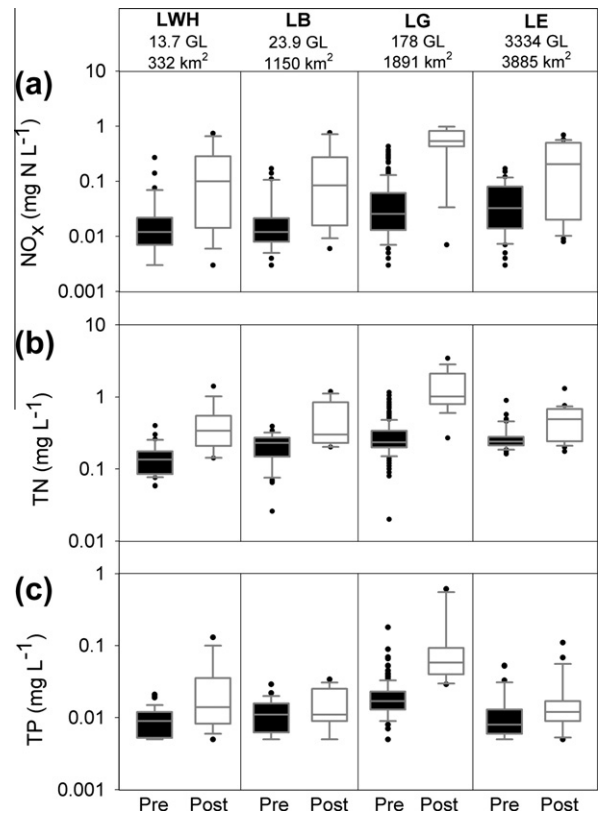

Fig. 3. Box plots of pre and post-fire (first year after fire) measurements at two–four weekly intervals of (a) NO_x; (b) TN; and (c) TP concentrations in four reservoirs (LWH: Lake William Hovell; LB: Lake Buffalo; LG: Lake Glenmaggie; LE: Lake Eildon) with catchments burned by wildfire in 2006/2007 in Victoria, south-eastern Australia. Box plots display the 10th, 25th, median, 75th, 90th percentiles and outliers. The reservoir capacity (GL) and catchment area (km^2) are listed below each reservoir label. Consecutive data prior to the 2006/2007 fire was available for 2003–2006 for LWH, LB and LE, whereas a longer record (1991–2006) was available for LG which included the effect of a wildfire that burned 17% of the catchment in 1998. Note that the catchment of LB was burned by wildfire in 2003 (35% of the catchment area) and again in 2006/2007 (near complete burn). Data for LWH, LB and LE was provided by Goulburn-Murray Water (L. Mattner, pers. comm., 18 May 2009), while data for Lake Glenmaggie was obtained through the Victorian Water Resources Data Warehouse (http://www.vicwaterdata.net/vicwaterdata/home.aspx).

TP concentrations, ranging from 1.3 to 11 times pre-2006/2007 fire levels, occurred in all reservoirs. These increases were statistically significant in all cases (Mann Whitney U test, 0.05 probability level), except for TP in two of the reservoirs (Lakes Buffalo and Eildon). Maximum concentrations in the first year after the 2006/2007 fire for NO_x, TN, and TP exceeded maximums recorded prior to this fire (Fig. 3), with both pre and post-fire monitoring occurring during a period of generally below average rainfall in south-eastern Australia (except for the longer pre-fire record at Lake Glenmaggie). The largest post-fire impact on reservoir water quality occurred in Lake Glenmaggie (catchment 90% burned) following debris flow (February 2007) and subsequent high magnitude floods (June and November 2007), with TN and TP concentrations in outflows only approaching pre-fire levels after 3 years (Fig. 4). In contrast, following the 2003 wildfires, Alexander et al. (2004) monitored nutrient levels in Dartmouth Reservoir (north-east Victoria) during the first year after fire. These authors reported elevated concentrations of TN (maximum 21 mg L^{-1}) and TP (8 mg L^{-1}) in tributary streams during flow events, but only a minor change was recorded in the reservoir near the dam wall.
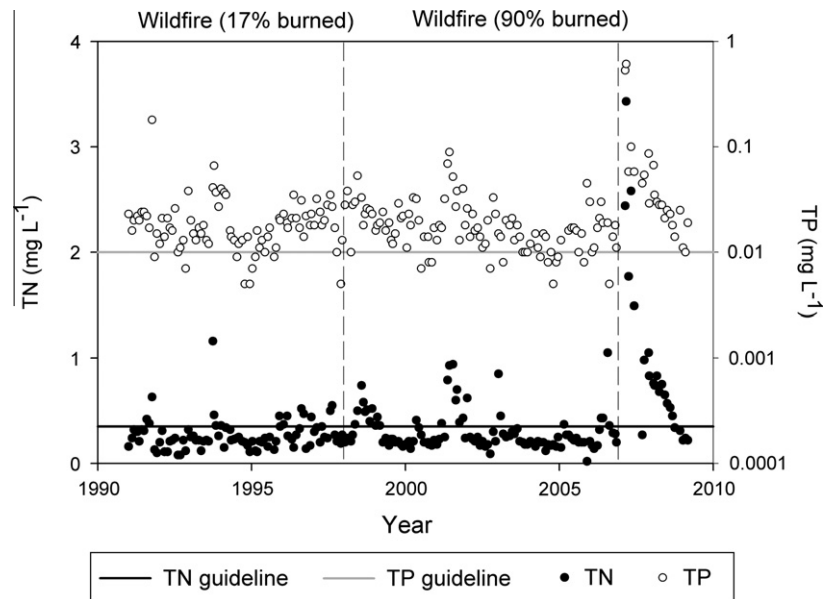
Fig. 4. Monthly TN and TP concentrations measured at the Lake Glenmaggie outflow (Macalister River) before and after wildfires in 1998 and 2006/2007, Victoria, southeastern Australia. The TN and TP guidelines indicated are for freshwater lakes or reservoirs in south-eastern Australia (ANZECC, 2000). Data was obtained through the Victorian Water Resources Data Warehouse (http://www.vicwaterdata.net/vicwaterdata/home.aspx). Note the difference in scales between TN and TP.

3.4. Trace elements

Contamination of streams and water supply reservoirs by post-fire inputs of various trace elements may be problematic for both health and aesthetic reasons. Elevated concentrations of Fe, Mn and Zn cause aesthetic problems (taste, colour, staining of pipes and fittings), whereas poisoning may occur from continued consumption of water containing high concentrations of Ba and Cu, with less severe gastrointestinal symptoms possible with Cu concentrations of 3–5 mg L^{-1} (NHMRC, 2004; WHO, 2008). As and Cr (specifically hexavalent Cr) may be carcinogenic, while Al, Pb and Hg are toxic when consumed in sufficient quantities for prolonged periods. However, information on the health effects of short duration exposure to highly elevated concentrations of these elements is generally unavailable (NHMRC, 2004; WHO, 2008).

The store of total and water soluble Mn has been reported to increase in soils following fire through additions of Mn in ash from burned vegetation and the physiochemical breakdown of Mn complexed with organic matter (Chambers and Attiwill, 1994; Parra et al., 1996). A similar pattern may be expected for Fe, Cu, and Zn (Certini, 2005). Notably, water soluble Mn levels were observed to decrease to control levels within 1–2 months, probably as a result of a rapid increase in microbial population and oxidation of Mn to less soluble higher oxides (Chambers and Attiwill, 1994). Hg may accumulate in forest ecosystems (largely in soil organic matter) by atmospheric deposition from natural (e.g. volcanoes) and anthropogenic (e.g. coal-fired power plants) sources and can be subsequently revolatilized by wildfires (Rea et al., 2002; Schwesig and Matzner, 2000; Biswas et al., 2008). Gaseous mercury (Hg^0) is oxidised to Hg^{2+} which is rapidly deposited and may be reduced to the toxic methylmercury, which bioaccumulates (Garcia and Carignan, 1999; Lin and Pehkonen, 1999; Biswas et al., 2008). Wildfire effects on levels and mobility of other trace elements in soils (Al, As, Ba, Cr, Pb) have not been reported.

Information on post-fire exports of trace elements is largely unavailable. A notable exception is the study by Townsend and Douglas (2004), which reported first year post-fire Fe and Mn exports of 1.2 kg ha^{-1} year^{-1} and 0.022 kg ha^{-1} year^{-1}, respectively, from a tropical dry savannah forest catchment (6.6 km^2), which represented a negligible change from pre-fire exports. Following

the 2003 wildfire in south-eastern Australia, Wasson et al. (2003) estimated individual event loads of Fe and Mn entering Corin reservoir (197 km^2; 98% burned), which supplies Canberra, from three storm events within 2 months after the fire. The storms generated approximate Fe/Mn loads of 139/35 kg (59 mm/day; 25.8 ML inflow), 755/19 kg (72 mm/2 days; 280 ML), and 476/143 kg (n/a rainfall; 153 ML). The first post-fire event was a high intensity, localised convective storm and generated maximum Fe and Mn concentrations of 131 and 34 mg L^{-1} (sampled one day after the event), respectively, which were well in excess of guideline values. Notably, the largest Fe load was generated by the second event, a lower intensity, widespread rainfall event with much higher inflows, despite much lower concentrations (Wasson et al., 2003).

Reports of post-fire concentrations of trace elements in streams and reservoirs are also limited. A small number of samples were collected following intense summer storm events within 1 month of the 2003 wildfire in north-east Victorian streams and analysed for various elements. Leak et al. (2003) recorded maximum Fe, As, Cr, and Pb concentrations (mg L^{-1}) of 740 (2470×), 0.28 (28×), 0.92 (18×), and 0.98 (98× WHO guideline value), respectively, in a sample taken from the Buckland River 30 km downstream of debris flows. These concentrations should not be considered event maximums given that the sample was collected on the receding limb of the hydrograph at 1.5 m^3 s^{-1}, compared to the peak flow of 68 m^3 s^{-1} that occurred less than 12 h earlier (Leak et al., 2003). Following another storm event 2 days later in the nearby Ovens River catchment (495 km^2; 55% burned), samples were collected upstream of the debris flow water quality impacts from the Buckland River (a tributary to the Ovens) and analysed for the local water authority. Concentrations of Fe (30 mg L^{-1}) greatly exceeded the WHO guideline value (100×), and remained highly elevated 6 weeks later at 22 mg L^{-1}, exceeding the pre-storm event (but post-fire) concentration of 0.64 mg L^{-1} (2.2× guideline value) (T. Smith, pers. comm., 22 May 2009). In contrast, both post and pre-storm event concentrations (mg L^{-1}) of Cu (post: 0.032/pre: 0.001), Zn (0.1/<0.002), and Cr (0.04/0.001) were below the guideline values, while post-event As (0.012/0.003) and Pb (0.033/0.001) concentrations exceeded the guideline by 1.2 and 3.3 times, respectively (T. Smith, pers. comm., 22 May 2009).

Monitoring of Fe and Mn concentrations in the Bendora reservoir (supplying Canberra) on the Cotter River (482 km^2; 98% burned) was undertaken following the 2003 wildfire in south-eastern Australia (White et al., 2006). Major water quality problems occurred, with post-fire Fe and Mn concentration peaks exceeding all previous peaks by factors of 3 and 5, respectively (White et al., 2006). The high influx of these metals, combined with the post-fire inflow of water that was five degrees warmer than previously recorded near the reservoir bottom, contributed to increased release of Fe and Mn from bottom sediments under increasingly anoxic conditions (White et al., 2006).

Following the Cerro Grande wildfire in 2000, which burned mixed-conifer forest near Los Alamos in New Mexico, USA, manual and automatic sampling of summer storm runoff immediately after the fire was undertaken by the Los Alamos National Laboratory (LANL) at 40 ephemeral stream sites and analysed for a large range of constituents (Gallaher et al., 2002). Maximum reported concentrations for Fe, Mn, and Zn were 560 (1870×), 102 (255×), and 3.6 (1.2× WHO guideline value) mg L^{-1}, respectively, from a total of 85 unfiltered samples (Gallaher et al., 2002). Elevated concentrations of As, Al, Ba, Cr, and Pb in stormflows were also reported, with maximum concentrations of 0.14 (14×), 995 (guideline value not available for total Al concentration), 20.7 (30×), 0.51 (10×), and 1.2 (120× WHO guideline value) mg L^{-1}, respectively. The maximum concentration of Hg (0.0013 mg L^{-1}) slightly exceeded the total Hg guideline value (0.001 mg L^{-1}), while Cu (0.61 mg L^{-1}) was below the guideline value. All element concentrations except Hg exceeded pre-fire maximums and were attributed to natural sources rather than from the LANL facility located downstream (Gallaher et al., 2002). Maximum filtered sample concentrations (n = 57) were also reported and were well below unfiltered concentrations (Gallaher et al., 2002). WHO guideline levels were exceeded by maximum filtered concentrations (mg L^{-1}) of Fe, Mn and As, which were 6.9 (23×), 2.0 (5×), and 0.012 (1.2× guideline value), respectively, while Ba, Cu, Cr, Hg, Pb, and Zn were all below guideline values. The unfiltered concentration of Al was high at 11.5 mg L^{-1}. Unfiltered element concentrations generally corresponded with the suspended sediment concentration (Gallaher et al., 2002). While the storm runoff in the Los Alamos streams is not used for water supply, downstream contaminant transport is a concern (Gallaher et al., 2002).

Further information on post-fire concentrations of trace elements in streams and reservoirs is not readily available but warrants investigation, particularly in fire-prone forest regions susceptible to high magnitude erosion events (such as debris flows or large floods) that may generate large suspended sediment loads. Information on the duration of elevated concentrations in streams and reservoirs is also required to determine the longevity of post-fire water quality impacts (White et al., 2006).

3.5. Chloride, sulfate and sodium

Elevated concentrations of Na$^+$ and Cl$^-$ in water supplies present aesthetic concerns (taste and corrosion of pipes and fittings), whereas SO$_4^{2-}$ may be problematic for both aesthetic (taste at concentrations over 250 mg L^{-1}) and health reasons (purgative effects are possible with concentrations over 500 mg L^{-1}) (WHO, 2008). Additional solutes (namely Ca^{2+}, Mg^{2+}, K$^+$) that have been measured in streams after fire do not have individual guideline values but are captured by measurement of total dissolved solids (TDS), although TDS is rarely reported in studies of fire effects on water quality (Neary et al., 2005).

Burning may increase the concentration of SO$_4^{2-}$ in surface soils through oxidation of sulfur in soil organic matter, while Na$^+$, SO$_4^{2-}$ and Cl$^-$ may be leached from burned plant litter (Khanna and Raison, 1986; Murphy et al., 2006b). Ash deposits contribute to Na$^+$,

Cl$^-$ and SO$_4^{2-}$ concentrations in burned soil, with 3, 9 and 3-fold increases, respectively, measured in soil solutions under ash beds compared to unburned sites (Khanna and Raison, 1986; Khanna et al., 1994).

Increased post-fire exports of Na$^+$, Cl$^-$ and SO$_4^{2-}$ relative to unburned areas have been observed. Ferreira et al. (2005) reported solute yields in overland flow after wildfire in *Pinus pinaster* forests of central Portugal, finding SO$_4^{2-}$ exports of 18.1 kg ha^{-1} year^{-1} (278 times unburned) at the plot-scale (16 m^2) and 13.2 kg ha^{-1} year^{-1} (4400 times unburned) at the catchment-scale (burned: 1.1 km^2; unburned: 0.61 km^2). These authors also measured burned catchment Na$^+$ and Cl$^-$ exports of 30.1 kg ha^{-1} year^{-1} (11 times unburned) and 39.9 kg ha^{-1} year^{-1} (19 times unburned), respectively. Most of the solute loss occurred during the first 4 months after fire and was associated with the removal of the easily mobilised surface ash layer (Ferreira et al., 2005). In contrast to this Mediterranean environment, increased solute losses in burned conifer catchments in North America have been associated with soil leaching and transfer to streams via sub-surface flow rather than storm-generated overland flow (Mast and Clow, 2008).

Reports of wildfire effects on solute concentrations in streams and lakes are mostly from coniferous forests in North America. Mast and Clow (2008) observed that wildfire increased levels of Cl$^-$ (4 times unburned) and SO$_4^{2-}$ (2.7 times unburned) in the first year after fire based on biweekly to monthly sampling in a subalpine conifer catchment (47.3 km^2) in north-west Montana. Despite the post-fire increase, maximum sampled Cl$^-$ concentrations remained <0.8 mg L^{-1}, with the peak occurring in the first spring snowmelt period after the fire. In a semi-arid environment, Gallaher et al. (2002) found post-fire maximum Cl$^-$ (53.2 mg L^{-1}) concentrations in stormflows only slightly exceeded the pre-fire maximum, while the maximum SO$_4^{2-}$ (16.7 mg L^{-1}) and Na$^+$ (14 mgL^{-1}) concentrations were below pre-fire. In the humid tropics (Malaysian Borneo), Malmer (2004) observed the effect of wildfire in small (<20 ha) forest catchment streams, which resulted in a small rise in Cl$^-$ baseflow concentrations for 2 months after fire.

Solute concentrations in lakes show a mixed response to burning. Wildfire increased exports of Cl$^-$ and SO$_4^{2-}$ to boreal shield lakes in Québec, Canada, resulting in up to a 6-fold increase in concentrations of both constituents over reference lakes, which declined over the 3 years monitoring period (Garcia and Carignan, 1999; Carignan et al., 2000; Lamontagne et al., 2000). However, maximum sampled concentrations of Cl$^-$ (<0.53 mg L^{-1}) and SO$_4^{2-}$ (<8 mg L^{-1}) after fire were very low by drinking water standards (Carignan et al., 2000). In contrast, Lathrop (1994) found negligible impact on all three solutes from a wildfire that burned 25% of the catchment areas of two lakes in Yellowstone National Park, and attributed this to the large size of the lakes which diluted increased post-fire inputs. Likewise, McEachern et al. (2000) found that fire did not significantly affect Cl$^-$ or Na$^+$ concentrations in boreal subarctic lakes of northern Alberta, Canada.

The effect of lower intensity prescribed fires on solute concentrations in streams has received some attention. Williams and Melack (1997) reported a 4 and 16-fold increase in volume-weighted mean concentrations of Cl$^-$ and SO$_4^{2-}$ (based on pre and post-fire 1–2 weekly sampling), respectively, in the first year after prescribed burning in a 13 ha mixed-conifer forest catchment in the Sierra Nevada, California. The large increase in mean concentration values was attributed to a succession of rain and snow events 4 months after the fire, although the maximum post-fire SO$_4^{2-}$ concentration (59 mg L^{-1}) was still well below the recommended limit. Stephens et al. (2004) also reported increased SO$_4^{2-}$ concentrations (13 times the mean of the unburned control) after a moderate-severity prescribed burn in the Lake Tahoe basin, California, but the maximum sampled concentrations remained

<10 mg L^{-1} and fire effects lasted for only 3 months. In contrast, both Davis (1989) and Richter et al. (1982), working in a 28 ha chaparral catchment (Arizona) and a 160 ha coastal pine forest catchment (South Carolina), respectively, reported no effect on Na$^+$, Cl$^-$ and SO$_4^{2-}$ concentrations from weekly stream sampling.

Based on this limited range of studies it is difficult to characterise Na$^+$, Cl$^-$ and SO$_4^{2-}$ responses to wildfire. It appears that exceedance of the recommended drinking water limits (based on aesthetic concerns) in streams and lakes after fire is unlikely to occur in North American coniferous forest catchments, while post-fire responses in most other forest environments are largely unknown.

3.6. Organic carbon

Wildfire may cause significant changes to the store of organic carbon on the forest floor and in surface soils, which, in conjunction with increases in post-fire erosion and leaching from the ash/soil, has implications for post-fire exports and concentrations of particulate and dissolved organic C (POC/DOC). No specific WHO drinking water guideline exists for POC or DOC, with turbidity used to infer the amount of suspended matter and colour (after 0.45 μm filtering) used as a general indicator of the level of dissolved organic matter in natural waters. In Ontario, Canada, a DOC guideline value of 5 mg L^{-1} has been set for aesthetic reasons, as well as to minimise disinfection by-products (Ministry of Environment, 2003). Chlorination of water with elevated dissolved organic matter can be problematic due to the formation of chlorinated by-products (e.g. trihalomethanes) that may present health concerns (NHMRC, 2004).

Forest floor (O horizon) loss of organic C after wildfire may be near complete, with reductions of >90% reported (Baird et al., 1999; Murphy et al., 2006a). However, deposited ash, primarily dark ash, may contain a sizable organic C component, with measured concentrations of up to 6.6% in ash from woodland burned at high severity in California (Goforth et al., 2005). Depending on the burn intensity, the effect on soil organic matter may range from minor (volatilization of some constituents), with charring (leading to formation of black carbon) and complete oxidation at higher temperatures (Giovannini et al., 1988; Tomkins et al., 1991; Giovannini and Lucchesi, 1997; Certini, 2005). Baird et al. (1999) reported soil organic C reduction of 10–17% in the surface horizons relative to unburned controls in conifer forests in Washington State, USA, 1 year after severe wildfire. An estimated 1% of the A-horizon organic C was lost through post-fire soil erosion relative to unburned control sites.

Increased post-fire erosion, combined with inputs of highly-erodible dark ash containing elevated organic C concentrations, may lead to increased POC exports after wildfire. Petticrew et al. (2006) reported a post-fire increase in the suspended organic sediment yield (burned: 3.2; unburned: 1.9 kg ha^{-1}) from a 135 km^2 catchment in British Columbia during a 7 month monitoring period, which included the spring snowmelt. These authors also observed a significantly higher proportion of organic matter in burned catchment composite suspended sediment (<500 μm) samples, which was attributed to either increased biofilm development (with increased light penetration following canopy removal by fire) and/or the transport of black carbon from ash deposits. In the 6 month period after the 2003 wildfire in south-eastern Australia, Wasson et al. (2003) estimated approximately 137 t (6.7 kg ha^{-1}) of POC entered the Corin reservoir based on sedimentation measurements, which exceeded the pre-fire mean annual POC input of 1.2 kg ha^{-1} year^{-1}.

More extensive research has been undertaken which examines DOC concentrations in streams and lakes after wildfire in the conifer forests of North America. Mast and Clow (2008) reported that wildfire had a minimal effect on DOC concentrations (burned

mean: 1.1 mg L^{-1}; unburned: 0.7 mg L^{-1}) over a 4 years period, with a concentration range of 0.5–2.3 mg L^{-1} in the burned catchment and <0.2–3.5 mg L^{-1} in the unburned. Comparison of paired burned and unburned streams in mixed conifer Rocky Mountain forest, central Idaho, revealed increased DOC levels in streams in burned catchments in the first year after fire during the peak spring flow period, although maximum sampled concentration remained <4 mg L^{-1} (Minshall et al., 2001). In boreal forests of northern Alberta, McEachern et al. (2000) observed a statistically significant 1.6-fold increase in DOC concentrations of burned catchment lakes (mean: 25 mg L^{-1}) compared to reference lakes (mean: 16 mg L^{-1}), as well as a 2.3-fold increase in mean colour of fire-affected lakes, with additional colour related to DOC in all lake waters. By contrast, Lamontagne et al. (2000) and Carignan et al. (2000) reported that wildfire did not cause a statistically significant increase in DOC stream exports or DOC concentrations (sampled maximums <11 mg L^{-1}) in burned catchment lakes compared to unburned in boreal forests, Québec, Canada.

Post-fire inputs of organic C to streams and reservoirs may be problematic, particularly from a water treatment perspective. POC flux appears to be contingent on the magnitude and timing of storm events after fire, and may be most problematic in those burned forest environments susceptible to large increases in runoff and erosion. Elevated post-fire DOC concentrations may reflect inputs from both overland and sub-surface flows. However, for the forest environments studied, wildfire effects on DOC were comparatively minor, with the concentrations measured in Canadian boreal lakes largely reflecting background conditions.

3.7. Cyanide

Cyanide release into stream water after burning as a result of ash leaching or aerial deposition has been reported (Barber et al., 2003). These authors found that available cyanide concentrations (comprised of free cyanides, HCN and CN$^-$, and several cyano-metal complexes) in ash leachate greatly exceeded that of unburned fuel in laboratory test burns. Furthermore, free cyanide concentrations measured in runoff from the first storm event following wildfire in North Carolina were an order of magnitude (mean 0.049 mg L^{-1}) higher than runoff from unburned areas (Barber et al., 2003). Both the test burns and wildfire generated available cyanide in similar or higher concentrations than the 96-h median lethal concentration for North American rainbow trout (0.045 mg L^{-1}) (Barber et al., 2003). Elevated post-fire concentrations of cyanide were also recorded following the Cerro Grande wildfire near Los Alamos (Gallaher et al., 2002). Maximum available cyanide (measured as cyanide amenable to chlorination) and total cyanide concentrations of 0.062 (median: 0.004) and 0.176 (median: 0.0116) mg L^{-1} were reported, respectively. The maximum available cyanide concentration, representing the potentially toxic fraction of cyanide, was only slightly below the WHO guideline value (0.07 mg L^{-1}). Importantly, increases in cyanide concentrations in stream water are probably of short duration during initial post-fire rainfall events and more likely to occur in small catchments where dilution is limited (Barber et al., 2003). In addition, Crouch et al. (2006) reported that the application of fire retardant to forest fires in North America had minimal effect on stream water quality, with cyanide concentrations in post-fire storm runoff unaffected by the presence of ferrocyanide in the retardant.

3.8. PAHs, PCDD/Fs and PCBs

Polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-ρ-dioxins and dibenzofurans (PCDD/Fs) and polychlorinated biphenyls (PCBs) may be produced during combustion in forest fires and released into the atmosphere or deposited in ash and

soil/sediments (Freeman and Cattell, 1990; Gabos et al., 2001; Kim et al., 2003; Gosh, 2007). Concern about PAHs, PCDD/Fs, and PCBs relates to their toxicity, carcinogenicity, environmental persistence, and tendency to bioaccumulate (Gabos et al., 2001; Olivella et al., 2006; Vila-Escalé et al., 2007).

Once released, PAHs are subject to various transformations and the different physiochemical properties of PAHs result in different interactions with ash, sediment and biota in streams (Olivella et al., 2006). Data on the release of PAHs after fire is limited. Kim et al. (2003) reported increased levels of PAHs in forest soils (15.5 times unburned maximums) 1 month after wildfire in Korea, with the difference attributed to ash inputs. Gosh (2007) concluded that elevated PAHs in sediment samples can be largely explained by the black carbon content. Vila-Escalé et al. (2007) observed increased post-fire PAH inputs to streams associated with increased overland flow and soil erosion in a Mediterranean region (Spain). PAH concentrations approached background levels 15 months after the fire and never reached levels of toxicological concern (Vila-Escalé et al., 2007). These authors also suggested low rainfall after fire may contribute to increasing PAH concentrations. This is supported by Olivella et al. (2006) who reported an increase in PAH concentrations in stream waters associated with atmospheric deposition of ash (in the absence of rainfall) 1 month after forest fires (also in Spain). With subsequent heavy rainfall, PAH concentrations decreased significantly due to dilution (which was not offset by increased PAH input with eroded ash and sediment), as well as because of the degradation of PAHs (due to photo-oxidation) and their adsorption onto deposited particles. Total PAH concentrations measured at all sampling sites and on all sampling dates remained within the European drinking water limit (Olivella et al., 2006).

PCDD/Fs and PCBs concentrations in sediment were studied following wildfire in northern Alberta, Canada (Gabos et al., 2001). These authors observed very low concentrations of both PCDD/Fs and PCBs that were consistent with background levels at all sites investigated. However, Kim et al. (2003) reported increased PCDD/Fs levels (2.3 times unburned maximums) in forest soils following wildfire in Korea 1 month after fire, with concentrations comparable to unburned soils 5 months later. The short-term increase was attributed to inputs of PCDD/Fs from ash (ash concentrations were higher than for corresponding soils), which was subsequently removed by wind and runoff.

4. Wildfire impacts on water supply: summary and future research

This review reveals a wide range of wildfire effects on levels of various physical and chemical constituents in forest catchment streams and reservoirs. Any examination of the risk of contamination and disruption to water supply following wildfire is confronted by this large range of potential water quality impacts. This reflects the many variables that influence post-fire runoff, erosion and downstream constituent flux combined with the capacity of receiving waters to attenuate increased constituent inputs. The likelihood of water supply disruption after fire also depends upon water treatment capacity, the availability of alternative supplies, and the size of the population dependent upon the catchment source. Attempting to determine the contamination risk associated with wildfire is an important step in evaluating the security of water supplies in fire-prone forest environments. This may guide decision making concerning future infrastructure investment or the diversification of water sources. In concluding this review, we (1) summarise findings and consider the potential contamination risk for various constituents after fire; (2) examine impacts on water supply following wildfires in a highly fire-prone region; and (3) outline directions for future research.

4.1. Summary of review findings

The following points summarise information on water quality changes after wildfire in forest catchments, the associated hydrological drivers, and the likelihood of contamination by various constituents from a drinking water supply and treatment perspective.

1. Catchment-scale constituent exports vary greatly after wildfire, as do estimates of export increases relative to unburned or pre-fire conditions. The majority of studies examining wildfire effects on exports focus on suspended sediment, which displayed a large range in first year post-fire export increases (1–1459 times unburned exports). Information on exports of various forms of N and P is less extensive, with reported changes in TN and TP yields after fire ranging from 0.3 to 431 times unburned. Published studies of post-fire exports of trace elements are largely unavailable. Changes in trace element fluxes after fire may be expected to reflect the magnitude of change in suspended sediment exports, given the strong tendency for sediment-association. There are also few studies that provide information on Na^+, Cl^-, SO_4^{2-} or POC exports, although short-term increases after fire may occur.

2. Constituent concentrations in streams and reservoirs after wildfire also vary widely. While TSS concentrations in streams have been extensively measured and large increases observed after wildfire, drinking water guidelines focus on turbidity. Limited post-fire turbidity data from reservoirs indicates the potential for significant increases at off-takes or outflows. NO_3^-, NO_2^-, and NH_3/NH_4^+ concentrations in streams and lakes or reservoirs may increase after wildfire but appear to present a generally low risk of exceeding drinking water guideline values. Large post-fire increases in TN and TP concentrations in streams and reservoirs have been observed, particularly in response to large erosion events. High post-fire suspended sediment concentrations were associated with elevated trace element concentrations (well in excess of guideline values), particularly for Fe, Mn, As, Cr, Al, Ba, and Pb. In contrast, Cu, Zn, and Hg have been recorded below or only slightly above guidelines, indicating a potentially lower risk of contamination for these elements. Reports of Na^+, Cl^- and SO_4^{2-} concentrations are mostly confined to coniferous forest areas in North America, where the maximum sampled values were well below recommended limits. Similarly, wildfire effects on DOC were generally minor but observations were restricted to studies in North America where concentrations largely reflected background conditions. Available cyanide concentrations may briefly approach levels of concern soon after fire in small catchments where dilution is limited. Post-fire stream concentrations of PAHs have been found to increase but did not exceed guidelines, while PCDD/Fs and PCBs in soils and sediments (in the absence of stream concentration data) remain unchanged or may experience a small increase over low levels measured under unburned conditions. Caveats on these findings include the location-specific nature of data, differences in sampling regimes, and the limited data available for many constituents. Therefore, the absence of impacts or guideline exceedance should not be interpreted as indicating that there is no post-fire risk of contamination by a particular constituent.

3. Large increases in exports and concentrations of some constituents after wildfire indicate the potential for substantial impacts on water supply. Sizable export and concentration increases at both small and large catchment scales demonstrate that post-fire impacts may extend large distances downstream. Thus wildfire in forested headwater sub-catchments may affect water supplies in downstream lowland areas, and distance from source may not necessarily act as an effective buffer against

Table 5
Summary of management actions taken to secure drinking water supplies in response to water quality impacts following wildfires in 2003 and 2006/2007 in south-eastern Australia.

Wildfire	Catchment	Management actions[a]
2003	Ovens River, Victoria	Boil water notices; increased water restrictions (level 4 of 4)
	Cotter River, ACT (Canberra)	Switched supply (1 year); water restrictions; new water treatment plant ($38 million AUD)
2006/2007	Ovens River, Victoria	Boil water (6 months); temporary water treatment plant installed at Bright
	Goulburn River, Victoria	Boil water notice for Eildon township (supplied from Lake Eildon)
	Macalister River, Victoria	Water treatment plant taken offline (Lake Glenmaggie); increased water restriction level; Water carting (February–September 2007)
	Mitchell River, Victoria	Water unsuitable for harvest to off-river storage; Installed water clarifiers and five settling dams ($6 million AUD); utilised groundwater to ensure supply

[a] White et al. (2006), Southern Rural Water (2007), North East Water (2008), State Government of Victoria (2008, 2009).

post-fire impacts on water quality. Large increases in post-fire exports and highly elevated constituent concentrations generally reflect the impact of large erosion events after wildfire. In particular, this review has emphasised the importance of short duration, high intensity storms as drivers of high magnitude, localised erosion processes (such as debris flows or flash floods) that have resulted in major water quality impacts after wildfires. The extent of downstream delivery of sediment and associated constituents is also dependent on the timing and magnitude of post-fire flow events. In-channel storage may occur in response to insufficient transport capacity of flows, potentially reducing or delaying the downstream flux of particulates. This combination of post-fire storm events, erosion processes, and the transport capacity of flow events may largely dictate the magnitude, duration and downstream extent of post-fire water quality impacts.

4. The risk to water supplies associated with contamination by various constituents after wildfire depends on the likelihood that concentrations will exceed guidelines, the duration of exceedance, and the availability of adequate treatment facilities to process contaminated water. Suspended sediment and sediment-associated contaminants (particularly nutrients, organic carbon and various trace elements) represent the constituents that are most likely to occur at elevated levels in water supplies after fire. In response, water treatment by coagulation (through use of coagulants such as aluminium sulfate or polyaluminium chloride) and filtration to remove flocculated particles may be required. Notably, for most toxic metals, elevated concentrations may reflect high sediment concentrations, which once removed would greatly reduce levels of these contaminants. At very high TSS/turbidity levels, treatment problems may be encountered that reduce the rate of water processing (e.g. Leak et al., 2003), potentially causing difficulties in maintaining a continuous supply of potable water. In the absence of adequate treatment facilities, water supplies may be vulnerable to more prolonged disruption from large post-fire increases in suspended sediment flux. Elevated turbidity levels may also necessitate increased disinfection and oxidation of metals or organics using various disinfectants/oxidants such as chlorine, ozone or hydrogen peroxide. This may result in the increased formation of disinfection by-products. For other constituents, such as NO_3^-, NO_2^-, Na^+, Cl^-, SO_4^{2-}, cyanide, PAHs, PCDD/Fs and PCBs, it appears less likely that concentrations of concern may occur after wildfire, although conventional treatment options are not available for many of these constituents.

4.2. Case study of wildfire impacts on water supply

The large wildfires that occurred in south-eastern Australia over the last decade burned numerous forest catchments containing streams and reservoirs utilised for water supply. This provides a case study of the extent to which wildfires may disrupt water supplies in a highly fire-prone region. Post-fire impacts on water quality that led to difficulties in maintaining the supply of potable water and the associated management actions taken in response are summarised in Table 5. Most notable was the disruption to the supply of drinking water to Canberra from reservoirs within the Cotter River catchment following the 2003 wildfire (White et al., 2006; Wade et al., 2008). Fortunately, an alternative unburned water storage reservoir was available, which, in conjunction with mandatory water restrictions, enabled the continued supply of potable water to the city. However, the impact of the fire was sufficient to prompt rapid construction of a $38 million (AUD) flocculation and filtration plant within 18 months that was capable of treating 270 ML d^{-1} of water with turbidity up to 20 NTU (White et al., 2006). Water supply difficulties also arose after the 2003 and 2006/2007 wildfires in Victoria (Table 5). In contrast, the 2009 wildfires burned 30% of Melbourne's water supply catchments and 9 months later no water quality impacts had been observed in storage reservoirs, with brief storm event turbidity peaks rapidly returning to baseline conditions (Frame et al., 2009). Similarly, the impact on water quality in Lake Burragorang (supplying Sydney) was negligible following wildfire in 2001, despite increased flow event TSS, TN and TP concentrations in tributaries (Wilkinson et al., 2007). Following the fire, rainfall and river flows were well below average, with much of the material generated by increased post-fire hillslope erosion entering channel storage (Wilkinson et al., 2009). This range of wildfire impacts on water supply across south-eastern Australia highlights both the dependency of water quality changes on post-fire rainfall events and the regional diversity of landscape controls (e.g. burn patterns, topography, soils, vegetation and recovery rates) influencing post-fire runoff, erosion and downstream constituent flux.

4.3. Future research

Given the current limitations in the understanding of wildfire effects on water quality, there are several areas which may form a focus for future research. Firstly, there is a paucity of data on stream exports or concentrations for various constituents (particularly trace elements) that may be generated and delivered to streams in burned forest catchments. In the absence of such data, assessing the potential contamination risk to water supplies across the range of constituents of concern is difficult. Establishing continuous monitoring programs after unplanned fire events is challenging, particularly from research funding and logistical perspectives. Nonetheless, such data from different forest environments is critical for identifying the range of post-fire impacts and for model validation.

Secondly, an expanded focus on research linking post-fire soil and hillslope hydrological properties to changes in runoff generation and erosion processes may contribute to development or

adaptation of models to better represent post-fire runoff, erosion and constituent delivery from hillslopes to streams (Istanbulluoglu et al., 2004; Rulli and Rosso, 2005; Doerr et al., 2006; Robichaud et al., 2007; Moody et al., 2009).

Thirdly, channel contributions have been shown to represent a large part of post-fire catchment sediment budgets in some forest environments (Moody and Martin, 2009). However, few studies have reported channel erosion responses to flow events after fire (White and Wells, 1979; Moody and Martin, 2001), although post-fire debris flow processes that scour steep, low-order stream channels have received more attention (Cannon and Reneau, 2000; Cannon, 2001; Meyer et al., 2001; Gartner et al., 2008; Santi et al., 2008). For this reason, greater insight into both post-fire channel adjustments and changes in catchment hydrology that influence the scour and transport capacity of flows are needed if the sources and transport of constituents are to be adequately represented in catchment models.

Finally, following from the previous point, there is a need for better accounting of the dominant sources of sediment and other constituents entering and transported through stream networks after wildfire, particularly at larger (10–100s km^2) catchment scales (Blake et al., 2009b; Wilkinson et al., 2009). Methods such as sediment fingerprinting/tracing (Collins and Walling, 2004), in conjunction with catchment monitoring of discharge and constituent fluxes, offer approaches suited to quantifying sources and fluxes at these larger spatial scales. Such information is particularly relevant to efforts to determine the potential magnitude of wildfire impacts on water resources at the scale of catchments commonly used for water supply.

Addressing these various areas would contribute to both our understanding of fundamental processes and add to the catalogue of reported wildfire impacts. It may also drive model development in a direction that services both an understanding of interactions between components within catchment systems disturbed by wildfire, while also providing guidance to managers concerned about the risk of water supply contamination after fire.

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References

Alexander, S.J., Grace, M., McKelvie, I., 2004. Effect of bushfires on receiving waters, eastern Victoria. First Interim Report to the Department of Sustainability and Environment, May 2004, Water Studies Centre, School of Chemistry, Monash University, Australia. <http://pandora.nla.gov.au/pan/47676/20050215-0000/www.dse.vic.gov.au/dse/nrence.nsf/fid/-50C870447326E485CA256ED10025C551/$file/Monash.pdf>.

Amiro, B.D., Sheppard, S.C., Johnston, F.L., Evenden, W.G., Harris, D.R., 1996. Burning radionuclide question: what happens to iodine, cesium and chlorine in a biomass fire? The Science of the Total Environment 187, 93–103.

ANZECC, 2000. Australian and New Zealand guidelines for fresh and marine water quality, volumes 1 and 2. Australia and New Zealand Environmental Conservation Council, Canberra.

Baird, M., Zabowski, D., Everett, R.L., 1999. Wildfire effects on carbon and nitrogen in inland coniferous forests. Plant and Soil 209, 233–243.

Barber, T.R., Lutes, C.C., Doorn, M.R.J., Fuchsman, P.C., Timmenga, H.J., Crouch, R.L., 2003. Aquatic ecological risks due to cyanide releases from biomass burning. Chemosphere 50 (3), 343–348.

Bayley, S.E., Schindler, D.W., Beaty, K.G., Parker, B.R., Stainton, M.P., 1992. Effects of multiple fires on nutrient yields from streams draining boreal forest and fen watersheds: nitrogen and phosphorus. Canadian Journal of Fisheries and Aquatic Science 49, 584–596.

Benavides-Solorio, J., MacDonald, L.H., 2001. Post-fire runoff and erosion from simulated rainfall on small plots, Colorado Front Range. Hydrological Processes 15 (15), 2931–2952.

Biswas, A., Blum, J.D., Keeler, G.J., 2008. Mercury storage in surface soils in a central Washington forest and estimated release during the 2001 Rex Creek fire. Science of the Total Environment 404, 129–138.

Bladon, K.D., Silins, U., Wagner, M.J., Stone, M., Emelko, M.B., Mendoza, C.A., Devito, K.J., Boon, S., 2008. Wildfire impacts on nitrogen concentration and production from headwater streams in southern Alberta's Rocky Mountains. Canadian Journal of Forest Research 38, 2359–2371.

Blake, W.H., Droppo, I.G., Wallbrink, P.J., Doerr, S.H., Shakesby, R.A., Humpreys, G.S., 2005. Impacts of wildfire on effective sediment particle size: implications for post-fire sediment budgets. In: Walling, D.E., Horowitz, A.J. (Eds.), Sediment Budgets, vol. 1, IAHS Publication 291, IAHS Press, Wallingford, UK, pp. 143–150.

Blake, W.H., Droppo, I.G., Humphreys, G.S., Doerr, S.H., Shakesby, R.A., Wallbrink, P.J., 2007. Structural characteristics and behavior of fire-modified soil aggregates. Journal of Geophysical Research F: Earth Surface 112 (2), F02020.

Blake, W.H., Wallbrink, P.J., Droppo, I.G., 2009a. Sediment aggregation and water quality in wildfire-affected river basins. Marine and Freshwater Research 60 (7), 653–659.

Blake, W.H., Wallbrink, P.J., Wilkinson, S.N., Humphreys, G.S., Doerr, S.H., Shakesby, R.A., Tomkins, K.M., 2009b. Deriving hillslope sediment budgets in wildfire-affected forests using fallout radionuclide tracers. Geomorphology 104 (3–4), 105–116.

Blake, W.H., Theocharopoulos, S.P., Skoulikidis, N., Clark, P., Tountas, P., Hartley, R., Amaxidis, Y., 2010. Wildfire impacts on hillslope sediment and phosphorous yields. Journal of Soils and Sediments 10, 671–682.

Brown, J.A.H., 1972. Hydrologic effects of a bushfire in a catchment in south-eastern New South Wales. Journal of Hydrology 15 (1), 77–96.

Cade-Menun, B.J., Berch, S.M., Preston, C.M., Lavkulich, L.M., 2000. Phosphorus forms and related soil chemistry of Podzolic soils on northern Vancouver Island, II. The effects of clear-cutting and burning. Canadian Journal of Fisheries and Aquatic Science 30, 1726–1741.

Campo, J., Andreu, V., Gimeno-Garcia, E., González, O., Rubio, J.L., 2006. Occurrence of soil erosion after repeated experimental fires in a Mediterranean environment. Geomorphology 82 (3–4), 376–387.

Canadian Council of Forest Ministers, 2006. Criteria and Indicators of Sustainable Forest Management in Canada – Indicator 2.3 Area of Forest Disturbed by Fire, Insects, Disease and Timber Harvest. <http://www.ccfm.org/ci/rprt2005/English/pg59-71.htm>.

Cannon, S.H., 2001. Debris-flow generation from recently burned watersheds. Environmental and Engineering Geoscience 7, 321–341.

Cannon, S.H., Reneau, S.L., 2000. Conditions for generation of fire-related debris flows, Capulin Canyon, New Mexico. Earth Surface Processes and Landforms 25, 1103–1121.

Cannon, S.H., Gartner, J.E., Wilson, R.C., Bowers, J.C., Laber, J.L., 2008. Storm rainfall conditions for floods and debris flows from recently burned areas in southwestern Colorado and southern California. Geomorphology 96, 250–269.

Carignan, R., D'Arcy, P., Lamontagne, S., 2000. Comparative impacts of fire and forest harvesting on water quality in Boreal Shield lakes. Canadian Journal of Fisheries and Aquatic Sciences 57, 105–117.

Cerdà, A., Doerr, S.H., 2008. The effect of ash and needle cover on surface runoff and erosion in the immediate post-fire period. Catena 74 (3), 256–263.

Cerdà, A., Lasanta, T., 2005. Long-term erosional responses after fire in the Central Spanish Pyrenees – 1. Water and sediment yield. Catena 60 (1), 59–80.

Certini, G., 2005. Effects of fire on properties of forest soils: a review. Oecologia 143 (1), 1–10.

Chambers, D.P., Attiwill, P.M., 1994. The ash-bed effect in Eucalyptus regnans forest: chemical, physical and microbiological changes in soil after heating or partial sterilisation. Australian Journal of Botany 42, 739–749.

Chessman, B.C., 1986. Impact of the 1983 wildfires on river water quality in East Gippsland, Victoria. Australian Journal of Marine and Freshwater Research 37 (3), 399–420.

Coelho, C.O.A., Ferreira, A.J.D., Boulet, A-K., Keizer, J.J., 2004. Overland flow generation processes, erosion yields and solute loss following different intensity fires. Quarterly Journal of Engineering Geology and Hydrogeology 37, 233–240.

Collins, A.L., Walling, D.E., 2004. Documenting catchment suspended sediment sources: Problems, approaches and prospects. Progress in Physical Geography 28 (2), 159–196.

Committee on Hydrologic Impacts of Forest Management, 2008. Hydrologic Effects of a Changing Forest Landscape. National Research Council, National Academy of Sciences, Washington, USA.

Covington, W.W., Sackett, S.S., 1992. Soil mineral nitrogen changes following prescribed burning in ponderosa pine. Forest Ecology and Management 54 (1–4), 175–191.

Crouch, R.L., Timmenga, H.J., Barber, T.R., Fuchsman, P.C., 2006. Post-fire surface water quality: comparison of fire retardant versus wildfire-related effects. Chemosphere 62 (6), 874–889.

Davis, E.A., 1989. Prescribed fire in Arizona chaparral: effects on stream water quality. Forest Ecology and Management 26 (3), 189–206.

Demeyer, A., Voundi Nkana, J.C., Verloo, M.G., 2001. Characteristics of wood ash and influence on soil properties and nutrient uptake: an overview. Bioresource Technology 77, 287–295.

Doerr, S.H., Shakesby, R.A., Blake, W.H., Chafer, C.J., Humphreys, G.S., Wallbrink, P.J., 2006. Effects of differing wildfire severities on soil wettability and implications for hydrological response. Journal of Hydrology 319, 295–311.

Doerr, S.H., Cerdà, A., Bryant, R., 2008. The role of ash in carbon fluxes in fire-affected environments. Geophysical Research Abstracts 10, European Geosciences Union General Assembly, EGU2008-A-06555.

Dragovich, D., Morris, R., 2002. Fire intensity, slopewash and bio-transfer of sediment in eucalypt forest, Australia. Earth Surface Processes and Landforms 27 (12), 1309–1319.

Drewry, J.J., Newham, L.T.H., Greene, R.S.B., Jakeman, A.J., Croke, B.F.W., 2006. A review of nitrogen and phosphorous export to waterways: context for catchment modelling. Marine and Freshwater Research 57, 757–774.

Droppo, I.G., 2001. Rethinking what constitutes suspended sediment. Hydrological Processes 15, 1551–1564.

Dudley, N., Stolton, S., 2003. Running Pure: The Importance of Forest Protected Areas to Drinking Water. Research Report for the World Bank and WWF Alliance for Forest Conservation and Sustainable Use. ISBN 2-88085-262-5.

Dyrness, C.T., Youngberg, C.T., 1957. The effects of logging and slash burning on soil structure. Soil Science Society of America Proceedings 21, 444–447.

Earl, S.R., Blinn, D.W., 2003. Effects of wildfire ash on water chemistry and biota in south-western USA streams. Freshwater Biology 48 (6), 1015–1030.

Ellis, S., Kanowski, P., Whelan, R., 2004. National inquiry on bushfire mitigation and management, Commonwealth of Australia, Canberra.

Environment Australia, 2002. Sources of dioxins and furans in Australia: air emissions, revised edition. Environment Australia, Commonwealth of Australia. <http://www.environment.gov.au/settlements/publications/chemicals/dioxins/dioxinsources.html>.

FAO, 2001. Global Forest Fire Assessment 1990–2000. Food and Agriculture Organization of the United Nations, Forestry Department, Forest Resources Assessment Programme Working Paper 55, Rome.

Ferreira, A.J.D., Coelho, C.O.A., Boulet, A.K., Lopes, F.P., 2005. Temporal patterns of solute loss following wildfires in Central Portugal. International Journal of Wildland Fire 14, 401–412.

Frame, J., Hand, J., Miles, N., Potter, M., Pettigrove, V., Lucas, A., Dabal, R., Crosbie, N.D., Yurisich, R., Tan, K.S., 2009. Melbourne Water's recovery response to the Black Saturday bushfires. In: Australian Water Association Specialty Conference: Sustaining the Rivers and Reservoirs, November 2009, Canberra, Australia. <http://www.awa.asn.au/>.

Freeman, D.J., Cattell, F.C.R., 1990. Woodburning as a source of atmospheric polycyclic aromatic hydrocarbons. Environmental Science and Technology 24, 1581–1585.

Gabet, E.J., Sternberg, P., 2008. The effects of vegetative ash on infiltration capacity, sediment transport, and the generation of progressively bulked debris flows. Geomorphology 101 (4), 666–673.

Gabos, S., Ikonomou, M.G., Schopflocher, D., Fowler, B.R., White, J., Prepas, E., Prince, D., Chen, W., 2001. Characteristics of PAHs, PCDD/Fs and PCBs in sediment following forest fires in northern Alberta. Chemosphere 43, 709–719.

Gallaher, B., Koch, R., Mullen, K., 2002. Quality of Storm Water Runoff at Los Alamos National Laboratory in 2000 with Emphasis on the Impact of the Cerro Grande Fire. Los Alamos National Laboratory LA-13926. <http://www.lanl.gov/environment/all/docs/cgf/LA-13926.pdf>.

Garcia, E., Carignan, R., 1999. Impact of wildfire and clear-cutting in the boreal forest on methyl mercury in zooplankton. Canadian Journal of Fisheries and Aquatic Sciences 56, 339–345.

Gartner, J.E., Cannon, S.H., Santi, P.M., Dewolfe, V.G., 2008. Empirical models to predict the volumes of debris flows generated by recently burned basins in the western US. Geomorphology 96, 339–354.

Gerla, P.J., Galloway, J.M., 1998. Water quality of two streams near Yellowstone Park, Wyoming, following the 1988 Clover-Mist wildfire. Environmental Geology 36 (1–2), 127–136.

Giovannini, G., Lucchesi, S., 1997. Modifications induced in soil physico-chemical parameters by experimental fires at different intensities. Soil Science 162 (7), 479–486.

Giovannini, G., Lucchesi, S., Giachetti, M., 1988. Effect of heating on some physical and chemical parameters related to soil aggregation and erodibility. Soil Science 146, 255–261.

Gluns, D.R., Toews, D.A.A., 1989. Effect of a major wildfire on water quality in southeastern British Columbia. In: Woessner, W.W., Potts, D.F. (Eds.), Headwaters Hydrology. American Water Resources Association, Bethesda, Maryland, pp. 487–499.

Goforth, B.R., Graham, R.C., Hubbert, K.R., Zanner, C.W., Minnich, R.A., 2005. Spatial distribution and properties of ash and thermally altered soils after high-severity forest fire, southern California. International Journal of Wildland Fire 14, 343–354.

Gosh, U., 2007. The role of black carbon in influencing availability of PAHs in sediment. Human and Ecological Risk Assessment 13, 276–285.

Hauer, F.R., Spencer, C.N., 1998. Phosphorus and nitrogen dynamics in streams associated with wildfire: a study of immediate and long-term effects. International Journal of Wildland Fire 8 (4), 183–198.

Hernandez, T., Garcia, C., Reinhardt, I., 1997. Short-term effect of wildfire on the chemical, biochemical, and microbiological properties of Mediterranean pine forest soils. Biology and Fertility of Soils 25, 109–116.

Horowitz, A.J., 1991. A Primer in Sediment-Trace Element Chemistry, second ed. Lewis Publishers, Chelsea, MI.

Horowitz, A.J., Elrick, K.A., 1987. The relation of stream sediment surface area, grain size and composition to trace element chemistry. Applied Geochemistry 2, 437–451.

Ice, G.G., Neary, D.G., Adams, P.W., 2004. Effects of wildfire on soils and watershed processes. Journal of Forestry 102, 16–20.

Istanbulluoglu, E., Tarboton, D.G., Pack, R.T., Luce, C.H., 2004. Modeling of the interactions between forest vegetation, disturbances, and sediment yields. Journal of Geophysical Research 109, F01009.

Johansen, M.P., Hakonson, T.E., Whicker, F.W., Breshears, D.D., 2003. Pulsed redistribution of a contaminant following forest fire: cesium-137 in runoff. Journal of Environmental Quality 32, 2150–2157.

Joint Fire Service Program, 2004. Joint Fire Service Program 2003 Business Summary. US Department of Agriculture, Forest Service, Pacific Northwest Research Station, Seattle, WA, USA.

Khanna, P.K., Raison, R.J., 1986. Effect of fire intensity on solution chemistry of surface soil under a Eucalyptus pauciflora forest. Australian Journal of Soil Research 24, 423–434.

Khanna, P.K., Raison, R.J., Falkiner, R.A., 1994. Chemical properties of ash derived from Eucalyptus litter and its effects on forest soils. Forest Ecology and Management 66, 107–125.

Kim, E.-J., Oh, J.-E., Chang, Y.-S., 2003. Effects of forest fire on the level and distribution of PCDD/Fs and PAHs in soil. The Science of the Total Environment 311, 177–189.

Kunze, M.D., Stednick, J.D., 2006. Streamflow and suspended sediment yield following the 2000 Bobcat fire, Colorado. Hydrological Processes 20 (8), 1661–1681.

Lamontagne, S., Carignan, R., D'Arcy, P., Prairie, Y.T., Paré, D., 2000. Element export in runoff from eastern Canadian Boreal Shield drainage basins following forest harvesting and wildfires. Canadian Journal of Fisheries and Aquatic Sciences 57, 118–128.

Lane, P.N.J., Sheridan, G.J., Noske, P.J., 2006. Changes in sediment loads and discharge from small mountain catchments following wildfire in south eastern Australia. Journal of Hydrology 331, 495–510.

Lane, P.N.J., Sheridan, G.J., Noske, P.J., Sherwin, C.B., 2008. Phosphorus and nitrogen exports from SE Australian forests following wildfire. Journal of Hydrology 361, 186–198.

Lathrop Jr., R.G., 1994. Impacts of the 1988 wildfires on the water quality of Yellowstone and Lewis Lakes, Wyoming. International Journal of Wildland Fire 4 (3), 169–175.

Lavee, H., Kutiel, P., Segev, M., Benyamini, Y., 1995. Effect of surface roughness on runoff and erosion in a Mediterranean ecosystem: the role of fire. Geomorphology 11 (3), 227–2384.

Leak, M., Passuello, R., Tyler, B., 2003. I've seen fire. I've seen rain. I've seen muddy waters that I thought would never clear again. Waterworks 6, 38–44.

Lin, C.J., Pehkonen, S.O., 1999. The chemistry of atmospheric mercury: a review. Atmospheric Environments 33, 2067–2079.

Lyon, J.P., O'Connor, J.P., 2008. Smoke on the water: Can riverine fish populations recover following a catastrophic fire-related sediment slug? Austral Ecology 33 (6), 794–806.

Mallik, A.U., Gimingham, C.H., Rahman, A.A., 1984. Ecological effects of heather burning 1. Water infiltration. Moisture retention and porosity of surface soil Journal of Ecology 72 (3), 767–776.

Malmer, A., 2004. Streamwater quality as affected by wild fires in natural and manmade vegetation in Malaysian Borneo. Hydrological Processes 18 (5), 853–864.

Malmon, D.V., Reneau, S.L., Katzman, D., Lavine, A., Lyman, J., 2007. Suspended sediment transport in an ephemeral stream following wildfire. Journal of Geophysical Research 112, F02006.

Mast, M.A., Clow, D.W., 2008. Effects of 2003 wildfires on stream chemistry in Glacier National Park, Montana. Hydrological Processes 22, 5013–5023.

Mayor, A.G., Bautista, S., Llovet, J., Bellot, J., 2007. Post-fire hydrological and erosional responses of a Mediterranean landscape: seven years of catchment-scale dynamics. Catena 71, 68–75.

McColl, J.G., Grigal, D.F., 1977. Nutrient changes following a forest wildfire in Minnesota: effects in watersheds with differing soils. Oikos 28, 105–112.

McEachern, P., Prepas, E.E., Gibson, J.J., Dinsmore, W.P., 2000. Forest fire induced impacts on phosphorous, nitrogen, and chlorophyll a concentrations in boreal subarctic lakes of northern Alberta. Canadian Journal Fisheries and Aquatic Science 57, 73–81.

Meyer, G.A., Pierce, J.L., Wood, S.H., Jull, A.J.T., 2001. Fire, storms, and erosional events in the Idaho batholith. Hydrological Processes 15 (15), 3025–3038.

Ministry of Environment, 2003. Technical Support Document for Ontario Drinking Water: Standards, Objectives and Guidelines. Ontario Ministry for the Environment, Canada.

Minshall, G.W., Brock, J.T., Andrews, D.A., Robinson, C.T., 2001. Water quality, substratum and biotic responses of five central Idaho (USA) streams during the first year following the Mortar Creek fire. International Journal of Wildland Fire 10, 185–199.

Moody, J.A., Martin, D.A., 2001. Initial hydrologic and geomorphic response following a wildfire in the Colorado Front Range. Earth Surface Processes and Landforms 26 (10), 1049–1070.

Moody, J.A., Martin, D.A., 2004. Wildfire impacts on reservoir sedimentation in the western United States. In: Proceedings of the Ninth International Symposium on River Sedimentation, October 2004, Yichang, China. Tsinghua University Press, China, pp. 1095–1102.

Moody, J.A., Martin, D.A., 2009. Synthesis of sediment yields after wildland fire in different rainfall regimes in the western United States. International Journal of Wildland Fire 18, 96–115.

Moody, J.A., Kinner, D.A., Úbeda, X., 2009. Linking hydraulic properties of fire-affected soils to infiltration and water repellency. Journal of Hydrology 379, 291–303.

Murphy, J.D., Johnson, D.W., Miller, W.W., Walker, R.F., Blank, R.R., 2006a. Prescribed fire effects on forest floor and soil nutrients in a Sierra Nevada forest. Soil Science 171, 181–199.

Murphy, J.D., Johnson, D.W., Miller, W.W., Walker, R.F., Carroll, E.F., Blank, R.R., 2006b. Wildfire effects on soil nutrients and leaching in a Tahoe Basin watershed. Journal of Environmental Quality 35, 479–489.

National Interagency Fire Centre, 2009. Fire Information – Wildland Fire Statistics: 1997–2008 large fires (<100,000 acres). <http://www.nifc.gov/fire_info/lg_fires.htm>.

Neary, D.G., Ryan, K.C., DeBano, L.F., 2005. Wildland Fire in Ecosystems: Effects of Fire on Soils and Water, US Department of Agriculture, Forest Service, General Technical Report RMRS-42, Ogden, Utah.

Neary, D.G., Ice, G.G., Jackson, C.R., 2009. Linkages between forest soils and water quality and quantity. Forest Ecology and Management 258, 2269–2281.

NHMRC, 2004. Australian Drinking Water Guidelines 6. National Health and Medical Research Council, Australian Government.

North East Water, 2008. Annual Water Quality Report 2007–2008. North East Water, Wodonga, Victoria, Australia. <http://www.nerwa.vic.gov.au/communications/publications/images/Annual_WQ_report_07_08_FinalVersion.pdf>.

Noske, P.J., Lane, P.N.J., Sheridan, G.J., 2010. Stream exports of coarse matter and phosphorus following wildfire in NE Victoria, Australia. Hydrological Processes 24, 1514–1529.

Nyman, P., Sheridan, G.J., Smith, H.G., Lane, P.N.J., in press. Evidence of debris flow occurrence after wildfire in upland catchments of south-east Australia. Geomorphology.

Olivella, M.A., Ribalta, T.G., de Febrer, A.R., Mollet, J.M., de las Heras, F.X.C., 2006. Distribution of polycyclic aromatic hydrocarbons in riverine waters after Mediterranean forest fires. Science of the Total Environment 355, 156–166.

Onda, Y., Dietrich, W.E., Booker, F., 2008. Evolution of overland flow after a severe forest fire, Point Reyes, California. Catena 72, 13–20.

Ongley, E.D., Krishnappan, B.G., Droppo, I.G., Rao, S.S., Maguire, R.J., 1992. Cohesive sediment transport: emerging issues for toxic chemical management. Hydrobiologia (235/236), 177–187.

Parliament of Victoria, 2008. Inquiry into the Impact of Public Land Management Practices on Bushfires in Victoria: Report of the Environment and Natural Resources Committee. Parliamentary Paper No. 116.

Parra, J.G., Rivero, V.C., Lopez, T.I., 1996. Forms of Mn in soils affected by a forest fire. The Science of the Total Environment 181, 231–236.

Petticrew, E.L., Owens, P.N., Giles, T.R., 2006. Wildfire effects on the quantity and composition of suspended and gravel-stored sediments. Water, Air, and Soil Pollution: Focus 6 (5–6), 647–656.

Plumlee, G.S., Martin, D.A., Hoefen, T., Kokaly, R., Hageman, P., Eckberg, A., Meeker, G.P., Adams, M., Anthony, M., Lamothe, P.J., 2007. Preliminary Analytical Results for Ash and Burned Soils from the October 2007 Southern California wildfires. United States Geological Survey Open File Report 2007-1407.

Prepas, E.E., Burke, J.M., Chanasyk, D.S., Smith, D.W., Putz, G., Gabos, S., Chen, W., Millions, D., Serediak, M., 2003. Impact of wildfire on discharge and phosphorous export from the Sakwatamau watershed in the Swan Hills, Alberta, during the first two years. Journal of Environmental Engineering Science 2, S63–S72.

Prosser, I.P., Williams, L., 1998. The effect of wildfire on runoff and erosion in native eucalyptus forest. Hydrological Processes 12, 251–265.

Raison, R.J., 1979. Modification of the soil environment by vegetation fires, with particular reference to nitrogen transformations: a review. Plant and Soil 51, 73–108.

Rea, A.W., Lindberg, S.E., Scherbatskoy, T., Keeler, G.J., 2002. Mercury accumulation in foliage over time in two northern mixed-hardwood forests. Water Air Soil Pollution 133, 49–67.

Reneau, S.L., Katzman, D., Kuyumjian, G.A., Lavine, A., Malmon, D.V., 2007. Sediment delivery after a wildfire. Geology 35 (2), 151–154.

Rhoads, C., Entwistle, D., Butler, D., 2006. Initial stream water response to the Hayman fire, Colorado Front Range. In: Elder, K., Dwire, K, Hubbard, R., Rhoades, C., Ryan, S., Young, M., Porth, L., Dixon, M., Goodbody, A., Proceedings of the Second Interagency Conference on Research in the Watersheds, May 16–19, 2006, Coweeta Hydrologic Laboratory, Otto, NC, pp. 89–98.

Richards, R.P., Holloway, J., 1987. Monte Carlo studies of sampling strategies for estimating tributary loads. Water Resources Research 23, 1939–1948.

Richter, D.D., Ralston, C.W., Harms, W.R., 1982. Prescribed fire: effects on water quality and forest nutrient cycling. Science 215, 661–663.

Robertson, D.M., Roerish, E.D., 1999. Influence of various water quality sampling strategies on load estimates for small streams. Water Resources Research 35, 3747–3759.

Robichaud, P.R., Elliot, W.J., Pierson, F.B., Hall, D.E., Moffet, C.A., 2007. Predicting postfire erosion and mitigation effectiveness with a web-based probabilistic erosion model. Catena 71 (2), 229–241.

Rulli, M.C., Rosso, R., 2005. Modeling catchment erosion after wildfires in the San Gabriel Mountains of southern California. Geophysical Research Letters 32, L19401.

Santi, P.M., deWolfe, V.G., Higgins, J.D., Cannon, S.H., Gartner, J.E., 2008. Sources of debris flow material in burned areas. Geomorphology 96, 310–321.

Schwesig, D., Matzner, E., 2000. Pools and fluxes of mercury and methylmercury in two forested catchments in Germany. Science of the Total Environment 260, 213–223.

Scott, D.F., 1993. The hydrological effects of fire in South African mountain catchments. Journal of Hydrology 150, 409–432.

Scott, D.F., Versfeld, D.B., Lesch, W., 1998. Erosion and sediment yield in relation to afforestation and fire in the mountains of the Western Cape Province, South Africa. South African Geographical Journal 80, 52–59.

Shakesby, R.A., Doerr, S.H., 2006. Wildfire as a hydrological and geomorphological agent. Earth-Science Reviews 74 (3–4), 269–307.

Shakesby, R.A., Coelho, C.O.A., Ferreira, A.D., Terry, J.P., Walsh, R.P.D., 1993. Wildfire impacts on soil erosion and hydrology in wet Mediterranean forest, Portugal. International Journal of Wildland Fire 3, 95–110.

Sheridan, G.J., Lane, P., Noske, P., 2007a. Quantification of hillslope runoff and erosion processes before and after wildfire in a wet Eucalyptus forest. Journal of Hydrology 343, 12–28.

Sheridan, G., Lane, P., Noske, P., Feikema, P., Sherwin, C., Grayson, R., 2007b. Impact of the 2003 Alpine Bushfires on Streamflow: Estimated Changes in Stream Exports of Sediment, Phosphorus and Nitrogen following the 2003 Bushfires in Eastern Victoria, Murray-Darling Basin Commission, MDBC Publication No. 22/08, Canberra, Australia.

Smith, H.G., 2008. Estimation of suspended sediment loads and delivery in an incised upland headwater catchment, south-eastern Australia. Hydrological Processes 22, 3135–3148.

Smith, H.G., Dragovich, D., 2008. Post-fire hillslope erosion response in a sub-alpine environment, south-eastern Australia. Catena 73 (3), 274–285.

Someshwar, A.V., 1996. Wood and combination wood-fired boiler ash characterization. Journal of Environmental Quality 25, 962–972.

Southern Rural Water, 2007. Safe Drinking Water 2006/2007 Annual Report. Southern Rural Water, Maffra, Victoria, Australia.

Spencer, C.N., Hauer, F.R., 1991. Phosphorus and nitrogen dynamics in streams during a wildfire. Journal of the North American Benthological Society 10, 24–30.

Spigel, K.M., Robichaud, P.R., 2007. First-year post-fire erosion rates in Bitterroot National Forest, Montana. Hydrological Processes 21 (8), 998–1005.

State Government of Victoria, 2008. Annual Report on Drinking Water Quality in Victoria, 1 July 2006–30 June 2007. Department of Health Services, State Government of Victoria, Melbourne, Victoria.

State Government of Victoria, 2009. Annual Report on Drinking Water Quality in Victoria, 1 July 2007–30 June 2008. Department of Health Services, State Government of Victoria, Melbourne, Victoria.

Stephens, S.L., Meixner, T., Poth, M., McGurk, B., Payne, D., 2004. Prescribed fire, soils, and stream water chemistry in a watershed in the Lake Tahoe Basin, California. International Journal of Wildland Fire 13, 27–35.

Thomas, A.D., Walsh, R.P.D., Shakesby, R.A., 2000. Solutes in overland flow following fire in eucalyptus and pine forests, northern Portugal. Hydrological Processes 14, 971–985.

Tomkins, I.B., Kellas, J.D., Tolhurst, K.G., Oswin, D.A., 1991. Effects of fire intensity on soil chemistry on a Eucalypt forest. Australian Journal of Soil Research 29 (1), 25–47.

Tomkins, K.M., Humphreys, G.S., Wilkinson, S.N., Fink, D., Hesse, P.P., Doerr, S.H., Shakesby, R.A., Wallbrink, P.J., Blake, W.H., 2007. Contemporary versus long-term denudation along a passive plate margin: the role of extreme events. Earth Surface Processes and Landforms 32 (7), 1013–1031.

Townsend, S.A., Douglas, M.M., 2000. The effect of three fire regimes on stream water quality, water yield and export coefficients in a tropical savanna (northern Australia). Journal of Hydrology 229, 118–137.

Townsend, S.A., Douglas, M.M., 2004. The effect of a wildfire on stream water quality and catchment water yield in a tropical savanna excluded from fire for 10 years (Kakadu National Park, North Australia). Water Research 38 (13), 3051–3058.

Tryhorn, L., Lynch, A., Abramson, R., Parkyn, K., 2008. On the meteorological mechanisms driving postfire flash floods: a case study. Monthly Weather Review 136 (5), 1778–1791.

Ulery, A.L., Graham, R.C., Amrhein, C., 1993. Wood–ash composition and soil pH following intense burning. Soil Science 156 (5), 358–364.

Victorian Bushfires Royal Commission, 2009. Interim Report of the 2009 Victorian Bushfires Royal Commission. Parliament of Victoria, Melbourne, Victoria. <http://www.royalcommission.vic.gov.au/getdoc/208e8bcb-3927-41ec-8c23-2cdc86a7cec7/Interim-Report>.

Victorian Department of Sustainability and Environment, 2009. Significant Fire Years: Major Bushfires in Victoria. <http://www.dse.vic.gov.au/DSE/nrenfoe.nsf/childdocs/-D79E4FB0C437E1B6CA256DA60008B9EF?open>.

Vila-Escalé, M., Vegas-Vilarrubia, T., Prat, N., 2007. Release of polycyclic aromatic compounds into a Mediterranean creek (Catalonia, NE Spain) after a forest fire. Water Research 41 (10), 2171–2179.

Wade, A., White, I., Worthy, M., Gill, A.M., Mueller, N., Wasson, R.J., 2008. Natural and human induced fire impacts on water quality in water supply catchments. In: Lambert, M., Daniell, T., Leonard, M. (Eds.), Proceedings of Water Down Under 2008: Incorporating 31st Hydrology and Water Resources Symposium, and, 4th International Conference on Water Resources and Environment Research, 14–17 April, 2008, Adelaide, Australia, pp. 1201–1212.

Walling, D.E., Webb, B.W., Woodward, J.C., 1992. Some sampling considerations in the design of effective strategies for monitoring sediment-associated transport. In: Bogen, J., Walling, D.E., Day, T.J. (Eds.), Erosion and Sediment Transport Monitoring Programmes in River Basins. IAHS Publication No. 210, IAHS Press, Wallingford, UK, pp. 279–288.

Wasson, R.J., Croke, B.F., McCulloch, M.M., Mueller, N, Olley, J., Starr, B., Wade, A., White, I., Whiteway, T., 2003. Sediment, Particulate and Dissolved Organic Carbon, Iron and Manganese Input to Corin Reservoir. Report to ActewAGL for the Cotter Catchment Fire Remediation Project, WF 30014, Centre for Resource and Environmental Studies, Australian National University.

Weston, C.J., Attiwill, P.M., 1990. Effects of fire and harvesting on nitrogen transformations and ionic mobility in soils of *Eucalyptus regnans* forests of south-eastern Australia. Oecologia 83, 20–26.

White, W.D., Wells, S.G., 1979. Forest-fire devegetation and drainage basin adjustments in mountainous terrain. In: Rhodes, D.D., Williams G.P. (Eds.), Adjustments of the Fluvial System: Proceedings of the Tenth Annual Geomorphology Symposia Series. Kendall Hunt Publishing, Binghamton, New York, pp. 199–223.

White, I., Wade, A., Worthy, M., Mueller, N., Daniell, T., Wasson, R., 2006. The vulnerability of water supply catchments to bushfires: impacts of the January 2003 wildfires on the Australian Capital Territory. Australian Journal of Water Resources 10 (2), 1–16.

WHO, 2008. Guidelines for drinking-water quality, third ed. World Health Organisation, Geneva.

Wilkinson, S.N., Wallbrink, P.J., Blake, W.H., Doerr, S.H., Shakesby, R.A., 2006. Impacts on Water Quality by Sediments and Nutrients Released during Extreme Bushfires: Report 3: Post-Fire Sediment and Nutrient Redistribution to Downstream Waterbodies, Nattai National Park, NSW. CSIRO Land and Water Science Report 64/06.

Wilkinson, S.N., Wallbrink, P.J., Hancock, G., Blake, W., Shakesby, R., Doerr, S., 2007. Impacts on Water Quality by Sediments and Nutrients Released During Extreme Bushfires: Report 4: Impacts on Lake Burragorang, CSIRO Land and Water Science Report 6/07.

Wilkinson, S.N., Wallbrink, P.J., Hancock, G.J., Blake, W.H., Shakesby, R.A., Doerr, S.H., 2009. Fallout radionuclide tracers identify a switch in sediment sources and transport-limited sediment yield following wildfire in a eucalypt forest. Geomorphology 110, 140–151.

Williams, M.R., Melack, J.M., 1997. Effects of prescribed burning and drought on the solute chemistry of mixed-conifer forest streams of the Sierra Nevada, California. Biogeochemistry 39, 225–253.

Woods, S.W., Balfour, V.N., 2008. The effect of ash on runoff and erosion after a severe forest wildfire, Montana, USA. International Journal of Wildland Fire 17 (5), 535–548.

Woodward, J.C., Walling, D.E., 2007. Composite suspended sediment particles in river systems: their incidence, dynamics and physical characteristics. Hydrological Processes 21, 3601–3614.

Wright, R.F., 1976. The impact of forest fire on the nutrient influxes to small lakes in northeastern Minnesota. Ecology 57, 649–663.

ASSESSMENT OF WATER QUALITY CONCENTRATIONS AND LOADS FROM NATURAL LANDSCAPES

Eric D. Stein
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Southern California Coastal Water Research Project

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Technical Report 500

EXECUTIVE SUMMARY

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

- What are the ranges of concentrations, loads, and fluxes of various metals, nutrients, solids, algae, and bacteria associated with storm and non-stormwater runoff from natural areas?

- How do the ranges of constituent concentrations and loads associated with natural areas compare with those associated with urban (developed) areas and existing water quality standards?

- How do the environmental characteristics of catchments influence constituent concentrations and loads from natural landscapes?

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

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

The results of this study yielded the following conclusions:

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

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

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

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

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

[a] Total fluxes are only for the eight months of the study from December 2005 through August 2006 during which the stream was flowing. No stream flow was present after August 2006 until the start of the next storm season.
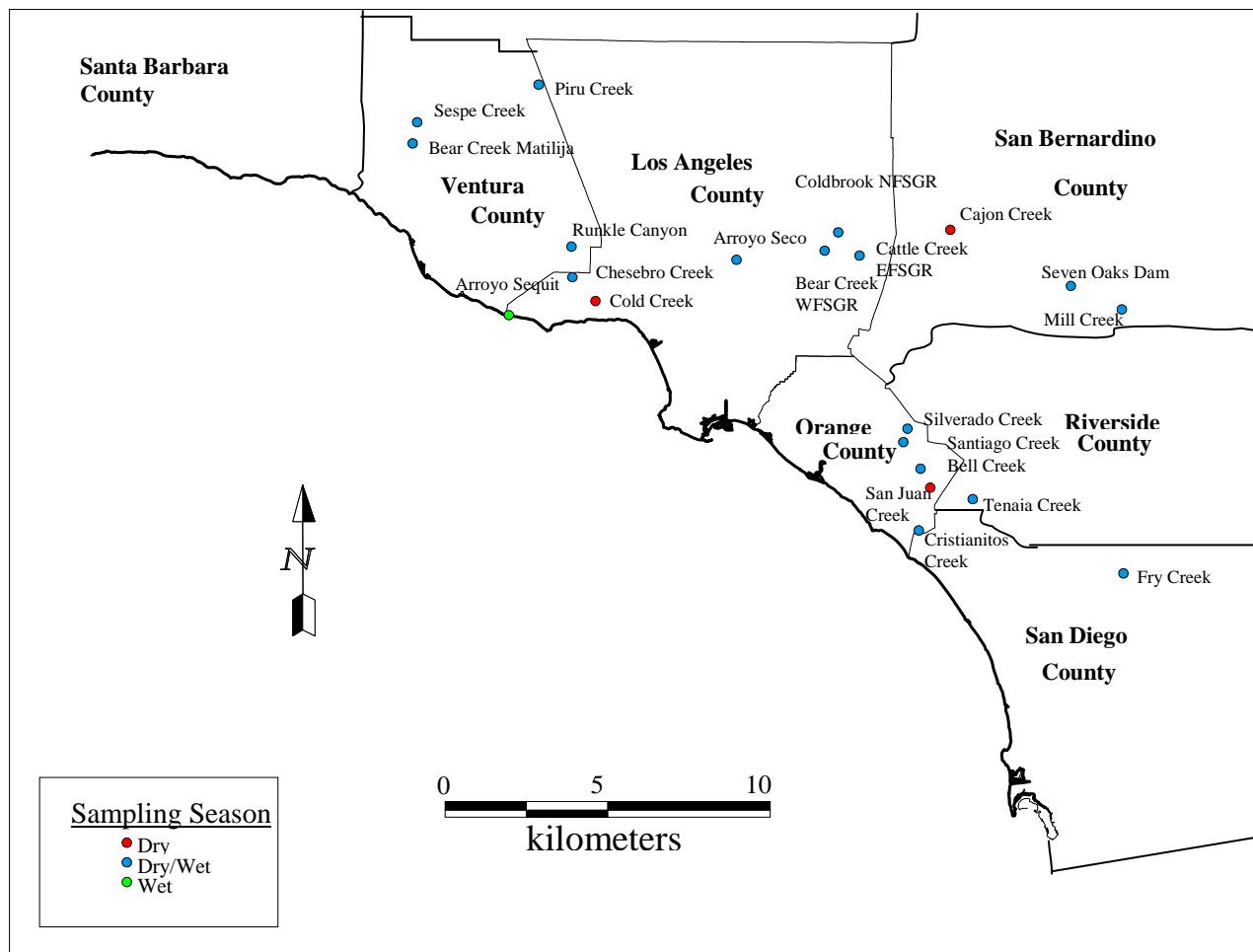
Figure ES-1. Study sites: red dots indicate sites sampled during dry weather only; blue dots indicate sites sampled in both dry and wet weather; and green dots indicate sites sampled during wet weather only.
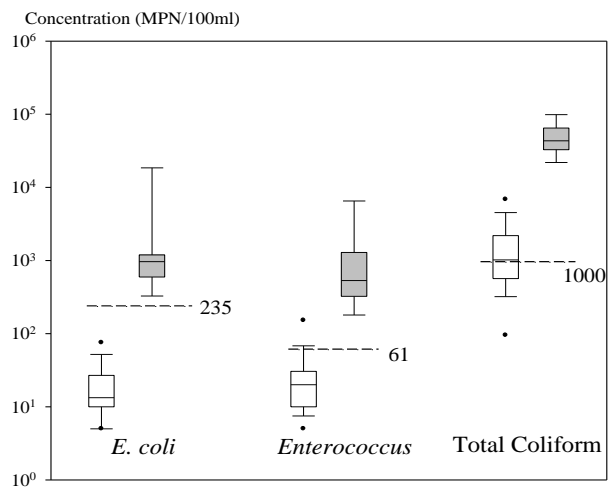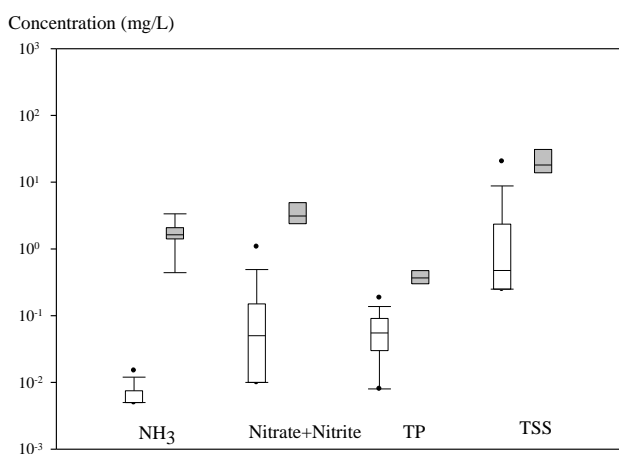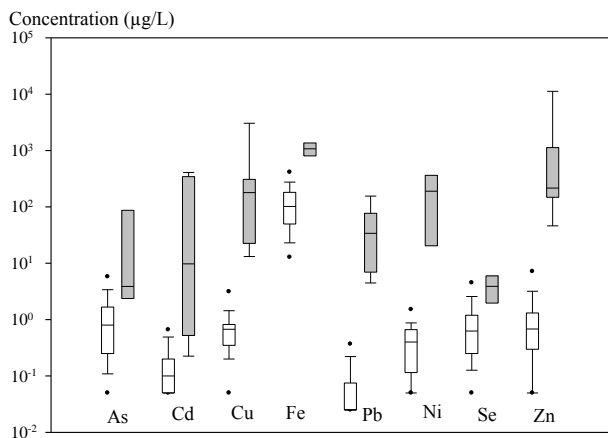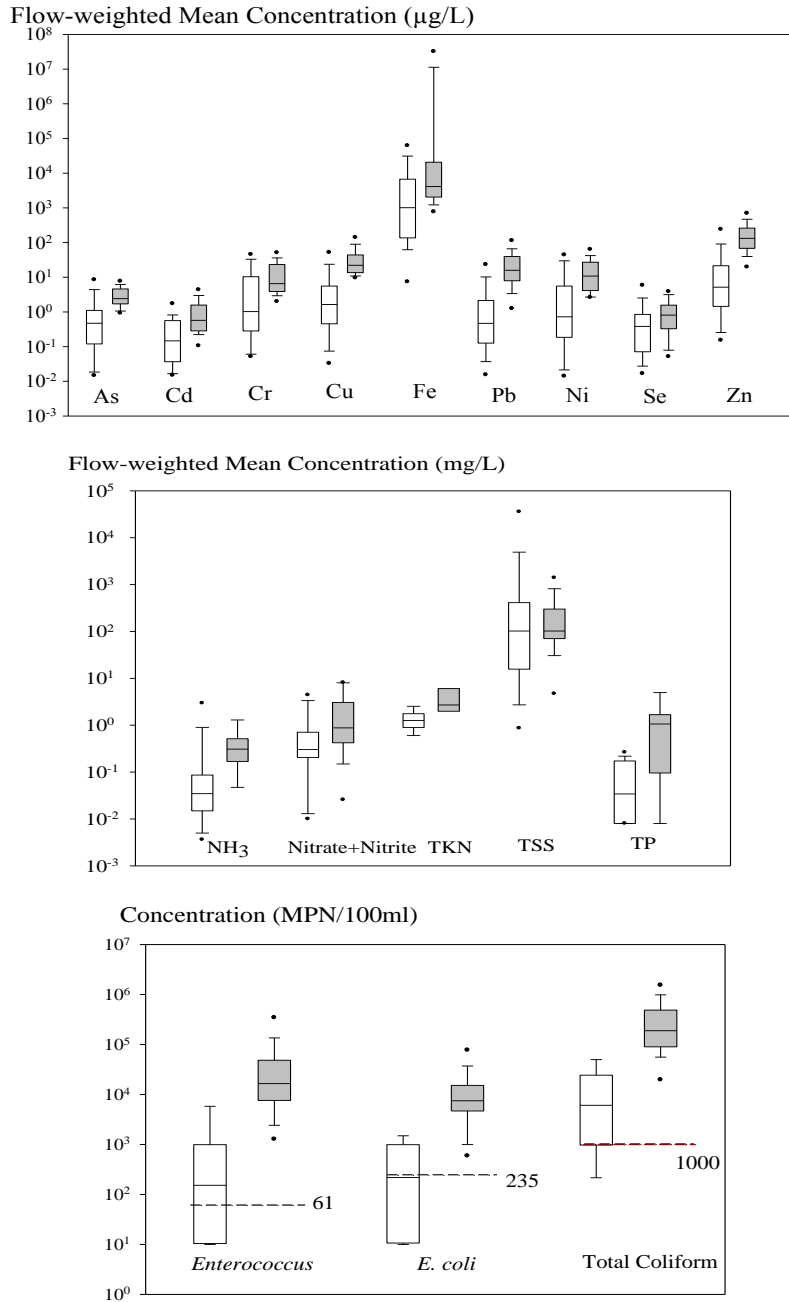
Figure ES-2. Comparison of dry weather concentrations of metals, nutrients, TSS, and bacteria between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. Solid lines within boxes indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots indicate 5th and 95th percentiles. The Y axis is in log scale. Dotted lines indicate Department of Health and Safety draft guidelines for freshwater recreation.

Flow-weighted Mean Concentration (µg/L)

Flow-weighted Mean Concentration (mg/L)

Concentration (MPN/100ml)

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

ACKNOWLEDGEMENTS

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INTRODUCTION

Background

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

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

To compensate for the lack of adequate information on natural sources of metals, nutrients, and bacteria, many TMDLs are written with load allocations based on data from other parts of the country or, worse yet, anecdotal data from previous time periods. As a result, these TMDLs may be developed with inefficient or overly stringent load allocations in order to meet numeric targets. The need for information on loading from undeveloped areas is amplified by the desire for many managers to use background concentrations or conditions as part of the numeric target for their TMDL. For example, the TMDL for

bacteria for Santa Monica Bay beaches used a watershed that was comprised of entirely open land use as a benchmark for success. Urbanized watersheds were required to generate no more bacterial exceedence days than the open, benchmark watershed. Unfortunately, little is known about the bacterial dynamics or wet and dry weather contributions from the open land uses, making the efficacy of this requirement difficult to assess.

Goals of the study

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

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

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

STUDY DESIGN

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

Compilation of existing data sources

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

Watershed characterization

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

Selection of sampling sites

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

General framework for site selection

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

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

Criteria for site selection

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

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

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

- Sites should have either year-round or prolonged dry weather flow that allows sampling during both storm and non-storm conditions. A stream with prolonged dry weather flow can be defined as one that still flows one to two months after the end of the last storm, even if it dries up later in the season.

- Sites should be targeted toward 3rd-order watersheds in which streams have large enough catchments to reliably generate flow during both storm and non-storm conditions. This position in the watershed also allows selection of sites for which catchments are small enough to have homogenous contributing drainage areas. Sites at this position in the watershed are representative of the watershed position of many of the less pristine waterbodies to which data from this study will be compared.

- Sites should not be within catchments that have burned during the previous three years. According to a study on the impact of wildfire in the Santa Monica Mountains (Gamradt and Kats 1997), erosion following the 1993 wildfire produced major changes in stream morphology and composition. These fire-induced landslides and siltation eliminated pools and runs, and altered habitats. Thus, streams that were impacted by wildfires were excluded from this study[2].

- The stream reach being sampled should be ratable for flow to allow computation of mass loadings of water quality constituents.

- Sites should be located in an area where sampling can be conducted safely.

- Field crews should be able to access the sampling location after hours and on weekends.

- Property owners and other responsible parties must provide permission for site access and sampling.

Selected sampling sites

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

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

Dry and wet weather sampling

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

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

Site characterization

Each catchment was characterized for its environmental settings: 1) land cover type (forest/shrub), 2) geology type (sediment/igneous), 3) catchment size, 4) average slope, 5) elevation, 6) latitude, and 7) percent canopy cover. Geologic and land cover type for the coastal watersheds in southern California were determined by plotting catchment boundaries over a digitized geology map (Strand 1962, Rogers 1965, 1967, Jennings and Strand 1969) and land cover map (NOAA CCAP 2003). The rest of catchment characteristics were assessed using ArcView GIS 3.2a (ESRI, Redlands, CA). Percent canopy cover was defined as a percent vegetation cover over the study reach based on field measurements using a spherical forest densitometer (Wildco, Buffalo, NY).

Dry weather sampling

Three dry weather sampling events were conducted: spring 2005, fall 2005, and spring 2006 (Table 3). Dry weather sampling was initiated following at least 30 consecutive days with no measurable rain to minimize effects of residual stormwater return flow. Water samples were collected as composite grab samples, with equivalent volumes collected from three different points across the stream (approximately 10, 50, and 90% distance across). A replicate water sample was collected in the same way 10 minutes after completion of the initial water sampling. Collected water samples were immediately placed on ice for subsequent analyses. At each sampling location and during each round of sample collection, temperature, pH, and dissolved oxygen (DO) were measured in the field using Orion 125 and Orion 810 field probes (Thermo Electron Corporation, Waltham, MA). Canopy cover was assessed using a spherical densitometer (Wildco, Buffalo, NY). Measurements were taken in triplicate at each transect. Stream discharge was measured as the product of the channel cross-sectional area and the flow velocity. Channel cross sectional area was measured in the field. At each sampling event, velocity was measured using a Marsh-McBirney Model 2000 flow meter (Frederick, MD). The flow meter measured velocity using the Faraday law of electromagnetic induction. The velocity was measured at three points along each transect, and the values from three transects were integrated to estimate overall flow at each site. To estimate biomass of algae, percent cover of algae was assessed visually at each site using the defined algal protocol (Appendix IV) as modified from the EPA Rapid Bioassessment Protocol (Barbour *et al.* 1999). Percent algal cover was estimated separately for benthic algae, algae attached to rocks or vascular plants, and free floating algae. Algae were sampled for chlorophyll-a analysis along each transect with a periphyton sampler modeled on the sampler described by Davies & Gee (1993). Algal samples were immediately frozen on dry ice for subsequent analyses. Details of the method of algal sampling and percent cover assessment are described in Appendix IV.

Wet weather sampling

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

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

Manual sampling (pollutograph)

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

Automatic sampling

When site accessibility and/or safety prohibited manual sampling, automatic samplers were used. Samplers were installed ahead of the storm event and streams were auto-sampled to collect four composite samples representing different portions of the storm hydrograph. The automatic sampler collected "microsamples" at set intervals during each portion of the storm. Samples were collected every five minutes for the first bottle. The interval between each microsample was increased for each subsequent bottle to allow a greater portion of the storm to be sampled. Samples for the second, third, and fourth bottles were taken at ten-, twenty-, and forty-minute intervals, respectively. Ultimately, each sample bottle consisted of a composite of 18 microsamples representing one portion of the storm. Intervals were determined based on expected duration of storm. If a storm was expected to last for several days, longer intervals were set. If a storm was expected to last for a short period of time, shorter intervals were set. In most cases, the four sample bottles were analyzed individually. In some cases two bottles were composited if analysis of the storm hydrograph revealed that they captured similar portions of the storm event. All sample tubing was triple purged with ambient and de-ionized water between samples. After collection, the samples were stored in pre-cleaned glass bottles on ice with Teflon®-lined caps until they were shipped to the laboratory for analysis.

Laboratory analysis

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

materials, duplicate analyses, matrix spike/ matrix spike duplicates, calibration standards traceable to the National Institute of Standards, and method blanks. Table 5 shows the list of analytes, along with minimum detection limits (MDLs) and applicable units for each analyte.

Data analysis

Dry weather

Three analyses were used to characterize dry weather water quality from natural areas. First the means, variances, and ranges of concentrations, loads, and fluxes were calculated to provide an estimate of expected natural (background) water quality. Loads were calculated as the product of flow and concentration for each sample (Equation 1):

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

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

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

Second, factors that impact variability in water quality of natural catchments were investigated. To explain variability in water quality among the natural catchments, relationships between environmental characteristics of the catchments and water quality constituent concentrations and fluxes were investigated using multivariate analyses. In this study, an ordination method, redundancy analysis (RDA) was used. RDA is a canonical extension of principal component analysis (PCA) and a form of direct gradient analysis that describes variation between two multivariate data sets (Rao 1964, ter Braak and Verdonschot 1995); and a matrix of predictor variables (e.g., environmental variables, explanatory variables, or independent variables) is used to quantify variation in a matrix of response variables (e.g., water quality variables, response variables, or dependent variables). For this study, RDAs were performed using the program CANOCO 4.54 (ter Braak and Smilauer 1997). Water quality variables used in the RDA were concentrations of all constituents. Environmental variables were geologic types (igneous rock vs. sedimentary rock), land cover types (forest vs. shrub), latitude of site, catchment area (km^2), elevation of site (km), slope of catchment, mean flow (m^3/sec), and percent canopy cover. Dummy values were assigned for the categorical variables; such as geology and land cover types. For example, a sampling site within a catchment dominated by igneous rock was assigned the value of one for igneous rock and a value of zero for sedimentary rock.

Prior to conducting the RDA, variables were log transformed to improve normality. Each set of variables was centered and standardized to normalize the units of measurement so that the coefficients would be comparable to one another. The environmental variables were standardized to zero mean and unit variance. Interaction terms were not considered.

The importance of the environmental variables was determined by stepwise selection. In each step the extra fit was determined for each variable, i.e., the increase in regression sum of squares over all constituents when adding a variable to the regression model. The variable with the largest extra fit was

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

then included, and the process was repeated until no variables remained that could significantly improve the fit of the model. The statistical significance of the effect of including a variable was determined by means of a Monte Carlo permutation test. The number of permutations to be carried out was limited to 199 because the power of the test increases with the number of permutations, but only slightly so beyond 199 permutations (Lepš and Šmilauer 2003).

The results of the multivariate analysis were visualized by means of biplots that represent optimally the joint effect of the environmental variables on water quality variables in a single plane (ter Braak 1990). In addition, the entire water quality data set was grouped based on the most influential environmental variables. Subsequent analyses, such as analysis of variance, ANOVA (Sokal and Rohlf 1995), were carried out to examine the significance of differences among the groups with a significance level of p <0.05.

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

Wet weather

Three analyses were used to characterize wet-weather water quality from natural areas. First the means, variances, and ranges of concentrations, loads, and fluxes were calculated to provide an estimate of expected baseline water quality. Event flow-weighted mean (FWM) concentrations, mass loadings, and flux rates were calculated for each site. Using only those samples for a single storm, the event FWM was calculated according to Equation 2:

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

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

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

Event mass loadings were calculated as the product of the FWM and the storm volume during the sampling period. Flux estimates facilitated loading comparisons among catchments of varying sizes. Flux calculated as the ratio of the mass loading per storm and contributing catchment area. All data were analyzed to determine if they were normally distributed. For those constituents that were not normally distributed, results were recorded as geometric means and upper/lower 95% confidence intervals. If the data were normally distributed, results were recorded as arithmetic means ± the 95% confidence interval.

Second, factors that impact variability in water quality from the natural catchments were investigated. To explain variability in water quality among different natural catchments, relationships between environmental characteristics of the catchments and concentrations were investigated using multivariate analyses. Variability within a storm event was also examined in terms of first flush. Variability of constituent levels within a storm event and between seasons was examined. First, flows and concentrations within storm events were evaluated by examining the time-concentration series relative to the hydrograph using a pollutograph. A first flush in concentration from individual storm events, defined as a peak in concentration preceding the peak in flow, is often observed in small urban watersheds (Characklis and Wiesner 1997, Sansalone and Buchberger 1997, Buffleben *et al.* 2002, Stein *et al.* 2006). This observation was quantified using cumulative discharge plots for which cumulative mass emission was plotted against cumulative discharge volume during a single storm event (Bertrand-Krajewski *et al.* 1998). When these curves are close to unity, mass emission is a function of flow discharge. A strong first flush was defined as ≥75% of the mass being discharged in the first 25% of runoff volume. A moderate first flush was defined as ≥30% and ≤75% of the mass being discharged in the first 25% of runoff volume. No first flush was assumed when ≤30% of the mass was discharged in the first 25% of runoff volume. Second, changes in proportions of metals between particulate phase and dissolved phase over the course of storm were examined and compared with concentrations of TSS, TDS, and flow. The Pearson correlation analysis was conducted to test correlation of the ratios with flow. Lastly, ANOVA was conducted in order to test if constituent concentrations differed significantly among different seasons. The %CV for each constituent was compared among different seasons in order to estimate the degree of seasonal variability.

Relationships between catchment characteristics and constituent concentration were investigated using RDA. Water quality variables used in the RDA were flow-weighted concentrations (FWMC) of all measured water quality constituents. Environmental variables used were geologic setting (igneous vs. sedimentary), land cover type (forest vs. shrub), latitude, catchment area (km^2), elevation of sampling location (km), slope of drainage area, total rainfall of storm event (cm), baseline flow (m^3/sec), mean flow (m^3/sec), peak flow of storm event (m^3/sec), total volume of stormwater runoff (m^3), and percent canopy cover (%). The RDA and subsequent analyses, such as ANOVA, were conducted in a similar manner to those of the dry weather data.

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

In addition to chemistry data, catchment hydrology was compared to that of developed watersheds. For each storm, the mean flow, peak flow, and total runoff volume was calculated relative to the total rainfall for that storm. Storm flow patterns relative to rainfall and catchment size were compared between developed and undeveloped watersheds to assess differences in hydrologic response using linear and log-linear regression analysis.

Estimation of annual loadings from natural landscapes

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

Flow data from USGS gauging stations

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

Flow monitoring using water level loggers

At the two ungauged intermittent streams, pressure transducers to measure water surface elevation (i.e., water level) were installed. Water level was monitored every 15 minutes during the 8-month study period from December 2005 through July 2006 using Hobo® model U20-001-01 water level logger (Onset Computer, Bourne, MA). Two water level loggers were deployed at each site. One was installed above the water level to measure atmospheric pressure and the other was installed under water level to measure combined pressure of atmospheric and water pressures. The water pressure was computed by subtracting the atmospheric pressure from the combined pressure. Water level was estimated based on the temperature that was logged with the pressure. Water level data were converted to flow data using flow-

rating curves that were obtained from previous sampling events conducted during the dry and wet seasons of 2004 through 2006. Separate rating curves for dry and wet weather flows were obtained. A rating curve with the highest correlation coefficient among possible linear or non-linear regressions was selected to convert a water level into flow for each site.

Storm flow *separation from non*-storm flow

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

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

where X_i was flow at time i.

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

Estimation of loads and fluxes

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

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

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

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

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

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

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

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

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

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

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

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

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

Analyte	Minimum Detection Limit	Analytical Method
pH	0.1 pH unit	SM4500H+B
Conductance	0.1 micromhos	SM2510B
DO	0.01 mg/L	SM4500OG
Temperature	0.01 °C	SM2550B
Hardness	1.0 mg/L	SM2340A EDTA titration
Nutrients		
NH$_3$	0.01 mg/L	SM 4500-NH3F
TKN	0.14 mg/L	EPA 351.2
Nitrate+Nitrite	0.02 mg/L	SM 4500-NO3/-NO2
TP/OP	0.016 mg/L	SM 4500-P C
TSS	0.5 mg/L	SM 2540-D
TDS	0.1 mg/L	SM 2540-C
TOC	0.5 mg/L	EPA 451.1
DOC	0.5 mg/L	EPA 451.1
Metals		
Arsenic	0.1 μg/L	EPA 200.8
Cadmium	0.1 μg/L	EPA 200.8
Chromium	0.1 μg/L	EPA 200.8
Copper	0.1 μg/L	EPA 200.8
Iron	1.0 μg/L	EPA 200.8
Lead	0.05 μg/L	EPA 200.8
Nickel	0.1 μg/L	EPA 200.8
Selenium	0.1 μg/L	EPA 200.8
Zinc	0.1 μg/L	EPA 200.8
Bacteria		
Total Coliform	10 MPN/100 ml	Idexx Quantitray
E. coli	10 MPN/100 ml	Idexx Quantitray
Enterococcus	10 MPN/100 ml	Idexx Quantitray
Algae		
Chlorophyll a	0.005 mg/L	EPA 446.0

Dissolved oxygen (DO); ammonia (NH$_3$); total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC); total Kjeldahl nitrogen (TKN); total phosphorus (TP); and orthophosphate (OP).

Table 6. Study site characteristics, including catchment size.

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

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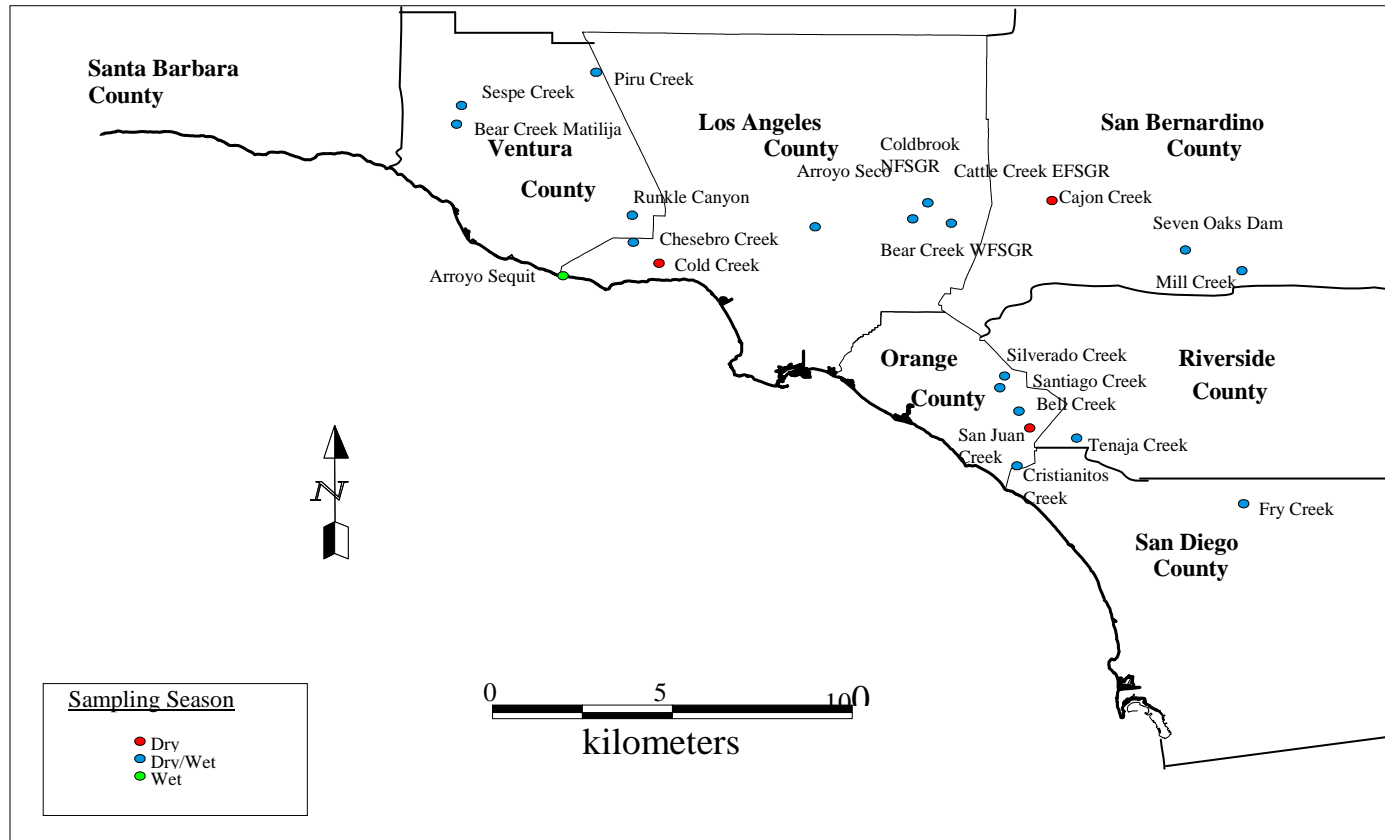
Figure 1. Study sites: red dots indicate sites sampled during dry weather only; blue dots indicate sites sampled in both dry and wet weather; and green dots indicate sites sampled during wet weather only.

DRY WEATHER

Background

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

Flow and field measurements

Seven of the nineteen streams sampled were intermittent, while the rest were perennial; intermittent streams included Chesebro Creek, Cristianitos Creek, San Juan Creek, Santiago Creek, Bell Creek, Fry Creek, and Tenaja Creek. Mean flow ranged from 0 to 0.72 m^3/sec with a mean of 0.33 m^3/sec. Dissolved oxygen was 6.14 ±3.4 mg/L (mean ± standard deviation), total hardness was 225.9 ±182.29 mg/L, pH was 8.0 ±0.4, water temperature was 16.77 ±3.04 °C, and percent canopy cover was 87 ±11 %.

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

Concentrations, loads, and fluxes ranges

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

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

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

Algal levels at natural catchments

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

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

Geologic type (sedimentary rock and igneous rock) and slope were the main sources of variance in the dry weather water quality data. The stepwise selection in RDA resulted in these variables significantly increasing the overall model fitness (Table 9). The remaining six variables did not appreciably increase the fitness of the model and were excluded in subsequent RDAs. Excluding less significant environmental variables increased the percent of variance explained by the model to 45.4%, compared to 20.3% for the model that included all nine variables (Table 10).

The predominant source of variability was geology. The first axis of the RDA model explained 66.4% of variance in the data set and was primarily determined by the two geology variables (Tables 10 and 11). Among the variables retained in the RDA model, slope contributed least to variation along the first axis and most along the second axis (Table 11). This indicates that geologic setting is a more important factor in defining dry weather water quality of natural catchments than the other environmental factors tested here.

Correlations between water quality and environmental variables are explained in the biplot (Figure 2). Copper, selenium, zinc, nickel, iron, TDS, TOC, and TKN were positively correlated with sedimentary rock. Nitrate+nitrite was negatively correlated with sedimentary rock and positively correlated with igneous rock. Arsenic was positively correlated with slope. Other constituents exhibited no strong correlation with any of the environmental variables.

Concentrations of several constituents exhibited significant differences between the different geology groups. Results of the ANOVA indicate that copper, iron, nickel, selenium, OP, and TDS concentrations were significantly higher in natural catchments underlain by sedimentary

rock than those underlain by igneous rock (p <0.05). Other constituents did not exhibit any significant differences between the geologic groups.

Comparison with developed catchments

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

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

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

Discussion

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

Dry weather concentrations were consistently lower than established water quality management targets. Mean concentrations of metals were below the chronic standards of the California Toxic Rules for inland surface waters (freshwater aquatic life protection standards; Table 14a). There are currently no established nutrient standards available for comparison to data collected from the natural catchments. However, in December 2000, USEPA proposed standards for TKN,

nitrate+nitrite, total nitrogen (TN), and TP, respectively, for Ecoregion III, 6, which includes southern California (USEPA 2000; Table 14b). Although these proposed standards have not been approved, they provide a reasonable basis of comparison to levels of potential environmental concern. The geometric means of all nutrients were below or similar to the proposed USEPA regional nutrient criteria. The USEPA criteria were developed for the entire year and do not separate dry weather condition from wet weather condition. When comparing geometric means from this study with the proposed USEPA nutrient criteria, it is important to realize that the USEPA criteria are averaged on the 25th percentiles of concentrations from four seasons that include wet and dry weather. As shown in this study, levels of nutrients can vary considerably between dry and wet weather. Therefore, it is important to consider storm and non-storm conditions separately in future criteria development.

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

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

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

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

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

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

This study showed that concentrations of metals, nutrients, and solids from natural catchments are highly variable. This may result from numerous factors, such as temporal and spatial variability and methods of data analysis. One factor that may influence data variability is treatment of non-detects (NDs). In this study, the percent of NDs for a given constituent ranged from 1.8% for TSS to 59.6% for TP (Table 15). Samples that are ND can be assigned a value ranging from zero to the MDL. In this study, zero was not considered because zero values do not allow calculation of geometric statistics. To be conservative, samples were assigned a value of one-half the MDL to ND samples used in this study. Use of the MDL instead of one-half MDL for ND samples would have resulted in less than a 2% increase in median concentration for most constituents. The exceptions were ammonia, nitrate+nitrite, OP, and TSS, which would have increased by 12, 18, 30, and 8%, respectively.

Environmental settings such as geology and land cover have been shown to affect water quality in natural catchments (Lakin and Byers 1941, Dunne and Leopold 1978, Ohlendorf *et al.* 1986, Larsen 1988, Ledin *et al.* 1989, Tracy *et al.* 1990, Tidball *et al.* 1991, Detenbeck *et al.* 1993, Presser *et al.* 1994, Hounslow 1995, Johnes *et al.* 1996, Richards *et al.* 1996, Johnson *et al.* 1997a, Gergel *et al.* 1999, Hibbs and Lee 2000). In this study, geology was the primary factor in determining dry weather water quality in natural catchments. Levels of TDS and other constituents were generally higher in streams draining sedimentary catchments than those draining igneous catchments. This difference can be explained by the higher erodibility of sedimentary rock resulting in the increased release of sediment and associated constituents into the water. Differences in constituent concentrations based on geologic setting were most pronounced for compounds that are typically associated with particles, such as copper, zinc, and nickel. Less difference was observed for compounds typically found primarily in the dissolved phase, such as arsenic and selenium.

Constituent concentrations also varied as a function of catchment slope. The likely mechanism for this effect is an increase in erosion and washoff associated with steeper watersheds (Naslas *et al.* 1994). Overall, the effect of both slope and geology was less pronounced for dry weather conditions than for wet weather conditions, most likely due to a lower amount of overland (surface) runoff.

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

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

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

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

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

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

Metals	Concentration (μg/L)			Mass Load (g/day)			Flux (g/km² day)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Arsenic	0.66	0.94	0.47	7.90	13.72	4.55	0.33	0.51	0.21
Cadmium	0.11	0.15	0.09	1.34	2.20	0.81	0.06	0.10	0.03
Chromium	0.17	0.22	0.13	2.03	3.22	1.28	0.08	0.14	0.05
Copper	0.56	0.72	0.43	6.64	10.59	4.16	0.28	0.43	0.18
Iron	83.90	109.83	64.10	997.79	1628.97	611.18	41.37	69.19	24.73
Lead	0.05	0.06	0.03	0.55	0.89	0.34	0.02	0.04	0.01
Nickel	0.30	0.41	0.22	3.56	6.03	2.10	0.15	0.24	0.09
Selenium	0.58	0.84	0.41	6.95	11.84	4.08	0.29	0.49	0.17
Zinc	0.56	0.82	0.39	6.70	10.52	4.27	0.28	0.50	0.16

Nutrients	Concentration (mg/L)			Mass Load (kg/day)			Flux (kg/km²day)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Ammonia	0.01	0.01	0.01	0.07	0.11	0.05	0.003	0.005	0.002
Nitrate+Nitrite	0.05	0.08	0.03	0.58	1.08	0.31	0.02	0.05	0.01
Total Kjeldahl Nitrogen	0.28	0.31	0.25	3.29	5.07	2.14	0.14	0.22	0.09
Dissolved Organic Carbon	2.68	3.39	2.12	31.87	49.86	20.37	1.32	2.17	0.80
Total Organic Carbon	2.85	3.37	2.41	33.88	51.18	22.43	1.40	2.18	0.91
Orthophosphate	0.02	0.02	0.01	0.20	0.33	0.13	0.008	0.014	0.005
Total Phosphorus	0.05	0.06	0.04	0.57	0.89	0.36	0.02	0.04	0.01

Solids	Concentration (mg/L)			Mass Load (kg/day)			Flux (kg/km²)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Total Dissolved Solids	274.43	411.49	183.02	3132.46	5804.84	1690.37	137.86	250.53	75.87
Total Suspended Solids	0.85	1.27	0.57	10.12	17.80	5.76	0.42	0.78	0.23

Microbes	Concentration (MPN/100ml)			Algae*	Percent Cover (%)			Chlorophyll-a (mg/m²)		
	Geomean	Upper CI	Lower CI		Mean	Min	Max	Mean	Min	Max
E. coli	15.83	20.11	12.46	Benthic	23.60	0.00	100.00	439.20	0.00	6946.20
Enterococcus	19.84	25.49	15.45	Attached	6.40	0.00	38.10	0.48	0.00	2.30
Total Coliform	1047.83	1429.96	767.82	Free floating	2.60	0.00	37.20	0.03	0.00	0.21

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

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

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

[a] Variables are given in the order of inclusion. The extra and cumulative fits are given as percentages relative to the total sum of squares over all water quality variables (comparable to the percentage explained variance in univariate regression). Number of observations: 1006. Total number of water quality variables: 18. Significance was determined by Monte Carlo permutation using 199 random permutations.

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

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

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

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

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

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

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

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

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

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

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

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

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

Constituent	No of ND	No of Sample	%ND
Arsenic	21	163	12.9
Cadmium	74	165	44.8
Chromium	45	164	27.4
Copper	18	164	11.0
Lead	5	163	3.1
Nickel	92	164	56.1
Selenium	31	165	18.8
Zinc	36	169	21.3
Ammonia	35	165	21.2
Dissolved Organic Carbon	67	115	58.3
Nitrate	4	104	3.8
Nitrite	24	120	20.0
Orthophosphate	64	119	53.8
Total Kjeldahl Nitrogen	32	108	29.6
Total Phosphorus	62	104	59.6
Total Dissolved Solids	21	108	19.4
Total Suspended Solids	2	109	1.8
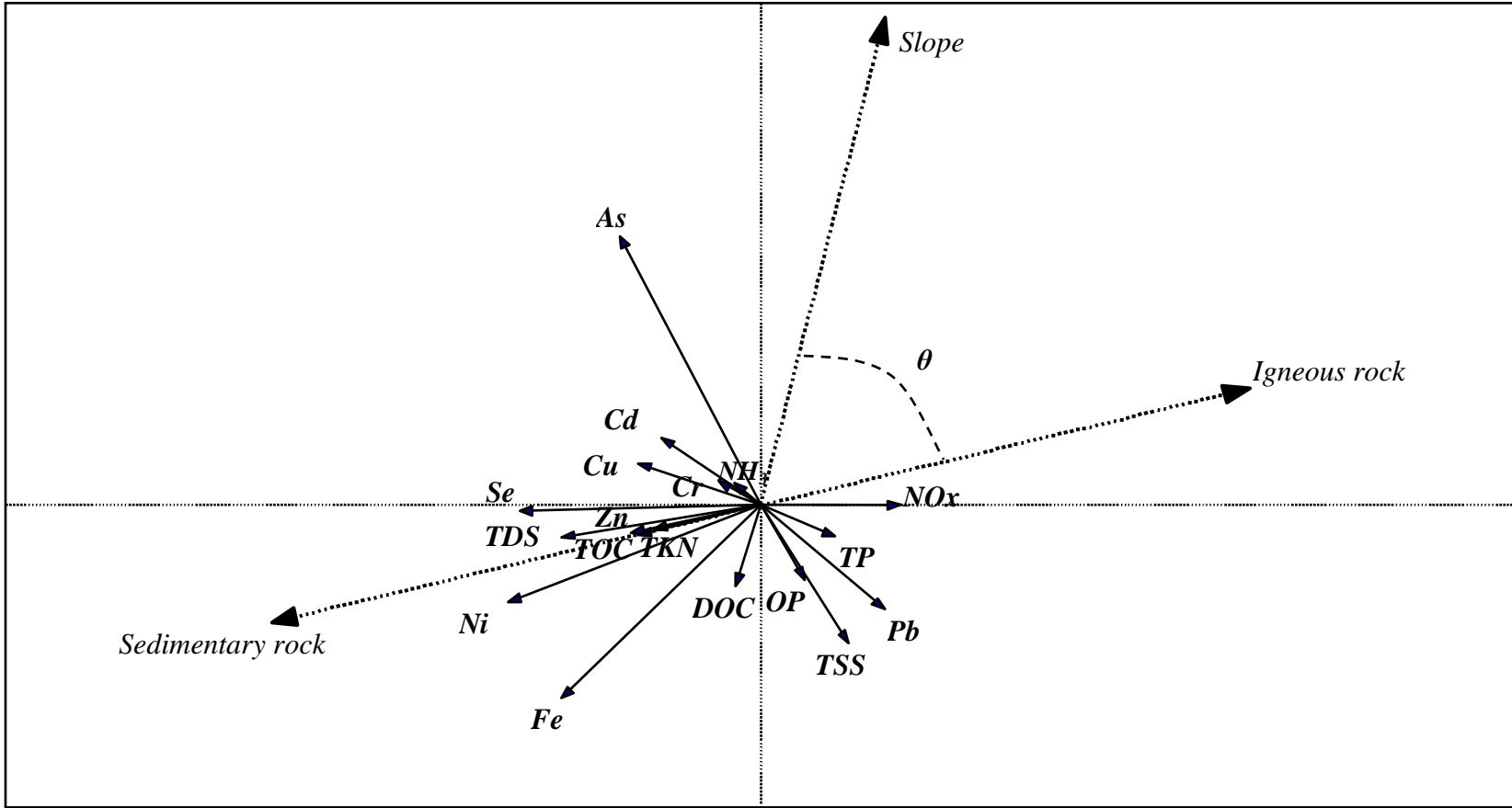
Figure 2. Correlation biplots showing relations between dry weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigen values: 0.151 and 0.0280 for the first (horizontal) and second (vertical). cos θ ≈ correlation coefficient between two variables (arrows). Longer arrows indicate which factor is more important in generating variability (Ter Braak, 1995). Total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC); total Kjeldahl nitrogen (TKN); total phosphorus (TP); orthophosphate (OP); and Nitrate+Nitrite (NOx).
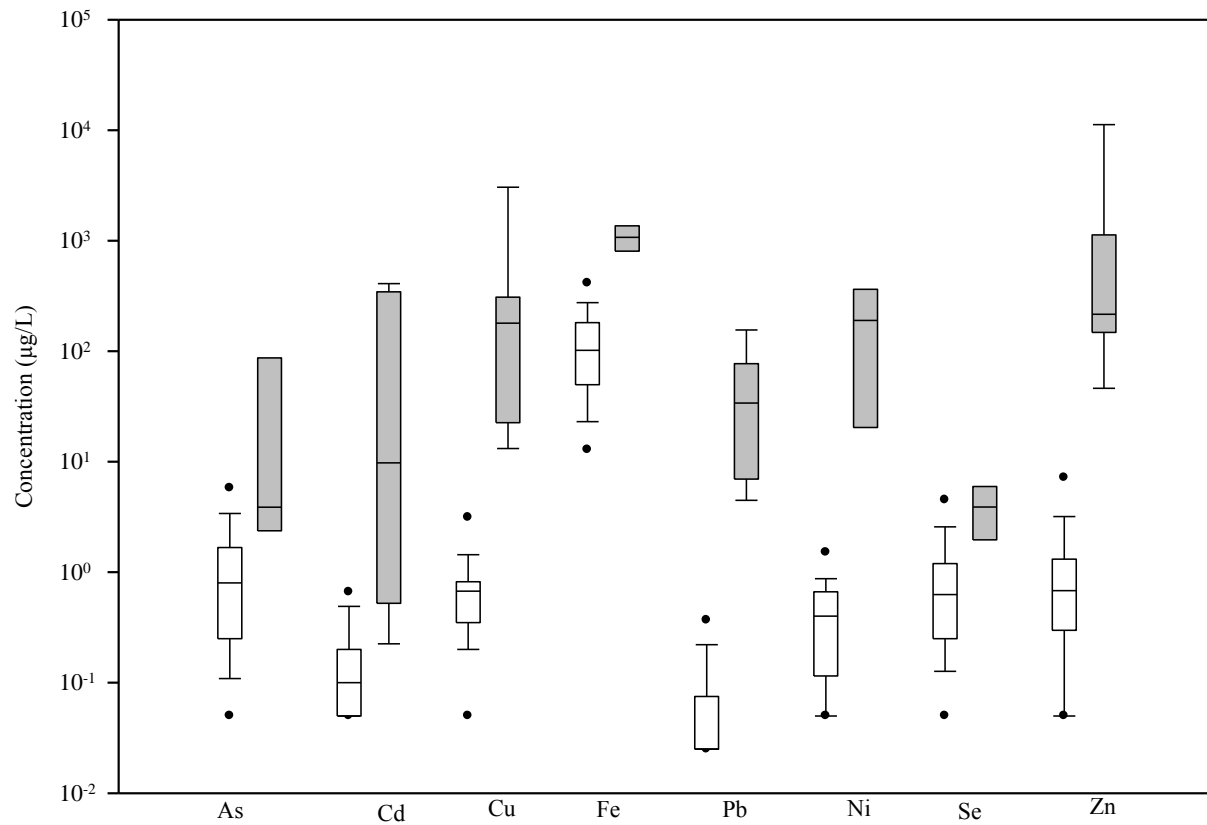
Figure 3a. Comparison of dry weather concentrations of metals between natural and developed catchments. White boxes represent natural sites, and gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles.. The Y axis is in log scale.
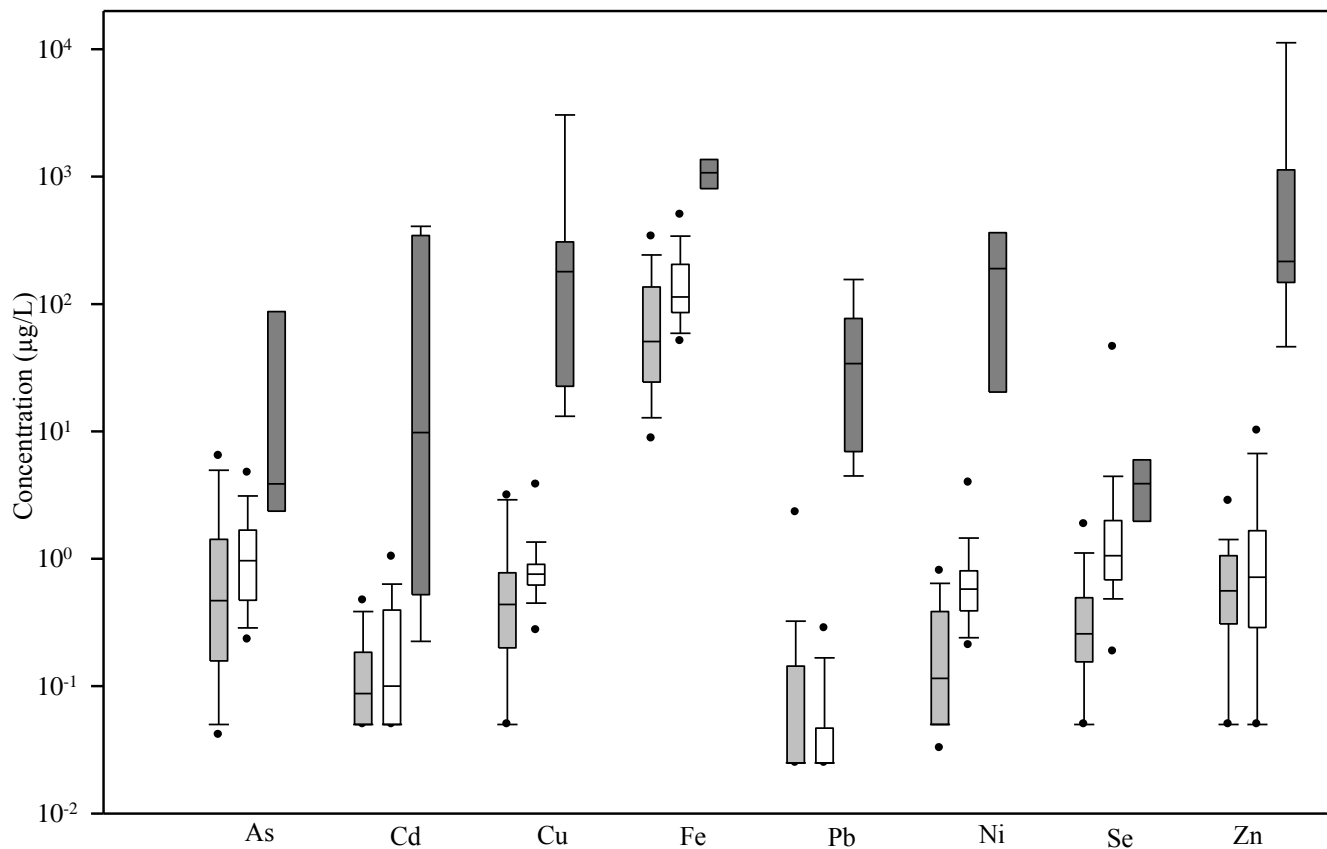
Figure 3b. Comparison of dry weather concentrations of metals between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock; white boxes represent natural sites underlain by sedimentary rock; and dark gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.
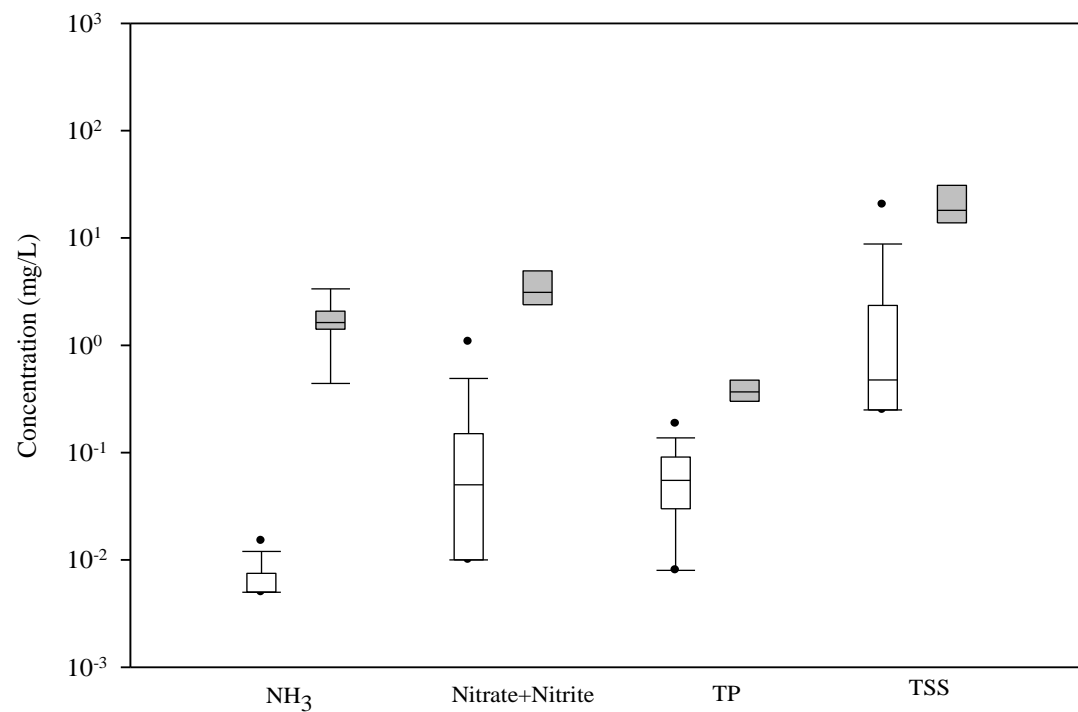
Figure 4a. Comparison of dry weather concentrations of ammonia (NH₃), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural sites, and gray boxes represent developed sites. The Y axis is in log scale.
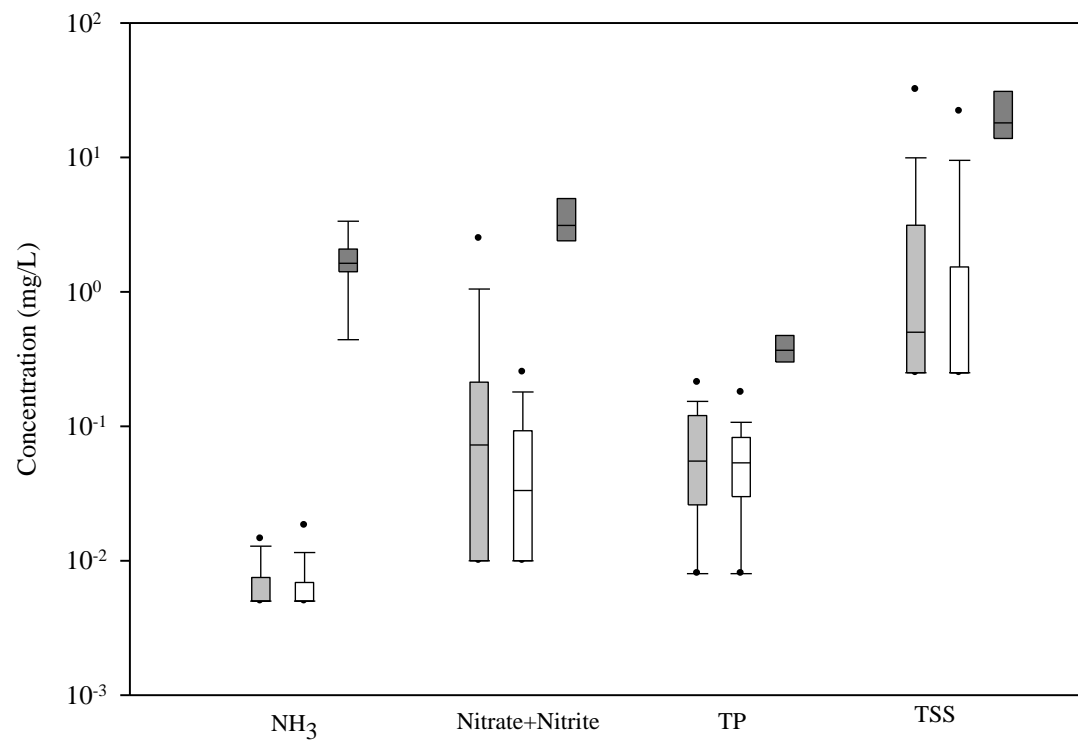
Figure 4b. Comparison of dry weather concentrations of ammonia (NH₃), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. The Y axis is in log scale.
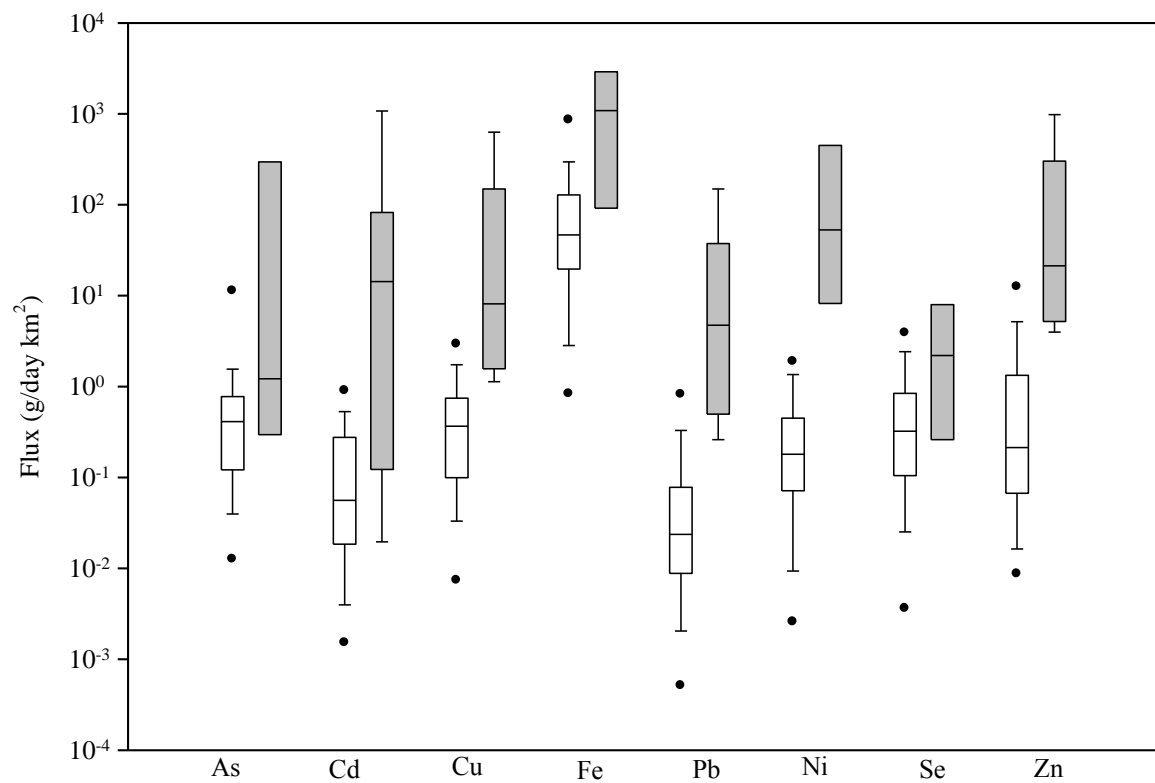
Figure 5. Comparison of dry weather fluxes of metals between natural and developed catchments. White boxes represent natural sites, while gray boxes represent developed sites. The Y axis is in log scale.
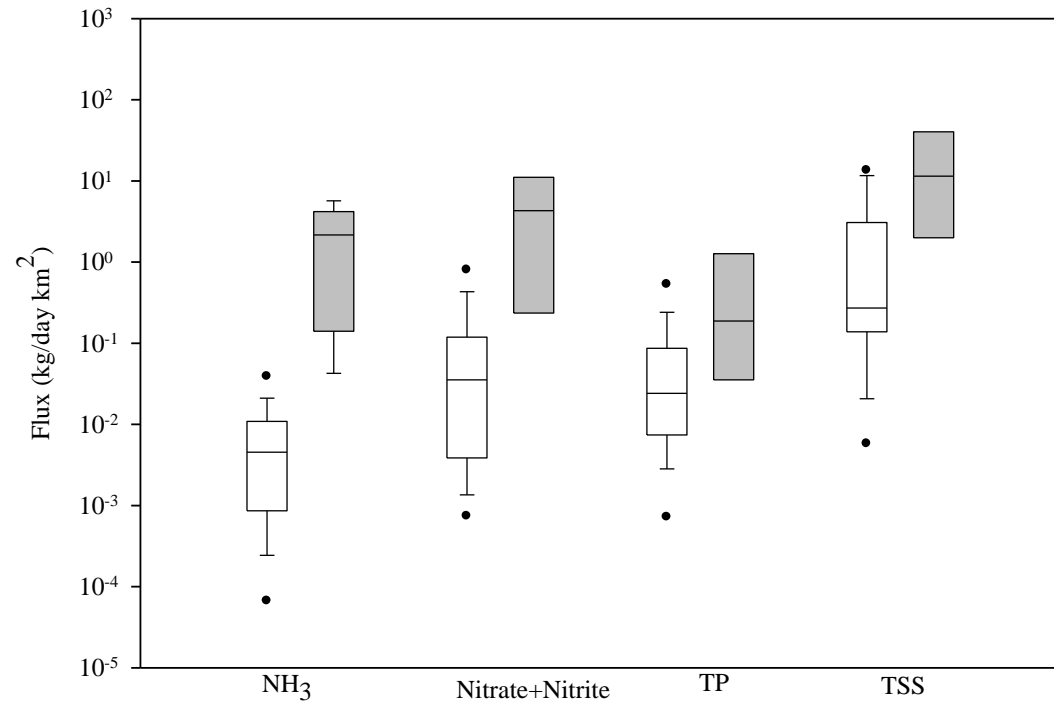
Figure 6. Comparison of dry weather fluxes of ammonia (NH_3), nitrate+nitrite, total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural sites, while gray boxes represent developed sites. The Y axis is in log scale.
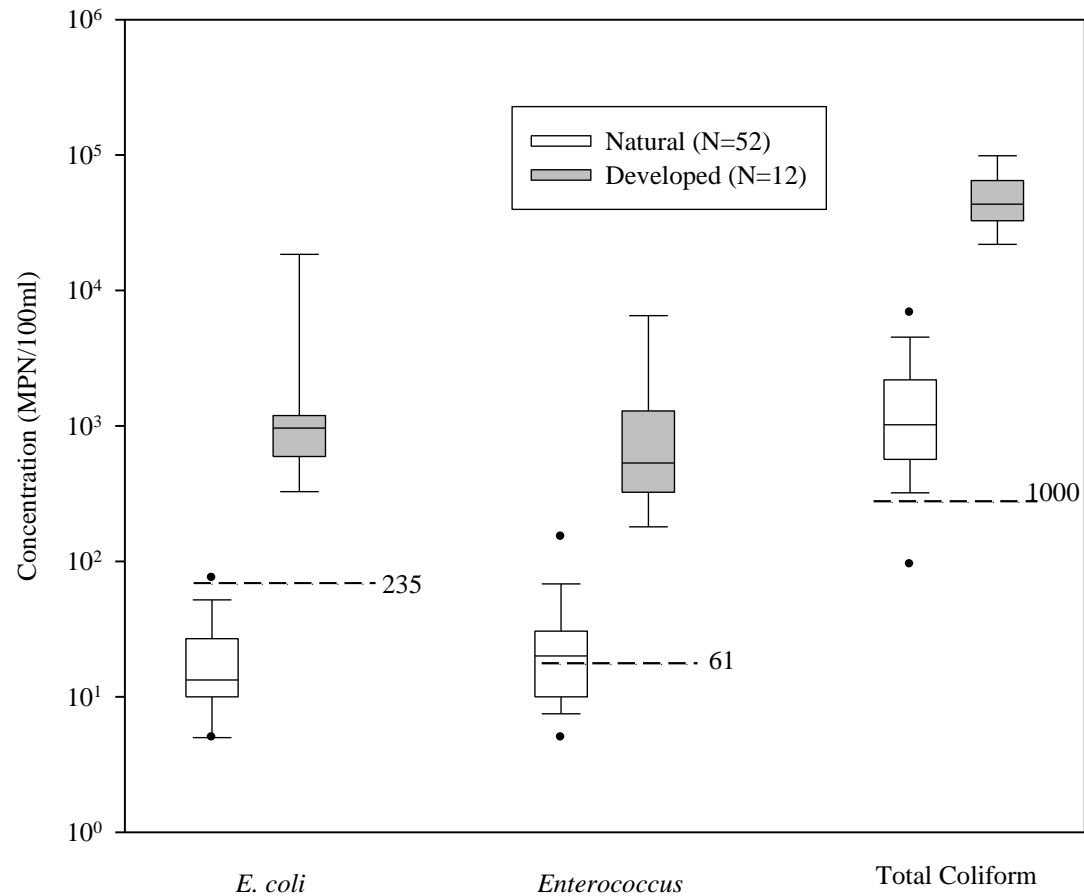
Figure 7. Comparison of dry weather bacteria concentrations between undeveloped and developed catchments. Blue boxes represent natural catchments, and yellow boxes represent developed catchments. The Y axis is in log scale. N is the number of samples per catchment type. Dotted lines are Department of Health and Safety draft guideline for freshwater recreation.

WET WEATHER

Background

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

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

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

Rainfall and flow

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

Event rainfall over the study period ranged from 0.81 to 17.20 cm. Mean storm flow was 1.39 ± 2.31 m^3/sec and flow varied from 1.51 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 mean total rainfall per storm event among the study catchments varied between the two years of sampling. During 2004-2005, mean rainfall was 7.3 cm/storm event, while in 2005-2006 it was 4.6 cm/storm event. The higher magnitude, frequency and duration of rainfall translated to average mean flows during 2004 being approximately four times larger than in 2005. Mean peak flow was 1.3 ± 1.6 m^3/sec in 2004-2005 vs. 8.1 $\pm$ 15.3 (m^3/sec) in 2005-2006.

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

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

Temporal variability in concentration and load

No first flush was observed in stormwater runoff from the natural catchments as indicated by the cumulative mass loading plots. In all cases less than 30% of total mass was discharged during the first 25% of the storm runoff volume. For example, the mass loading for Piru Creek was roughly proportional to the percent volume discharged in Piru Creek (Figure 9). From a concentration perspective, concentrations varied over the course of the storm; however, peak concentrations for metals, nutrients, and solids occurred after the peak flow, unlike the pattern typically observed in developed catchments, where peak concentrations occur during the rising limb of the hydrograph. An example of the pollutograph for Piru Creek shows that the peak concentration of copper occurred on the decreasing limb of the hydrograph (Figure 10), and the pollutograph was more spread out in natural areas than typically observed in developed watersheds.

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

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

Particulate vs. dissolved concentrations of metals in storm runoff

Ratios of particulate to dissolved metals concentrations changed over the course of storms. Particulate metals increased with increased flow, and were significantly associated with an increase in the concentration for TSS (p <0.05). Figure 11 shows an example of this pattern from a storm event at Bear Creek. The concentration of TSS sharply increased with the increase in rainfall and flow, while the concentration of TDS dropped, primarily due to dilution by increased runoff. Once the flow dropped, the concentration of TSS also dropped, but the concentration of TDS did not return to the pre-storm levels for approximately two days (Figure 11). The pattern of TSS concentration was synchronized with the increase in particulate metals and inversely related to TDS concentrations. Although this pattern was consistent among all metals, the ratio of particulate to dissolved concentration varied by metal. Arsenic (As) and selenium (Se) exist primarily in a dissolved phase throughout storms, indicated by the fact that all samples were

below the 1:1 reference line of equal distribution between the two phases (Figure 11). At peak flow, the ratio of particulate over dissolved metals for As and Se increased by approximately two orders of magnitude coincident with an increase in TSS. Copper (Cu), lead (Pb), and zinc (Zn) existed primarily in the dissolved phase during baseflow conditions. However, during peak flow particulate metals increased by three orders of magnitude and the majority of metals in storm runoff occur in the particulate phase. Increased particulate metal concentrations persisted long after flow subsided; the ratio of particulate to dissolved metals did not return back to the pre-storm levels for two days following peak flow.

Environmental factors that influence variability in constituent concentrations

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

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

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

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

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

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Comparison with developed catchments

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

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

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

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

Discussion

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

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

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

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

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

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

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

The role of aerial deposition, which was not accounted for in this study, is another factor that could have influenced the this study's estimates. If aerial deposition had been considered, the natural background levels estimated by this study would have been even lower. Atmospheric deposition can be a significant factor that affects loadings in natural areas. For example, in Midwestern and Northeastern streams, atmospheric deposition of nitrogen can account for nearly all downstream nitrogen loads (Smith *et al.* 1987, Puckett 1995). Studies show that rates of atmospheric nitrogen deposition were high in the xeric wet region, which includes a majority of coastal catchments in southern California (Clark *et al.* 2000). The study by Smith *et al.* (2003) reported that loadings of TN and TP could be 16 to 30% lower when corrected with atmospheric deposition rate. This suggests that the nutrient levels in the natural catchments could be lower than values presented in this study. Sabin *et al.* (2005) showed that atmospheric deposition potentially accounted for as much as 57 to 100% of the total trace metal stormwater loads to a small impervious urban catchment in Los Angeles, CA. Mountainous areas within the South Coast air basin, which include portions of four counties in the Los Angeles area, received the highest nitrogen deposition in the country (Fenn and Kiefer 1999, Fenn *et al.* 2003). This suggests potential strong contribution of atmospheric deposition to metals and nutrients in the natural catchments of southern California. Consequently, the contribution of atmospheric deposition should be investigated to assess more accurate natural contribution to loadings.

Geology and elevation were the two factors that controlled most variability in among natural catchments. In this study, land cover did not significantly impact water quality. This result differs from previous studies which have reported that land use and land cover types have a significant impact on water quality (Larsen 1988, Detenbeck *et al.* 1993, Johnes *et al.* 1996, Richards *et al.* 1996, Johnson *et al.* 1997a, Gergel *et al.* 1999). Previous studies have focused on the influence of natural vs. developed land cover on surface water quality or on the effect of different types of developed land use/land cover. The influence of different types of natural land cover on water quality has not been extensively examined prior to this study. Our ANOVA

results showed that levels of constituents were not significantly different between two different land cover groups (forest and shrub). This suggests that any differences that might occur due to different types of natural land cover are subtle, and not a key deterministic factor in water quality, unlike the relatively dramatic differences between natural vs. developed land cover previously investigated. However, Miller *et al.*' study (2005) addressed the importance of land cover on natural water quality, indicating that the ecosystem in mature forested Sierra catchments could be a significant source for nutrients. The concentrations of ammonia, nitrate, and phosphate were high in surface runoff from forested systems: as high as 87.2 mg/L, 95.4 mg/L, 24.4 mg/L for ammonia, nitrate, and phosphate, respectively. These values are even greater (one-order of magnitude) than maximum values for developed land uses observed in southern California coastal catchments (Ackerman and Schiff 2003). Values from Miller *et al.* were one to two orders of magnitude higher than the upper ends of 95% CI values for nutrients presented in this study. Miller *et al.* suggested that nutrients that were driven from mature organic horizons (O-horizons[8]) might have had little contact with mineral soil or root zone where strong retention and/or uptake of these ions would be expected. The major difference in nutrient levels between the Sierran catchments and the natural catchments examined in this study may be due to difference in abundance of O-horizon. The coastal catchments in southern California are characterized by young soils with poorly-developed O-horizons and substantially lower standing biomass than the Sierran catchments (Griffin and Critchfield 1972 (reprinted with supplement, 1976)). The Lake Tahoe region and the southern California mountainous areas are located in California, but they are categorized as different ecoregions[9] and the nutrient levels vary by up to two orders of magnitudes. This highlights the importance of identifying region-specific background water quality and potentially significant impact of land cover on water quality.

Other environmental factors, such as catchment size, flow-related factors, rainfall, slope, and canopy cover, as well as land cover, did not significantly affect the variability of water quality. This suggests that the findings of this study may be extrapolated as natural background water quality to the southern California's coastal region. For example, natural catchments in this study were relatively small because few large undeveloped watersheds exist in the coastal region of southern California. In general, concentrations would be expected to vary with increasing catchment size due to loss processes that reduce constituent mass as it travels downstream through stream channels (Alexander *et al.* 2000, Peterson *et al.* 2001). However, no significant difference of natural background concentrations among catchments with different size was observed in this study. This allows extrapolation of this study's findings to natural background water quality for other larger or smaller developed watersheds.

Temporal patterns (within and between storm variability) were different in natural catchments than those observed in developed catchments. No first flush was observed in natural catchments, even for small catchments where first flush is most commonly observed in developed areas. The

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[8] O-horizon: At the top of the profile is the O horizon. The O horizon is primarily composed of organic matter. Fresh litter is found at the surface, while at depth all signs of vegetation structure has been destroyed by decomposition. The decomposed organic matter, or humus, enriches the soil with nutrients (nitrogen, potassium, etc.), aids soil structure (acts to bind particles), and enhances soil moisture retention.
[9] Ecoregions denote areas of general similarity in ecosystems and in the type, quality, and quantity of environmental resources. They are designed to serve as a spatial framework for the research, assessment, management, and monitoring of ecosystems and ecosystem components. By recognizing the spatial differences in the capacities and potentials of ecosystems, ecoregions stratify the environment by its probable response to disturbance. These general purpose regions are critical for structuring and implementing ecosystem management strategies across federal agencies, state agencies, and nongovernmental organizations that are responsible for different types of resources within the same geographical areas (http://www.epa.gov/wed/pages/ecoregions.htm).

observation of first flush occurs because pollutants deposited onto exposed areas can be dislodged and entrained by the rainfall-runoff process. In developed areas, the stormwater that initially runs off an area will be more polluted than the stormwater that runs off later, after the rainfall has 'cleansed' the catchment. The first flush can occur up to several hours prior than the peak flow during a storm (Hoffman *et al.* 1984, Smith *et al.* 2000, Stein *et al.* 2006). The existence of first flush should not be assumed in all cases. Intensive monitoring of stormwater runoff from some (usually larger) catchments has failed to observe this phenomenon, mainly due to the complex commingling of flows from different areas within a large catchment (New South Wales Environment Protection Authority 2005). The lack of first flush in the natural catchments may be explained by the fact that first flush is generally seen only where the supply of pollutants is limited (New South Wales Environment Protection Authority 2005). For example, in natural catchments, sediment, as well as and associated bound pollutants, generated from soil erosion will not exhibit a first flush because the supply of soil particles is practically unlimited. As long as rainfall continues and generates storm runoff, there is a continuous input of the sediments (TSS and TDS). Thus, there is also almost no limitation of TSS-correlated constituents, especially metals, during storms, as indicated by the spread observed in the pollutograph of natural areas. This may partially explain the comparability of TSS FWMC for natural and developed areas. Differences in pollutant delivery timing for natural areas compared to developed areas may provide some ability to segregate downstream loads that are anthropogenic in origin and most prevalent in the early part of storms, from those that are natural in origin and most prevalent later in the storm. This should be investigated further through additional empirical and modeling analysis.

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

Metals	FWMC (μg/L)			Mass Load (g)			Flux (g/km^2)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Arsenic	0.39	0.71	0.21	17.40	44.63	6.78	0.87	1.91	0.40
Cadmium	0.14	0.24	0.08	6.26	15.46	2.53	0.31	0.73	0.14
Chromium	1.40	3.09	0.63	62.59	188.88	20.74	3.13	7.98	1.23
Copper	1.54	3.17	0.75	68.84	201.07	23.57	3.45	8.68	1.37
Iron	962	2313	400	43100	139746	13293	2158	6160	756
Lead	0.51	1.06	0.24	22.80	64.84	8.02	1.14	2.94	0.44
Nickel	1.03	2.46	0.43	46.24	152.10	14.06	2.32	6.36	0.84
Selenium	0.33	0.60	0.18	14.93	41.22	5.41	0.75	1.85	0.30
Zinc	5.32	11.16	2.54	238.44	680.97	83.49	11.94	31.52	4.52

Nutrients	FWMC (mg/L)			Mass Load (kg)			Flux (kg/km^2)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Ammonia	0.04	0.08	0.02	1.91	4.68	0.78	0.10	0.21	0.04
Dissolved Organic Carbon	6.26	9.54	4.11	338.67	915.76	125.25	11.83	30.35	4.61
Nitrate+Nitrite	0.34	0.58	0.19	15.01	36.20	6.22	0.75	1.54	0.37
Orthophosphate	0.04	0.06	0.02	1.91	4.35	0.84	0.10	0.20	0.05
Total Kjeldahl nitrogen	1.21	1.55	0.95	70.74	255.66	19.58	2.63	7.18	0.96
Total Organic Carbon	6.28	9.91	3.98	339.54	935.81	123.20	11.86	31.31	4.49
Total Phosphorus	0.12	0.21	0.07	1.12	4.54	0.28	0.09	0.55	0.02

Solids	FWMC (mg/L)			Mass Load (kg)			Flux (kg/km^2)		
	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI	Geomean	Upper CI	Lower CI
Total Dissolved Solids	251	338	187	11200	25300	4990	637	1260	320
Total Suspended Solids	98.12	280.84	34.28	5069.70	20983.90	1224.84	257.25	854.39	77.46

Microbes	Concentration (MPN/100ml)		
	Geomean	Upper CI	Lower CI
E. coli	125	399	39.70
Enterococcus	140	511	38.80
Total coliform	4460	13100	1510

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Constituent	No of ND	No of Sample	%ND
Arsenic	62	355	17.5
Cadmium	96	355	27.0
Chromium	11	355	3.1
Copper	9	254	3.5
Lead	76	355	21.4
Nickel	21	355	5.9
Selenium	56	355	15.8
Ammonia	73	216	33.8
Nitrate	44	220	20.0
Nitrite	93	218	42.7
Orthophosphate	41	210	19.5
Total Phosphorus	112	212	52.8
Total Suspended Solids	34	213	16.0
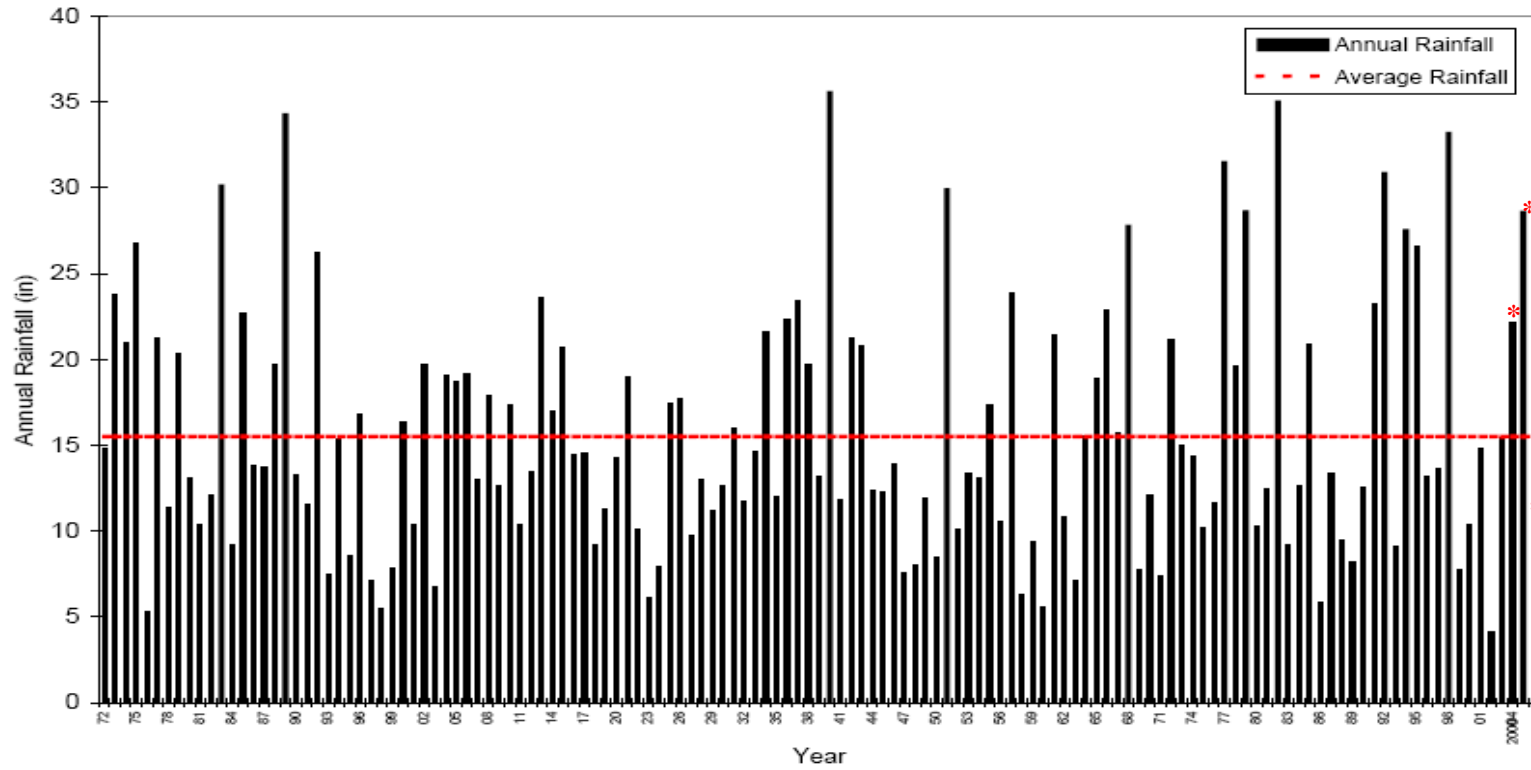
Figure. 8. Comparison of annual rainfall (wet season) at LADPW station #716, Ducommun St., Los Angeles in 2004, 2005, and 2006 with the average rainfall over 135 years. Red dotted line indicates the average annual rainfall of 135 years. * indicates the period of this study from 2004 through 2006.
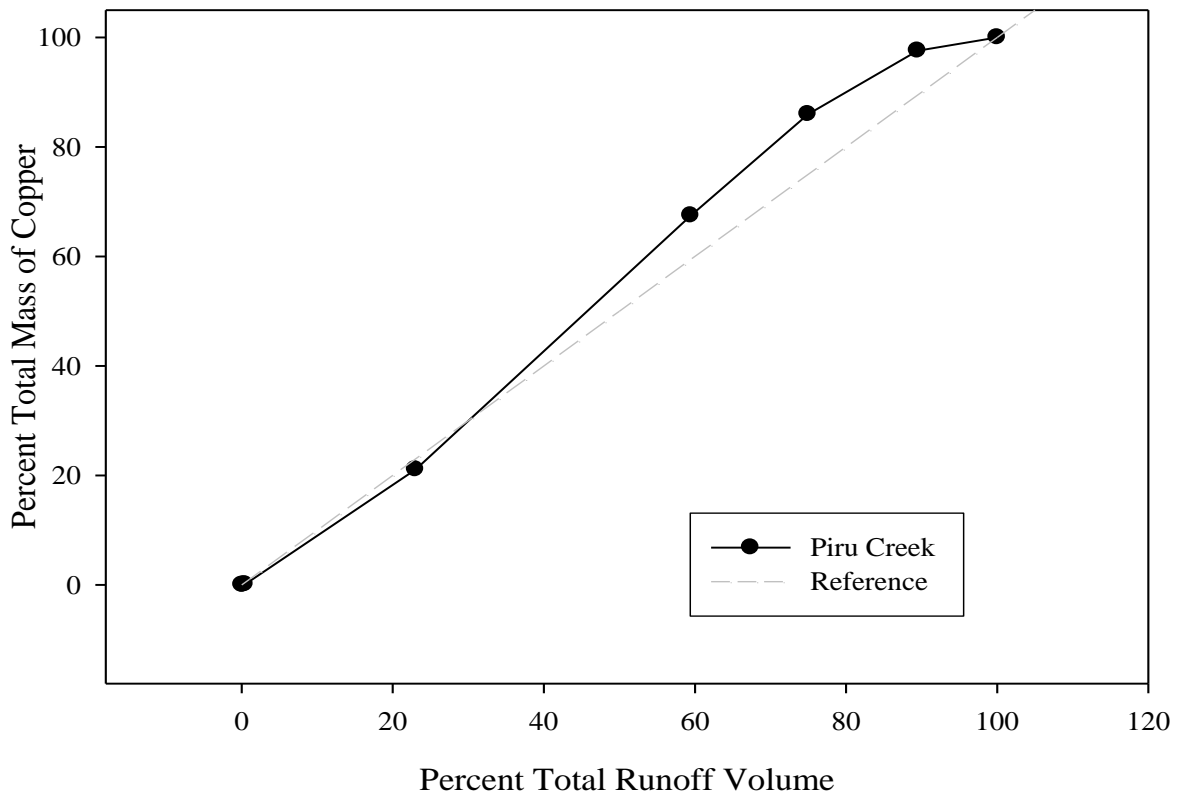
Figure 9. Cumulative copper mass loads for a storm (February 27 through March 1, 2006) at Piru Creek. Reference line indicates a 1:1 relationship between volume and mass loading. Portions of the curve above the line indicate proportionately higher mass loading per unit volume.
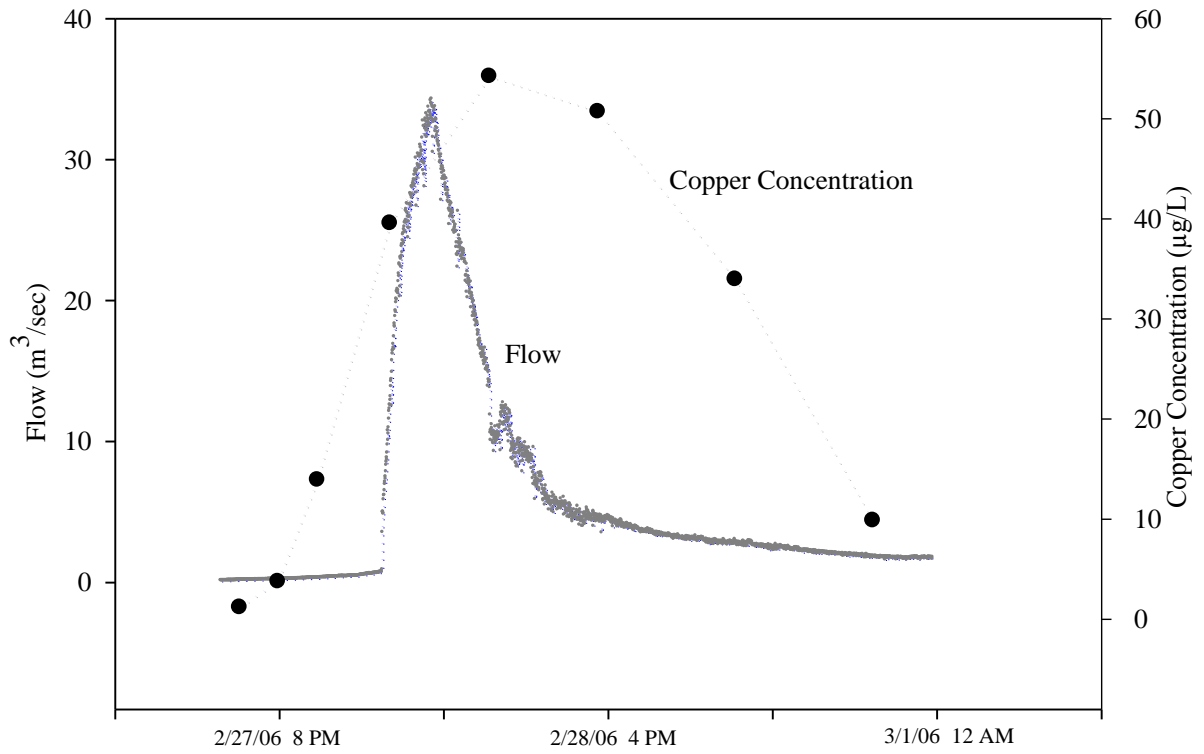
Figure 10. Variation in total copper concentrations with time for storm event in Piru Creek from February 27 through March 1, 2006.
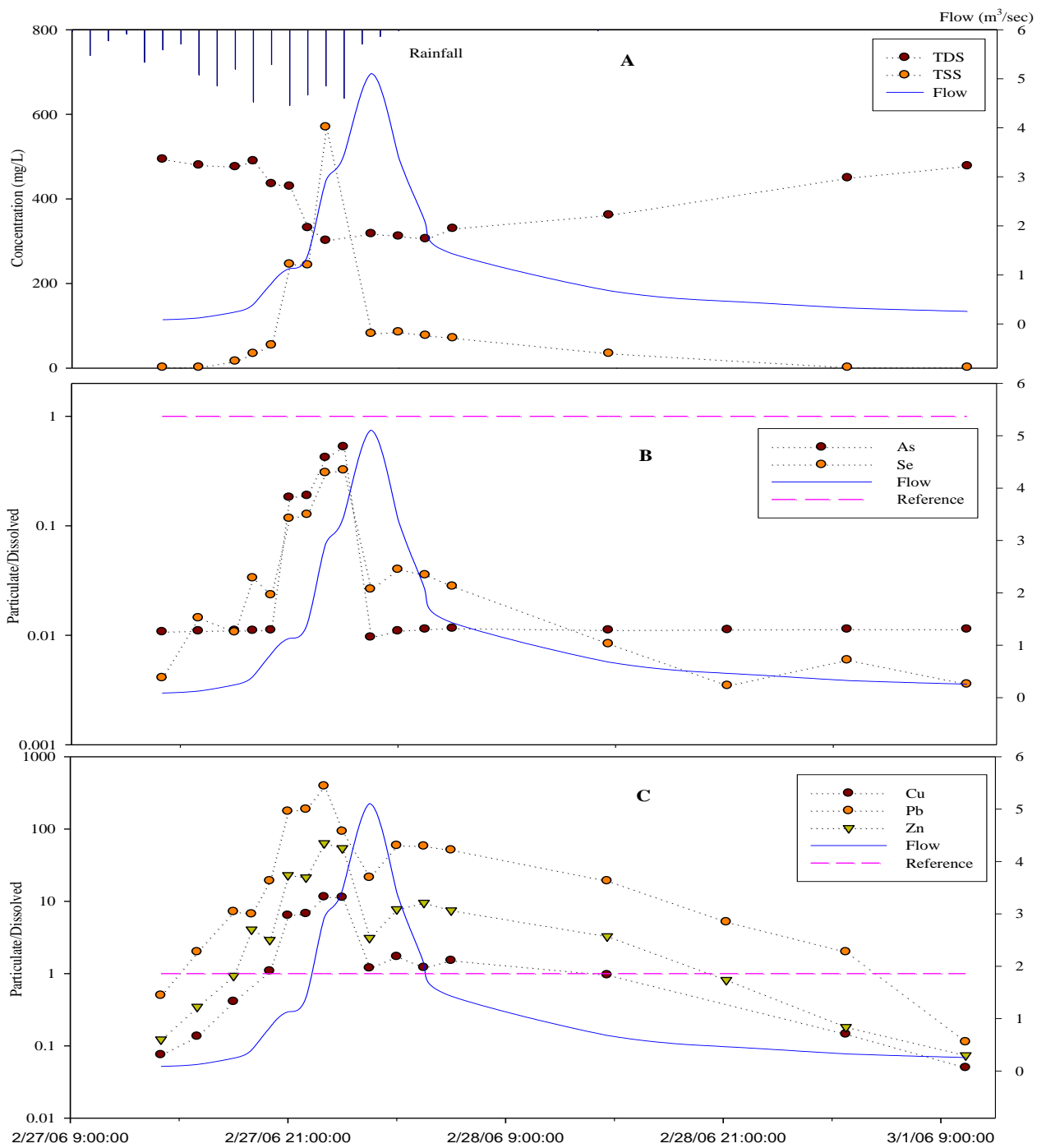
Figure 11. Change in the ratio of particulate metals over dissolved metals over the course of a storm event at Bear Creek, a tributary to North Fork Matilija, CA.
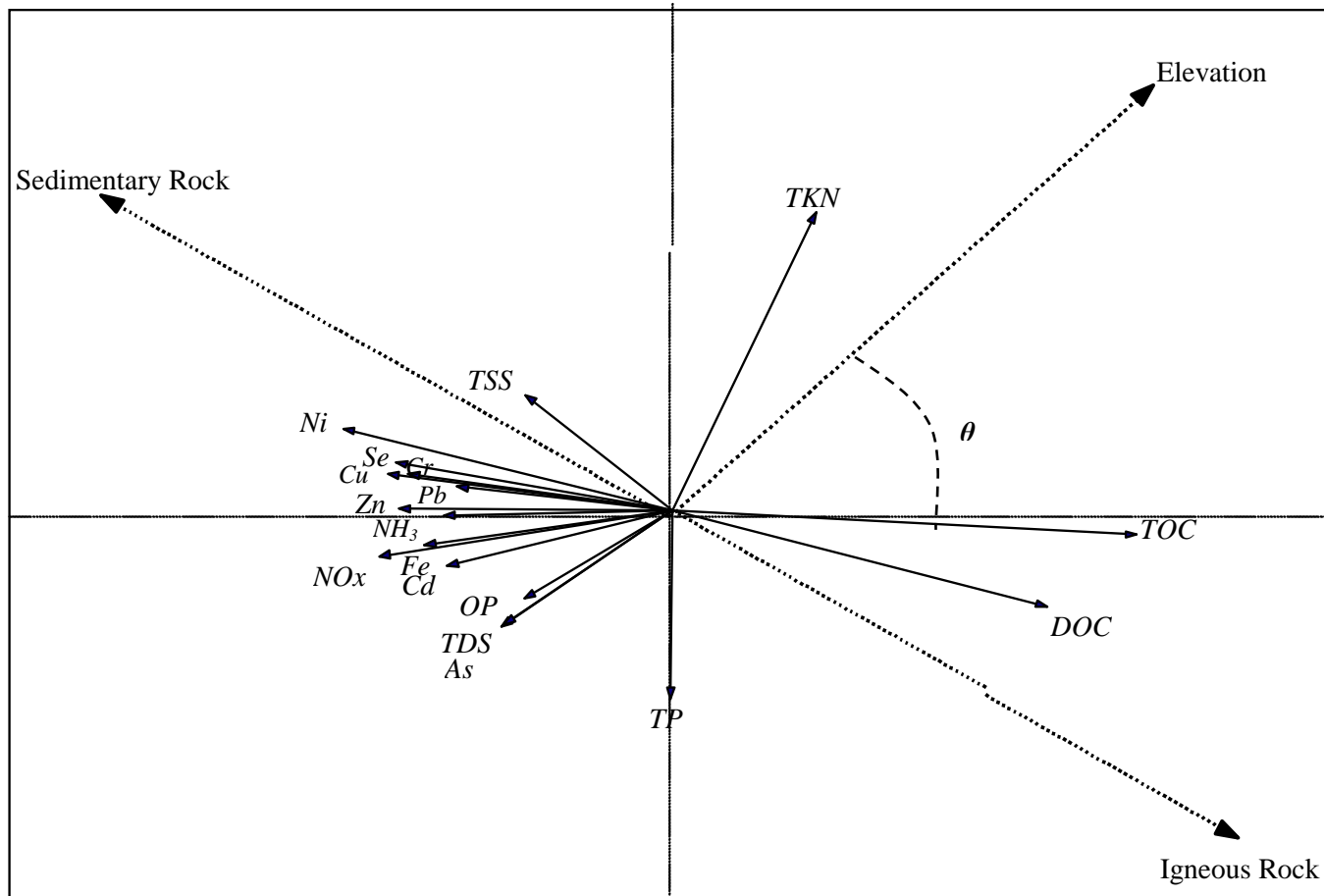
Figure 12. Correlation biplots showing the relations between wet weather concentrations of metals, nutrients, and solids (solid arrows) and environmental variables (dotted arrows). Eigenvalues: 0.151 and 0.0280 for the first (horizontal) and second (vertical) axes. *cos θ* ≈ correlation coefficient between two variables (arrows). Longer arrow indicates which factor is more important in generating variability. total dissolved solids (TDS); total suspended solids (TSS); total organic carbon (TOC); dissolved organic carbon (DOC; total Kjeldahl nitrogen (TKN); total phosphorus (TP); orthophosphate (OP); and Nitrate+Nitrite (NOx).
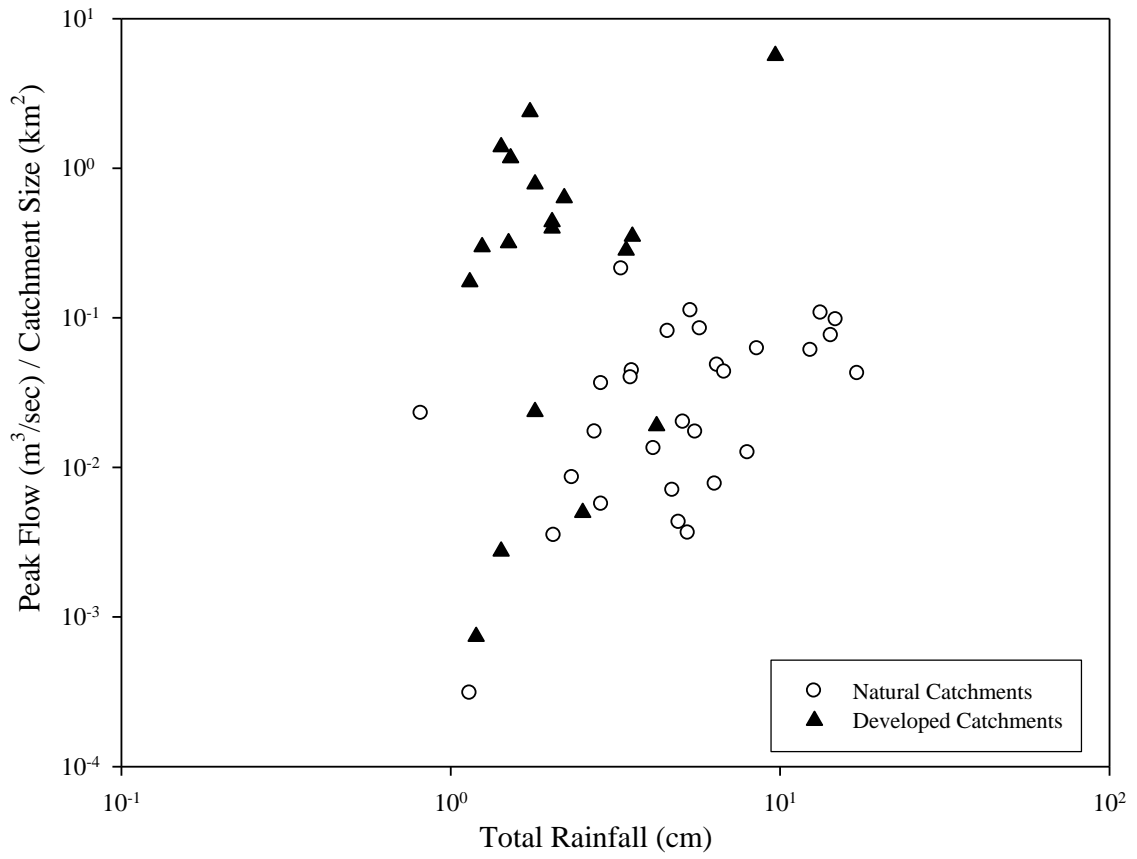
Figure 13a. Comparison of peak flow over catchment size vs. rainfall between natural catchments and developed catchments; X and Y axes are in log scale.

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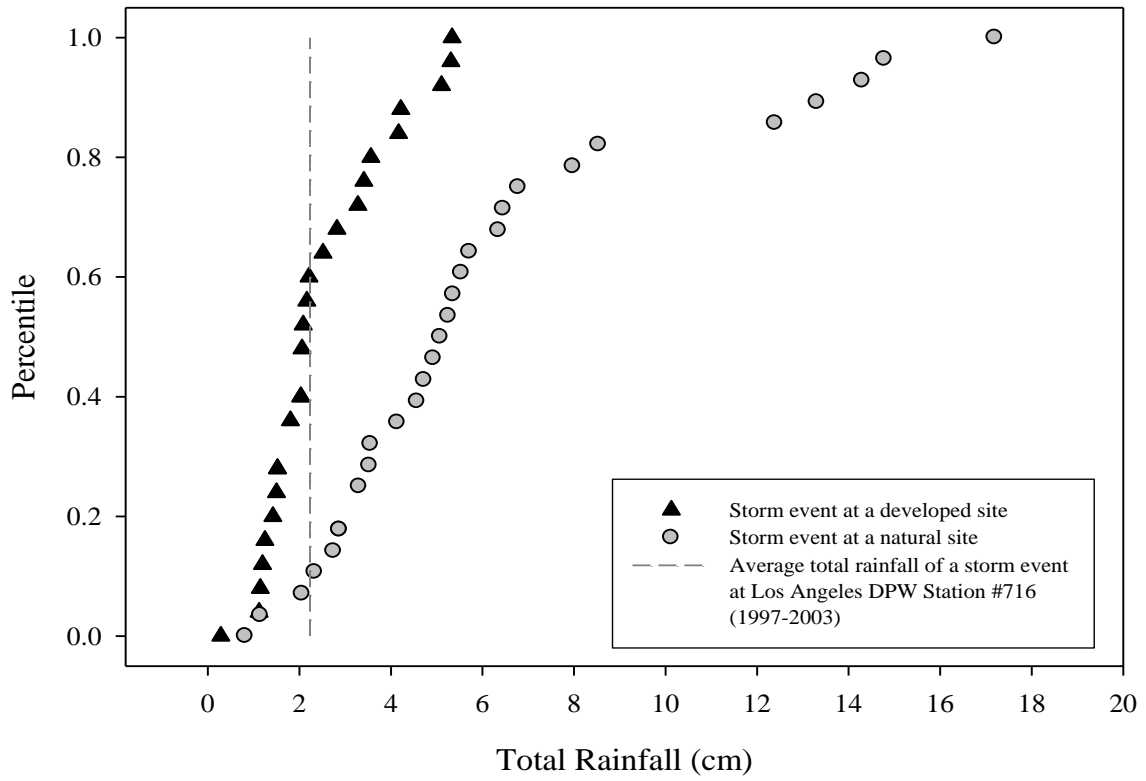
Figure 13b. Distribution of storm events in terms of total rainfall per storm event.
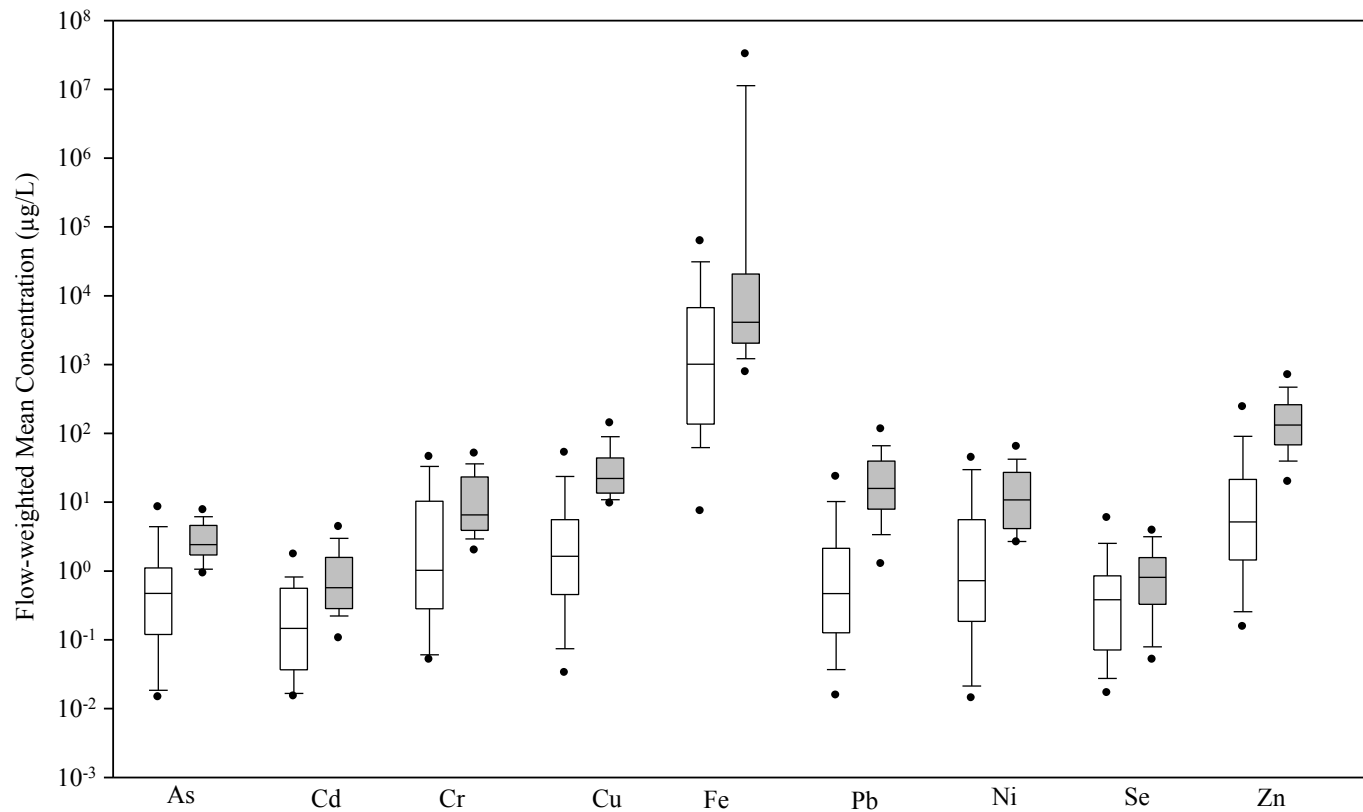
Figure 14a. Comparison of wet weather flow-weighted concentrations of metals between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.
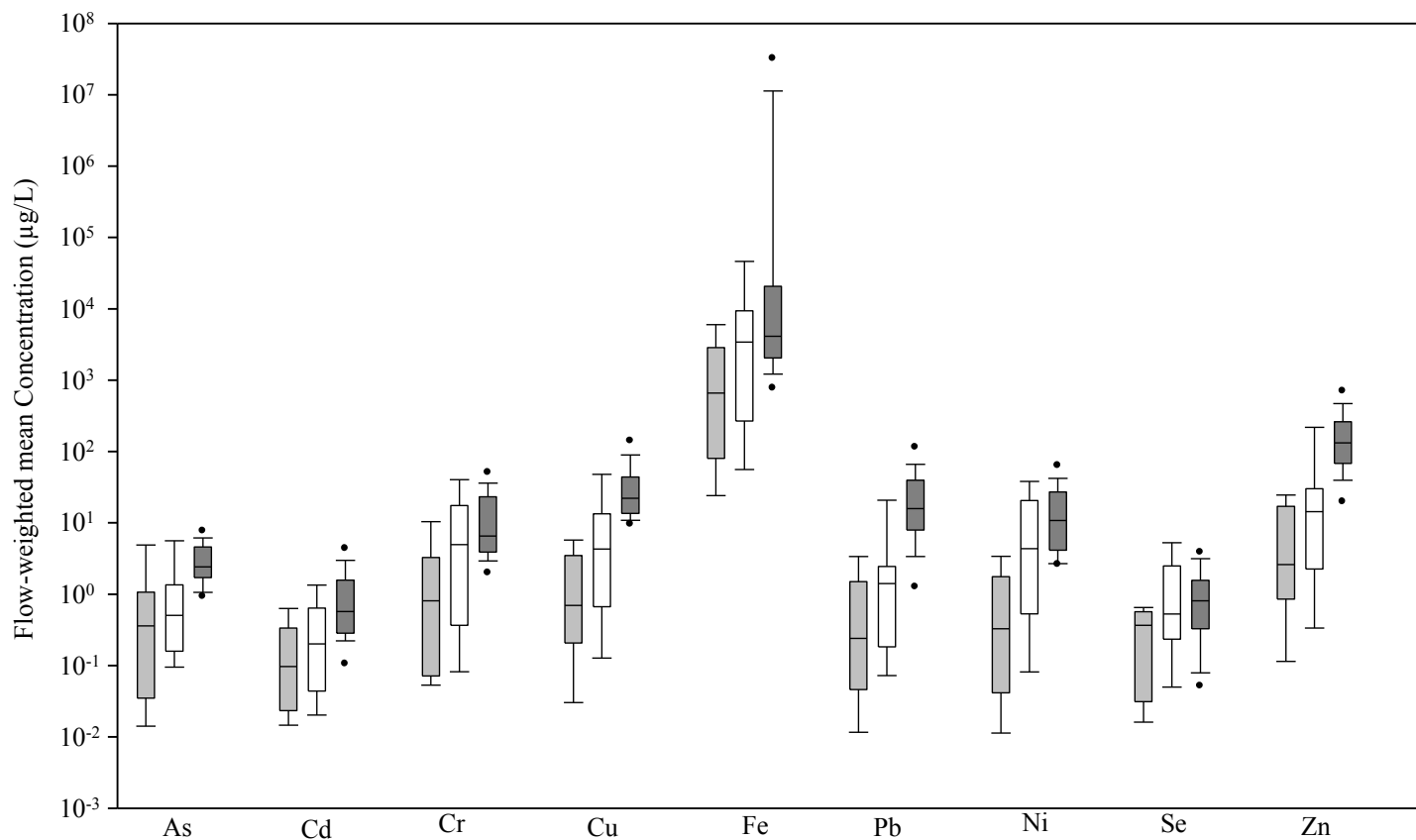
Figure 14b. Comparison of wet weather flow-weighted concentrations of metals between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.
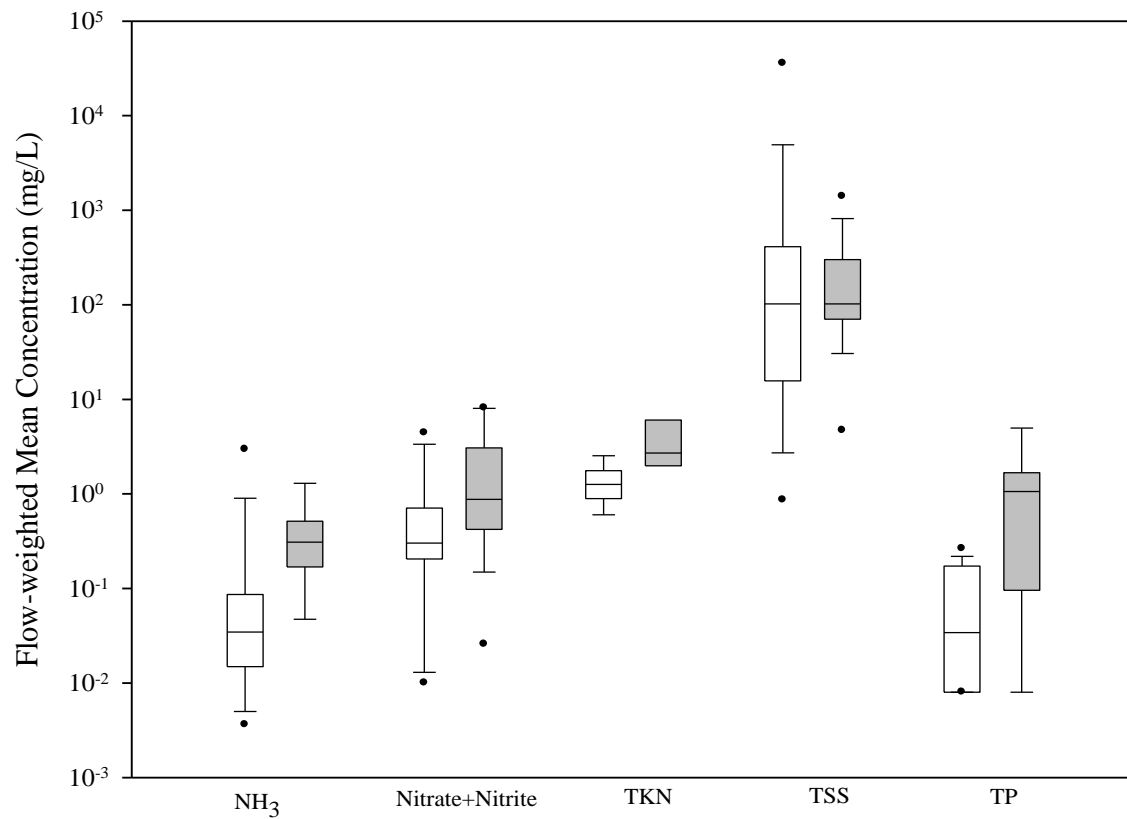
Figure 15a. Comparison of wet weather flow-weighted concentrations of ammonia (NH$_3$), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total suspended solids (TSS), and total phosphorous (TP) between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. The Y axis is in log scale.
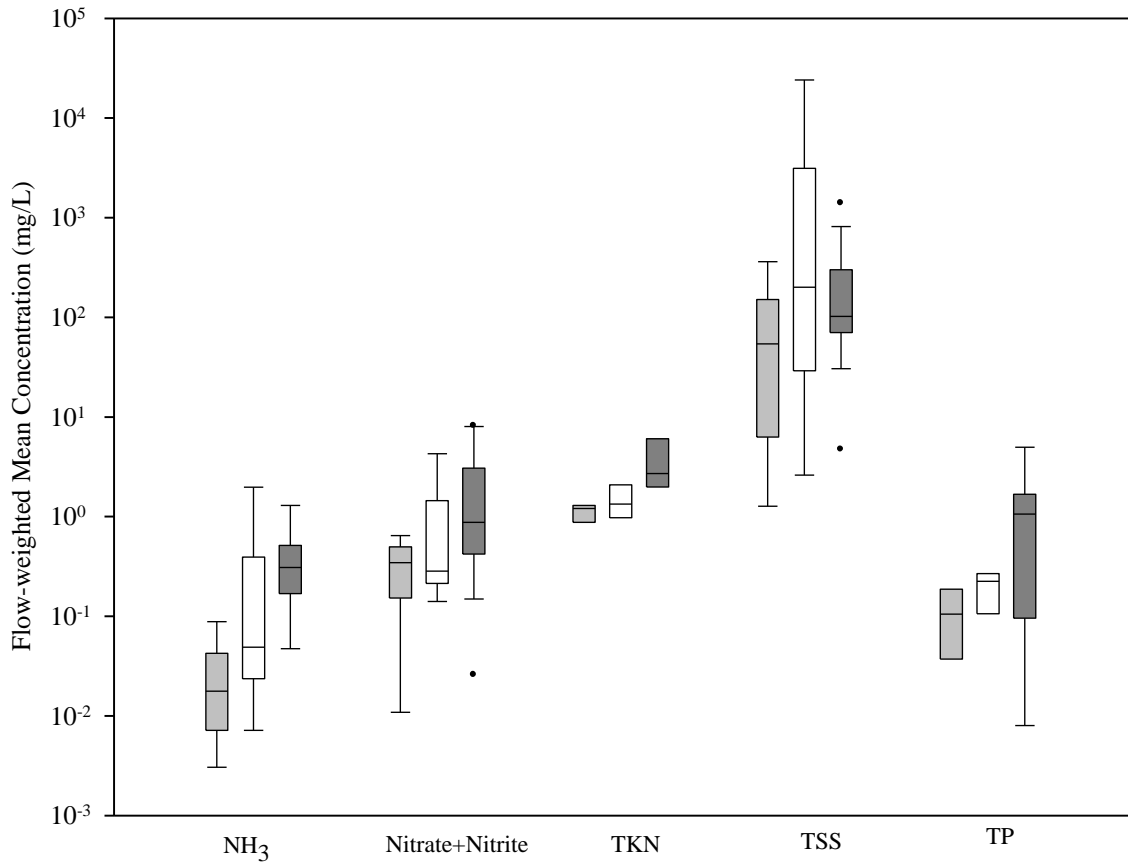
Figure 15b.   Comparison of wet weather flow-weighted concentrations of ammonia (NH$_3$), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total suspended solids (TSS), and total phosphorous (TP) between natural and developed catchments. Light gray boxes represent natural sites underlain by igneous rock, white boxes represent natural sites underlain by sedimentary rock, and dark gray boxes represent developed sites. Y axis is in log scale.
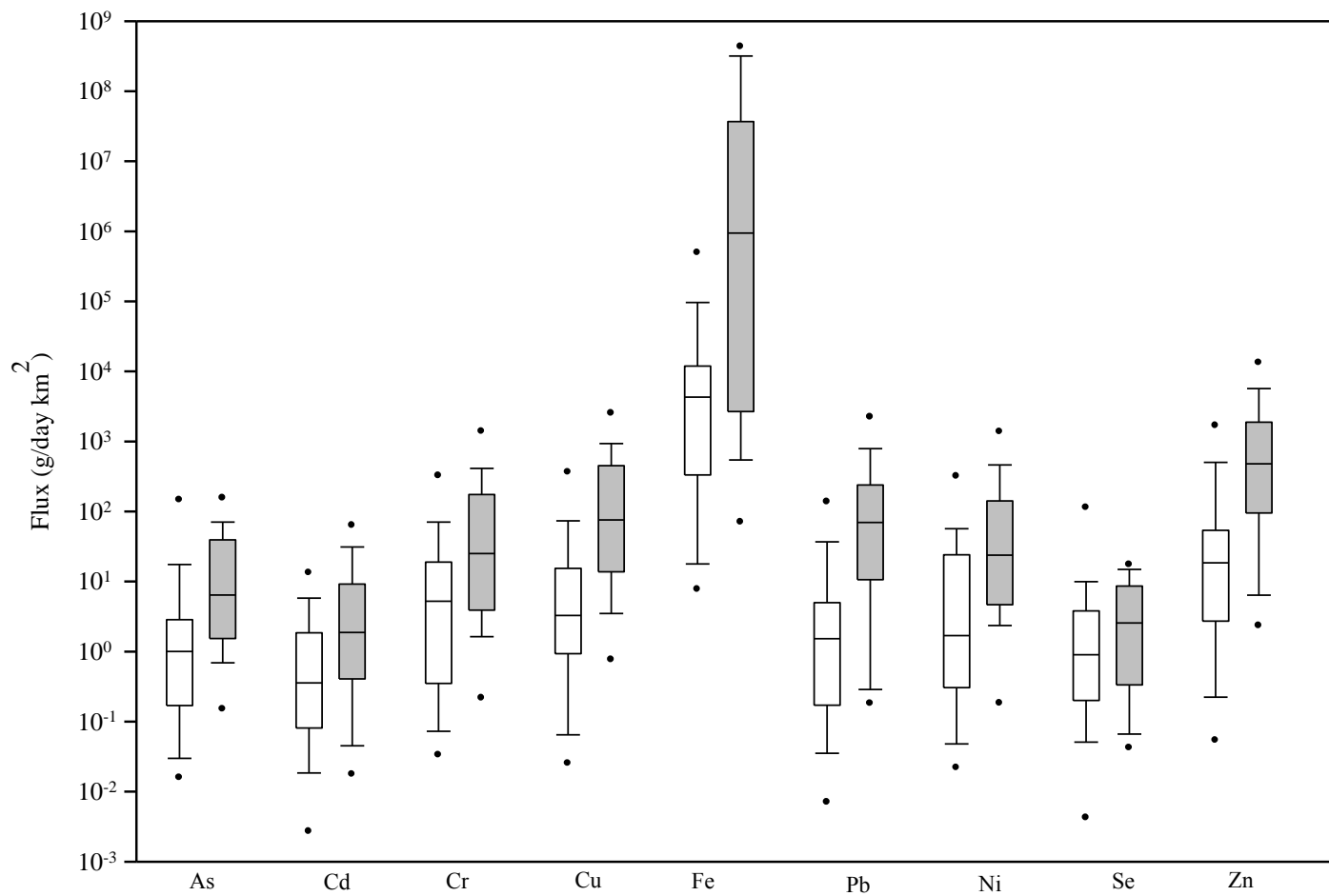
Figure 16. Comparison of wet weather fluxes of metals between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. Y axis is in log scale
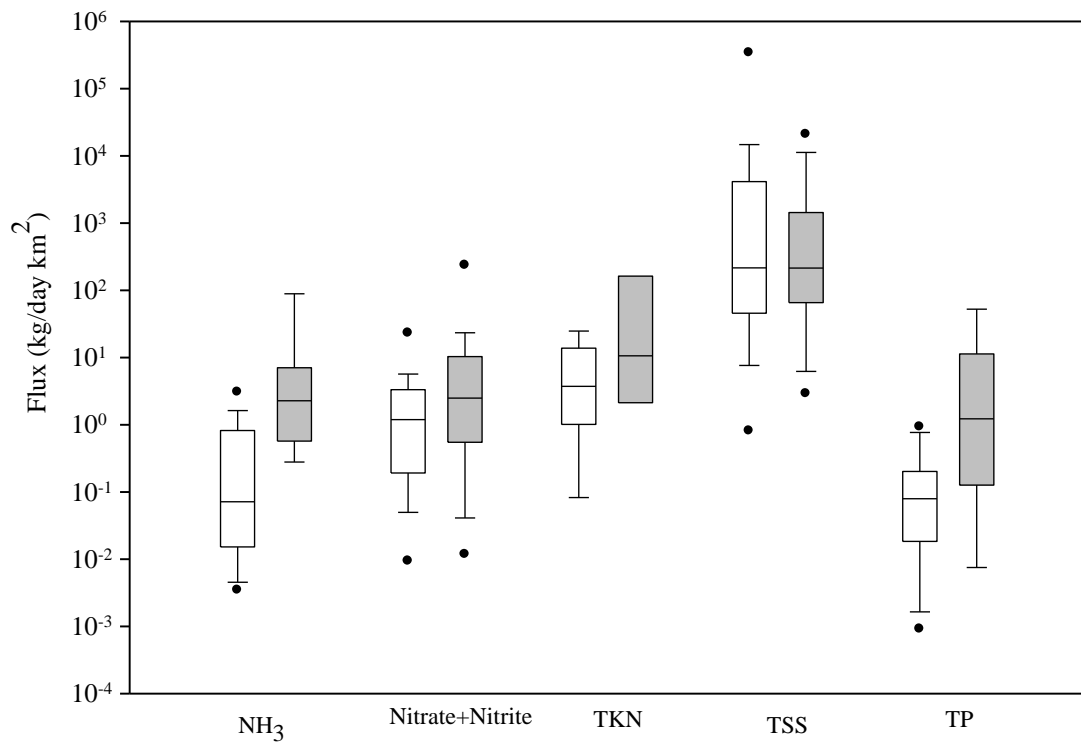
Figure 17. Comparison of wetweather fluxes of ammonia (NH$_3$), nitrate+nitrite, total Kjeldahl nitrogen (TKN), total phosphorus (TP), and total suspended solids (TSS) between natural and developed catchments. White boxes represent natural catchments, while gray boxes represent developed catchments. All fluxes are expressed in kg/day km^2. Y axis is in log scale.
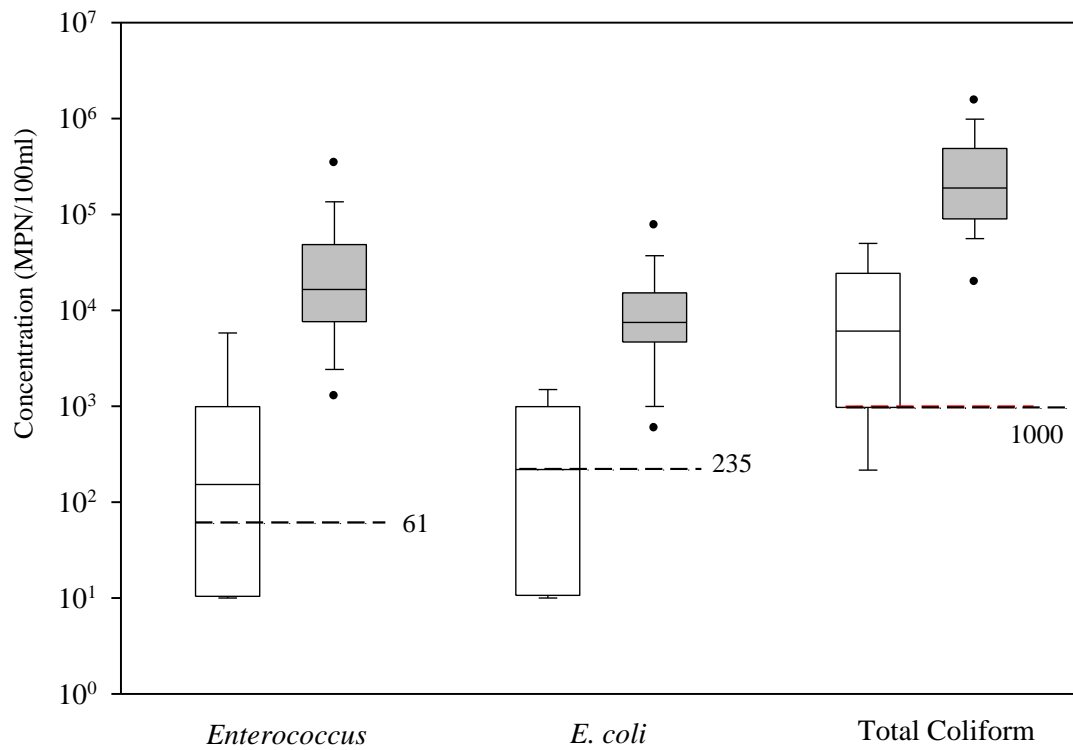
Figure 18. **Comparison of wet weather flow-weighted concentrations of bacteria between natural and developed catchments. White boxes represent natural catchments, and gray boxes represent developed catchments. .Y axis is in log scale. Dotted lines represent Department of Health and Safety draft guideline for freshwater recreation.**
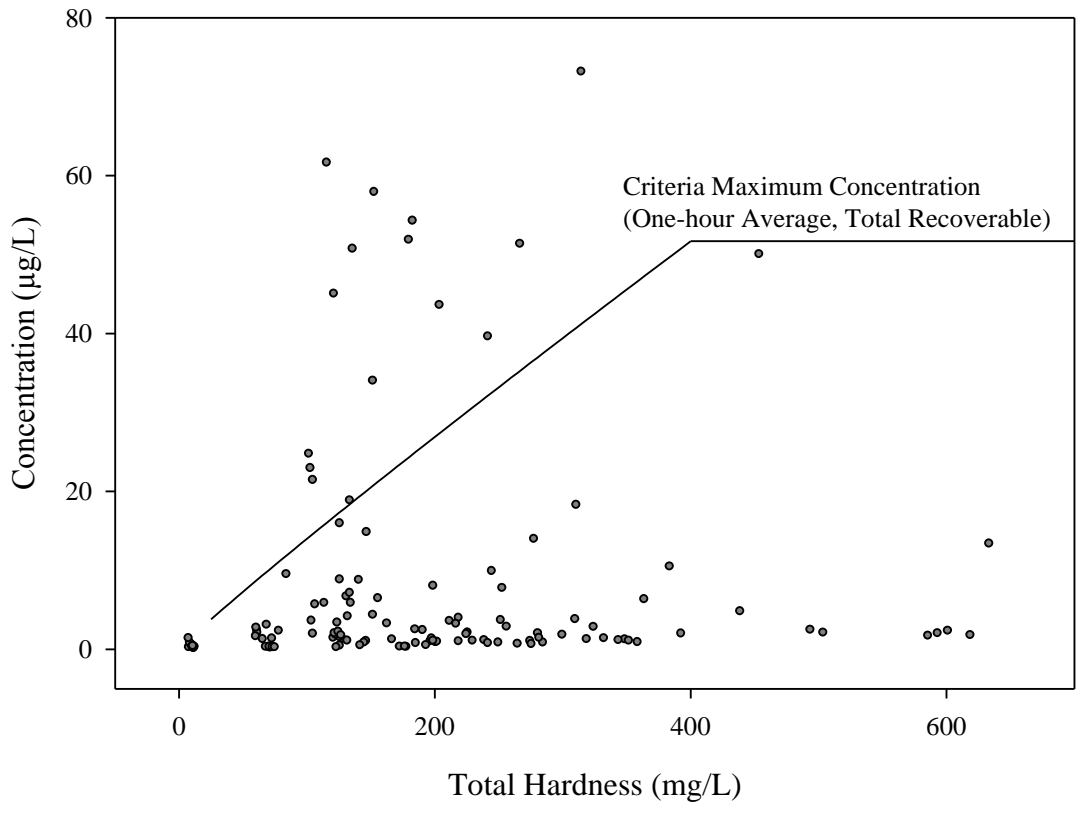
Figure 19a. Copper concentrations at natural catchments compared with the hardness-adjusted standard under the California Toxics Rule (CTR). The stormwater concentrations are compared with the acute standard.
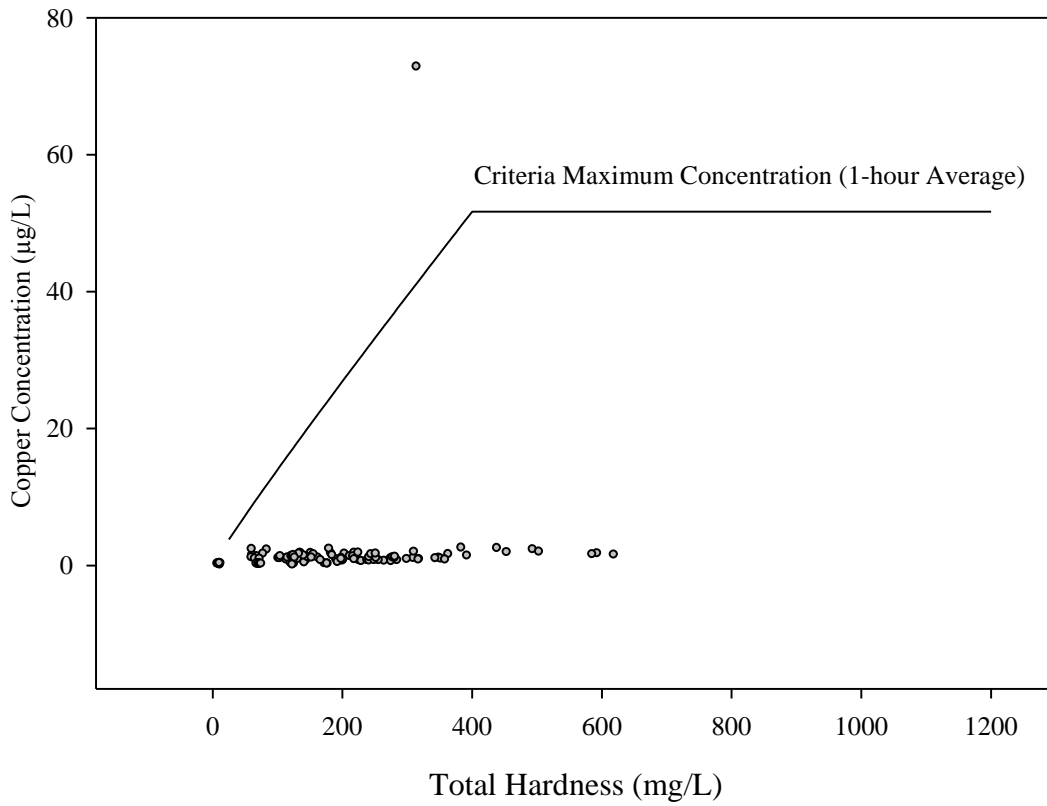
Figure 19b. Wet weather dissolved copper concentrations at natural catchments compared with the hardness-adjusted standard under the California Toxics Rule (CTR). The stormwater concentrations are compared with the acute standard.

ESTIMATION OF ANNUAL LOADS

Background

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

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

Flow

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

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

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

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

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

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

Loading in perennial vs. intermittent streams

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

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

Discussion

Annual flux rates were significantly lower in natural catchments than in developed catchments in southern California (Table 27). This difference can be illustrated by comparing this study's results to data from Ballona Creek, which is located in southern California and includes a significant portion of the City of Los Angeles, California. Approximately 85% of the 330 km^2 catchment is charactarized by urban land uses (Wong *et al.* 1997). Annual fluxes of Cr, Cu, Pb, Ni, Zn, and TSS for Ballona Creek were based on the load values presented in studies by McPherson *et al.* (2005) and Tiefenthaler *et al.* (in review). Annual fluxes of Cr, Cu, Pb, Ni, and Zn were one to two orders of magnitude higher at Ballona Creek than at natural streams. In

contrast, fluxes of TSS was two to three orders of magnitude higher at Piru Creek and Sespe Creek than that at Ballona Creek. This is expected due to storm-induced erosion of soil from open areas in the natural catchments. Unlike urban catchments with larger impervious area and concrete-bottom channels, the five natural catchments are mainly open lands that can contribute large volumes of sediment (and hence TSS). In addition, in-channel erosion of natural streams, which can be a substantial source of TSS (Trimble 1997, Pons 2003) does not occur in concrete lined channels, such as Ballona Creek.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

[a] Total fluxes are only for the eight months of the study from December 2005 through August 2006.
[b] McPherson *et al.* 2005
[c] Tiefenthaler *et al.* in review
[d] Clark *et al.* 2000
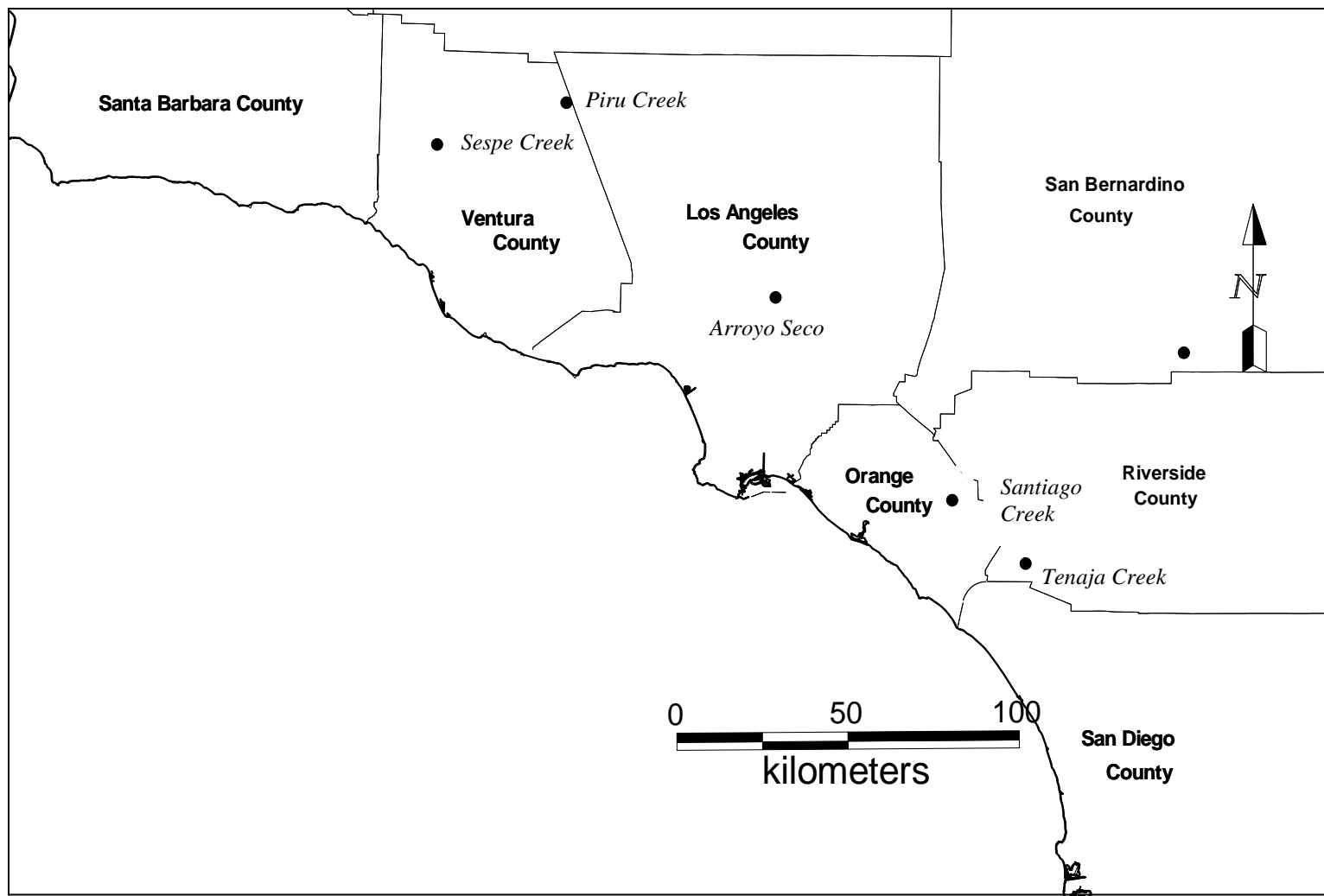
Figure 20. Map of study sites for the estimation of annual loads.
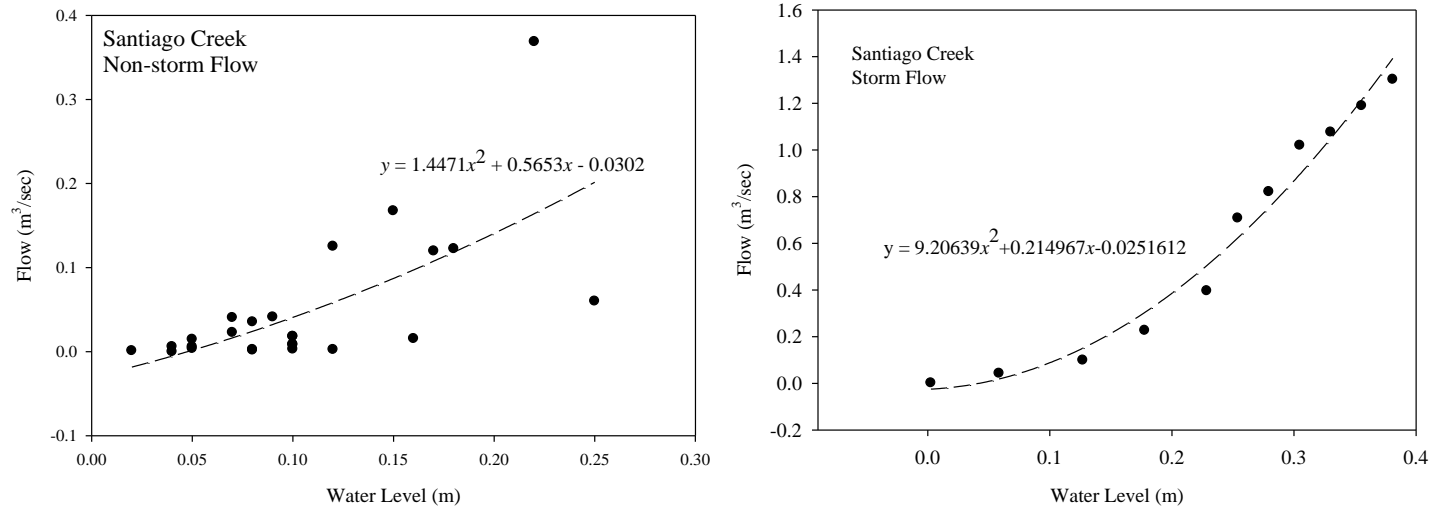
Figure 21a. Rating curves at Santiago Creek for non-storm and storm flows. r^2 Values are 0.43 and 0.97 for non-storm and storm flows, respectively.
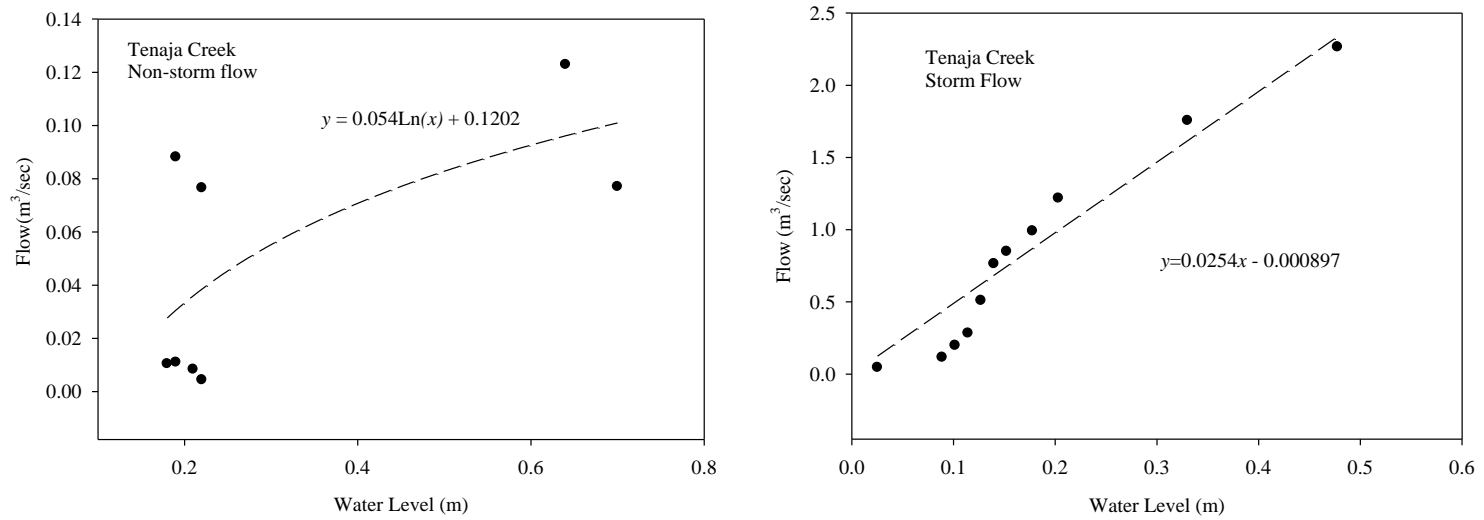
Figure 21b. Rating curves at Tenaja Creek for non-storm flow and storm flows. r^2 Values are 0.43 and 0.97 for non-storm and storm flows, respectively.
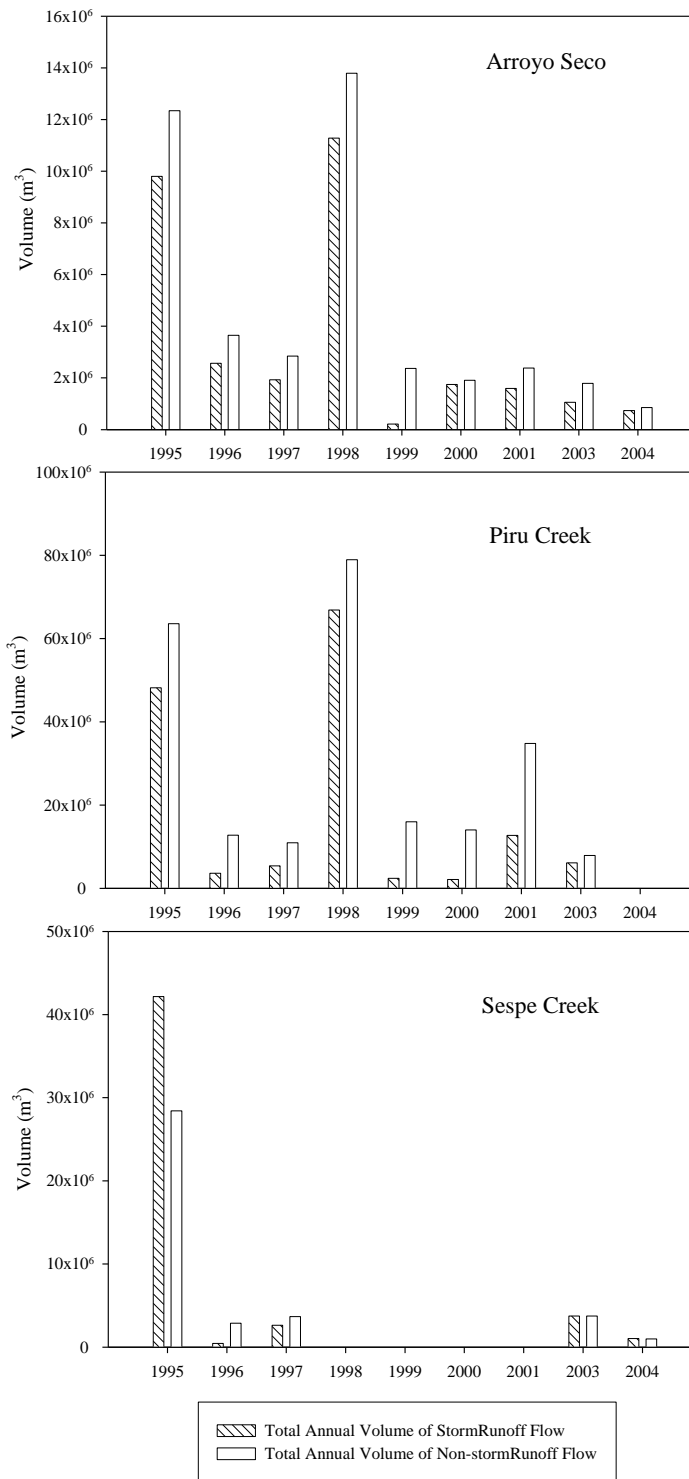
Figure 22. Comparison of annual storm flow and non-storm flow volumes. The flow data for the 2004 water year for Piru Creek and for the 1998 to2001 water years for Sespe Creek are not available. The flow data of the water year 2002 for Arroyo, Piru, and Sespe Creeks were not included in the analysis due to the insufficient quality of the data set.
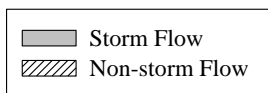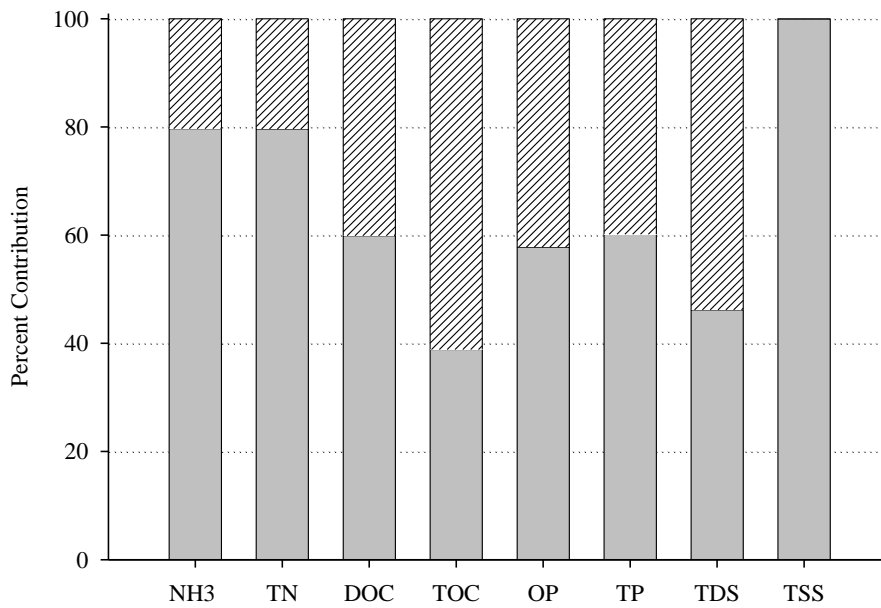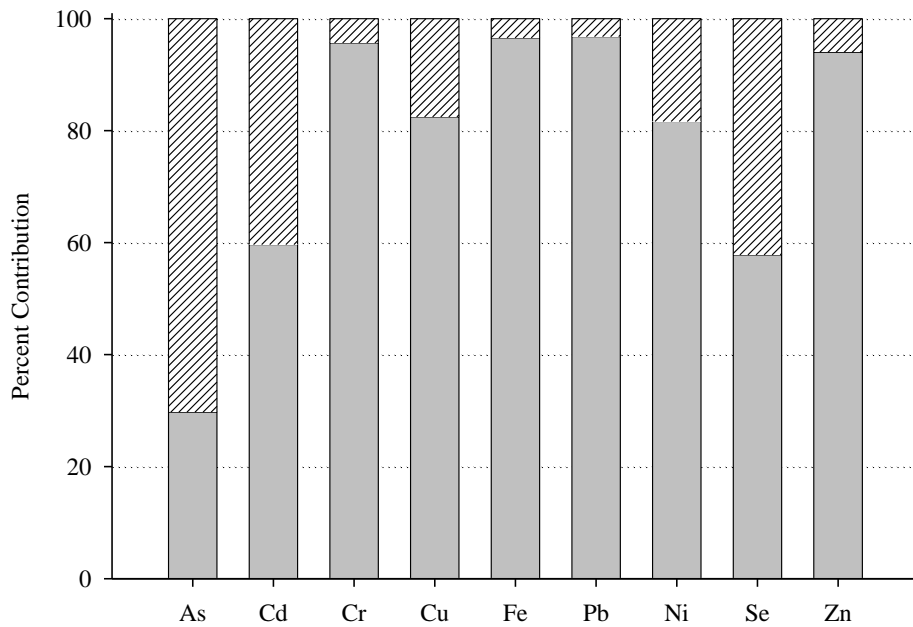
Figure 23. Percent contribution of storm flow and non-storm flow to total annual fluxes of metals, nutrients, and solids; ammonia (NH$_3$,); total nitrogen (TN); dissolved organic carbon (DOC); total organic carbon (TOC); orthophosphate (OP); total phosphorus (TP); total dissolved solids (TDS); and total suspended solids (TSS).
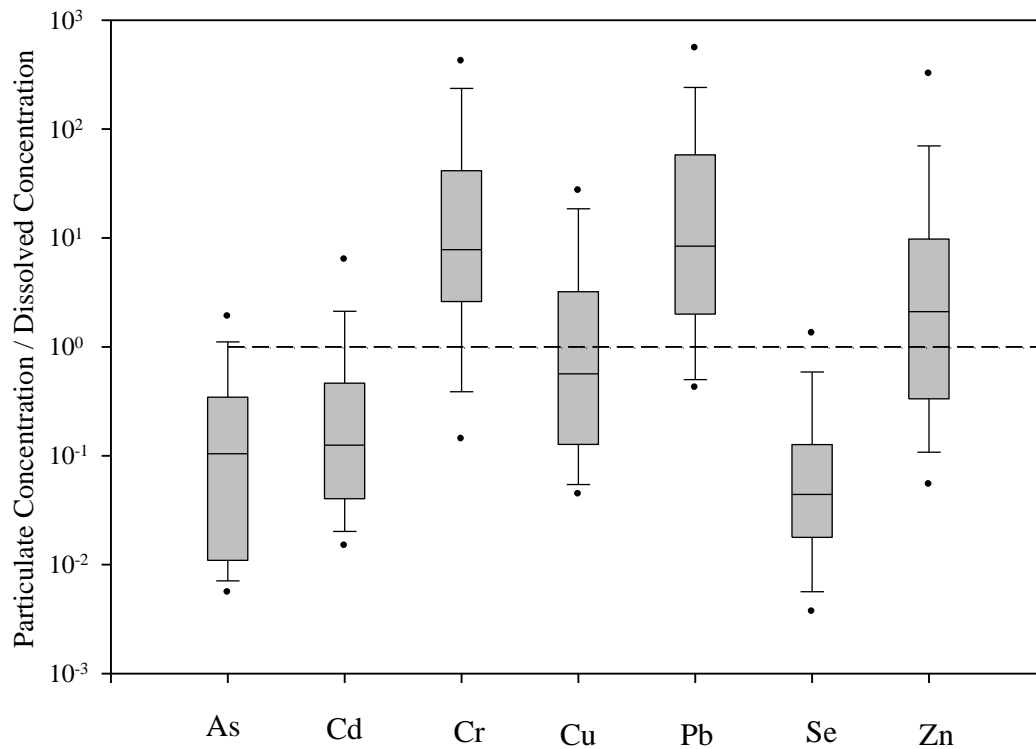
Figure 24. Ratios of particulate concentrations over dissolved concentrations for metals in storm flow. The dissolved and particulate concentrations were analyzed with samples of storm, which were collected in the winter of 2006. The dotted line references a 1:1 ratio; Solid lines indicate the median of all values in the category. Boxes indicate 25th and 75th percentiles, and error bars indicate 10th and 90th percentiles. Solid dots represent 5th and 95th percentiles. The Y axis is in log scale.

CONCLUSIONS

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

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

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

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

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

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

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

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

8. Concentrations of several nutrients were higher than the USEPA proposed nutrient guidelines for Ecoregion III, 6. It is important to note that the ultimate approach for nutrient

criteria adopted in the State of California will likely differ from the approach used in the proposed EPA guidelines. Furthermore, the proposed guidelines were based on a combination of both wet and dry weather data. Nevertheless, this result indicates that background nutrient levels in southern California may be higher than in other portions of the country.

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

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

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

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

APPLICATIONS AND NEXT STEPS

Natural background water quality estimates

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

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

Geology-specific loadings

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

Further studies

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

weighted mean concentrations of this study provide relevant background water quality concentrations for the southern California region.

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

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

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

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

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

LITERATURE CITED

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

Ackerman, D., K.C. Schiff, H. Trim and M. Mullin. 2003. Characterization of water quality in the Los Angeles River. *Bulletin of Southern California Academy of Sciences* 102:17-25.

Ackerman, D. and S.B. Weisberg. 2003. Relationship between rainfall and beach bacterial concentrations on Santa Monica Bay beaches. *Journal of Water and Health* 1:85-89.

Agency, U.S.E.P. 1983. Methods for chemical analysis of water and waste, Report EPA-600/4-79-020. U.S. Environmental Protection Agency. Cincinnati, OH.

Ahn, J.H., S.B. Grant, C.Q. Surbeck, P.M. Digiacomo, N.P. Nezlin and S. Jiang. 2005. Coastal water quality impact of stormwater runoff from an urban watershed in southern California. *Environmental Science and Technology* 15:5940-5953.

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

Bay, S. and D.J. Greenstein. 1996. Toxicity of dry weather flow form the Santa Monica Bay watershed. *Bullentine of southern California Academy of Science* 95:33-45.

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

Biggs, B.J.F. and H.A. Thomsen. 1995. Disturbance in stream periphyton by perturbations in shear stress: time to structural failure and differences in community resistance. *Journal of Phycology* 31:233-241.

Buffleben, M.S., K. Zayeed, D. Kimbrough, M.K. Stenstrom and I.H. Suffet. 2002. Evaluation of urban non-point source runoff of hazardous metals entering Santa Monica Bay, California *Water Science and Technology* 45:263-268.

Bytnerowicz, A. and M.E. Fenn. 1996. Nitrogen deposition in California forests: Review. *Environmental Pollution* 92:127-146.

Characklis, G.W. and M.R. Wiesner. 1997. Particles, Metals, and Water Quality in Runoff from Large Urban Watershed. *Journal of Environmental Engineering* 123:753-759.

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

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

Detenbeck, N., C.A. Johnston and G. Niemi. 1993. Wetland effects on lake water quality in the Minneapolis/St. Paul metropolitan area. *Landscape Ecology* 8:39-61.

Dickert, P.F. 1966. Tertiary Phosphatic Faces of the coast ranges, in geology of Northern California. Vol. Bulletin 190. California Division of Mines and Geology.

Dodds, W.K., J.R. Jones and E.B. Welch. 1998. Suggested classification of stream trophic state: Distributions of temperate stream types by chlorophyll, total nitrogen, and phosphorus. *Water Research* 32:1455-1462.

Driscoll, E., P.E. Shelley and E.W. Strecker. 1990. Pollutant loadings and impacts from highway stormwater runoff, Volume III: Analytical investigations and research report,. Federal Highway Administration, Woodward-Cylde Consultant. Oakland, CA.

Duke, L.D., T.S. Lo and M.W. Turner. 1999. Chemical constituents in storm flow vs. dry weather discharges in California storm water conveyances. *Journal of American Water Resources Association* 35:821-835.

Dunne, T. and L.B. Leopold. 1978. Water in Environmental Planning. WH Freeman. New York, NY.

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

Fenn, M.E. and J.W. Kiefer. 1999. Throughfall deposition of nitrogen and sulfur in a Jeffrey pine forest in the San Gabriel Mountains, southern California. *Environmental Pollution* 104:179-187.

Fenn, M.E., M.A. Poth and M. Arbaugh. 2002. A throughfall collection method using mixed bed ion exchange resin columns. *the International symposium on passive sampling of gaseous air pollutants in ecological effects research* 2:122-130.

Gamradt, S.C. and L.B. Kats. 1997. Impact of chaparral wildfire-induced sedimentation on oviposition of stream-breeding California newts. *Oecologia* 110:546-549.

Gergel, S.E., M.G. Turner and T.K. Kratz. 1999. Dissolved organic carbon as an indicator of the scale of watershed influence on lakes and rivers. *Ecological Applications* 9:1377-1390.

Gray, J.R., G.D. Glysson, L.M. Turcios and G.E. Schwarz. 2000. Comparability of Suspended-Sediment Concentration and Total Suspended Solids Data. U.S. Geological Survey, Office of Surface Water.

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

Griffin, J.R. and W.B. Critchfield. 1972 (reprinted with supplement, 1976). The Distribution of Forest Trees in California. USDA Forest Service, Pacific Southwest Forest and Range Experiment Station. Berkeley, CA.

Hatje, V., K. Rae and G.F. Birch. 2001. Trace metal and total suspended solids concentrations in freshwater: the importance of small-scale temporal variation. *Journal of Environmental Monitoring* 3:251-256.

Hibbs, B.J. and M.M. Lee. 2000. Sources of selenium in the San Diego Creek watershed, Orange County California. Technical Contract Report prepared for Defend The Bay Foundation and the California Urban Environmental Research and Education Center Hydrogeology Program California State University, Los Angeles. Los Angeles, CA.

Hoffman, E.J., G.L. Mills, J.S. Latlmer and J.G. Quinn. 1984. Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters. *Environmental Science and Technology* 18:1984.

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

Hounslow, A.W. 1995. Water quality data:analysis and interpretation. pp. 86-87. CRC Lewis Publishers. Boca Raton, FL.

Jennings, C.W. and R.G. Strand. 1969. Geologic map of California, Los Angeles sheet. Olaf P Jenkins ed.: California Department of Conservation, Division of Mines and Geology.

Johnes, P., B. Moss and G. Phillips. 1996. The determination of total nitrogen and total phosphorous concentrations in freshwaters from land use, stock headage and population data: testing a model for use in conservation and water quality management. *Freshwater Biology* 36:451-473.

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

Johnson, L.B., C. Richards, G.E. Host and J.W. Arthur. 1997b. Landscape influences on water chemistry in Midwestern stream ecosystems. *Freshwater Biology* 37:193-208.

Kruskall, W.H. 1952. A Nonparameteric Test for the Several Sample Problem. *Ann. Math. Statist.* 23:525-540.

Kruskall, W.H. and W.A. Wallis. 1952. Use of Ranks in One-criterion Analysis of Variance. *J. A. Statist. Assoc* 47:583-621.

Lakin, H.W. and H.G. Byers. 1941. Selenium occurrence in certain soils in the United States, with a discussion of related topics: sixth report. Department of Agriculture Washington DC.

Larsen, D.P. 1988. A region approach for assessing attainable surface water quality: an Ohio case study. *J. Soil and Water Conservation* March-April 1988:171-176.

Lau, S.-L., M.K. Stenstrom and S. Bay. 1994. Assessmetn of stormdrain sources of contaminants to Santa Monica Bay. Santa Monica Bay Restoration Project. Monterey Park, CA.

Ledin, A., C. Pettersson, B. Allard and M. Aastrup. 1989. Background concentration ranges of heavy metals in Swedish groundwaters from crystalline rocks:a review. *Water Air and Soil Pollution* 47:419-426.

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

Lepš, J. and P. Šmilauer. 2003. Multivariate analysis of ecological data using CANOCO. Cambridge University Press. New York, NY.

McPherson, T.N., S. Burian, M.K. Stenstrom, H.J. Turin, M.J. Brown and I.H. Suffet. 2005. Trace metal pollutant load in urban runoff from a southern California watershed. *Journal of Enviromental Engineering* 131:1073-1080.

McPherson, T.N., S.J. Burian, H.J. Turin, M.K. Stenstrom and I.H. Suffet. 2002. Comparison of the pollutan loads in dry and wet weatehr runoff in a southern California urban watershed. *Water Science and Technology* 45:255-261.

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

Mizell, S.A. and R.H. French. 1995. Beneficial use potential of dry weather flow in the Las Vegas valley, Nevad. *Water Resources Bulletin* 31:447-461.

Naslas, G.D., W.W. Miller, R.R. Blank and G.F. Gifford. 1994. Sediment, nitrate, and ammonium in surface runoff from two Tahoe Basin soil types. *Water Resources Bulletin* 30:409-417.

National Oceanographic and Atmospheric Administration, C.S.C. 2003. Southern California 2000-Era Land Cover/Land Use. [Data set]. Charleston, SC: NOAA Coastal Services Center.

New South Wales Environment Protection Authority. Stormwater first flush pollution. http://http://www.environment.nsw.gov.au/mao/stormwater.htm

Nezlin, N.P. and E.D. Stein. 2005. Spatial and temporal patterns of remotely-sensed and field-measured rainfall in southern California. *Remote Sensing of Environment* 96:228-245.

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

Nolan, B. and K. Hitt. 2003. Nutrients in Shallow Ground Waters Beneath Relatively Undeveloped Areas in the Conterminous United. USGS. Denver, Colorado.

Ohlendorf, H., A. Kilness, J. Simmons, R. Stroud, D. Hoffman and J. Moore. 1988. Selenium toxicosis in wild aquatic birds. *Journal of Toxicology and Enviromental Health* 24:67-92.

Ohlendorf, H.M., D.J. Hoffman, M. Saiki and T. Aldrich. 1986. Mortality and abnormalities of aquatic birds:apparent impacts of selenium from irrigation drainwater. *The Science of the Total Evironment* 52:49-63.

Paulson, C. and G. Amy. 1993. Regulating Metal Toxicity in Stormwater. *Water Environment & Technology WAETEJ* 5:44-49.

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

Pitt, R.E., R. Field, M. Lalor and M. Brown. 1995. Urban Stormwater Toxic Pollutants: Assessment, Sources, and Treatability. *Water Environment Research* 67:260-275.

Pons, L. 2003. Helping states slow sediment movement. *Agricultural research magazine* 51:12-14.

Presser, T.S., M.A. Sylvester and W.H. Low. 1994. Bioaccumulation of selenium from natural geologic sources in the Western United States and its potential consequences. *Environmental Management* 18:423-436.

Puckett, L.J. 1995. identifying the major sources of nutrient water pollution. *Environmental Science and Technology* 29:408-414.

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

Richards, C., L.B. Johnson and G.E. Host. 1996. Landscape-scale influences on stream habitats and biota. *Can. J. Fish. Aquat. Sci.* 53:295-311.

Rogers, T.H. 1965. Geologic map of California, Santa Ana sheet. Olaf P. Jenkins ed.: California Department of Conservation, Division of Mines and Geology.

Rogers, T.H. 1967. Geologic Map of California: San Bernardino Sheet. Olaf p. Jenkins ed.: California Department of Conservation, Division of Mines and Geology.

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

Sansalone, J.J. and S.G. Buchberger. 1997. Characterization of solid and metal element distributions in urban highway stormwater. *Water Science and Technology* 36:155-160.

Schiff, K. 2000. Sediment chemistry of the southern California Bight. *Marine Pollution Bulletin* 40:286-276.

Schiff, K.C. and L.L. Tiefenthaler. 2000. Anthropogenic versus natural mass emission from an urban watershed. 1999-2000 Annual Report. Southern California Coastal Water Research Project:. Westminster, CA.

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

Smith, J., M. Sievers, S. Huang and S. Yu. 2000. Occurrence and phase distribution of polycyclic aromatic hydrocarbons in urban storm-water runoff *Water Quality Management In Asia* 42:383-388.

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

Smith, R.A., R.B. Alexander and M.G. Wolman. 1987. Water-quality trends in the nation's rivers. *Science* 235:1607-1615.

Sokal, R. and F.J. Rohlf. 1995. Biometry: the principles and practice of statistics in biological research (3rd edition ed.). WH Freeman and Co. New York, NY.

Stein, E.D. and D. Ackerman. 2007. Dry Weather Water Quality Loadings In Arid, Urban Watersheds of the Los Angeles Basin, California, USA. *Journal of the American Water Resources Association* 43:1–16.

Stein, E.D., D. Ackerman and K. Schiff. 2003. Watershed-based sources of contaminants to San Pedro Bay and Marina del Rey: patterns and trends. Technical Report #413. Southern California Coastal Water Research Project. Westminster, CA.

Stein, E.D. and L. Tiefenthaler. 2005. Dry-weather metals and bacteria loading in an arid, urban watershed: Ballona Creek, California. *Water, Air, & Soil Pollution,* 164:367-382.

Stein, E.D., L.L. Tiefenthaler and K. Schiff. 2007. Understanding sources, patterns, and mechanisms of pollutant loading from urban, arid watersheds and land-uses of the greater Los Angeles, California, USA. SCCWRP. Westminster, CA.

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

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

Strand, R.G. 1962. Geologic Map of California, San Diego-El Centro Sheet. Olaf P Jenkins ed.: California Department of Conservation, Division of Mines and Geology.

ter Braak, C.J.F. 1990. Interpreting canonical correlation analysis through biplots of structure correlations and weights. *Psychometrika* 55:519-531.

ter Braak, C.J.F. and P. Smilauer. 1997. Canoco for Windows Version 4.54 ed. Wageningen, The Netherlands: Biometris-Plant Research International.

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

Tidball, R.R., R.C. Severson, T.S. Presser and W.C. Swain. 1991. Selenium sources in the Diablo Range, western Freson County, California. The 1990 Bilings Land Reclamation

Symposium on Selenium in Arid and Semarid Environments, Western United States. Denver, CO.

Tracy, J.E., J.D. Oster and R.J. Beaver. 1990. Selenium in the southern coast range of California: well waters, mapped geological units, and related elements. *Journal of Environmental Quality* 19:46-50.

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

Trimble, S.W. 1997. Contribution of Stream Channel Erosion to Sediment Yield from an Urbanizing Watershed *Science* 278:1442-1444.

Turekian, K. and K. Wedepohl. 1961. Distribution of the elements in some major units of the earth's crust. *Geological Society of Ameria Bulletin* 72:175-192.

USEPA. 1995. National water quality inventory; 1994 Report to Congress. Environmental Protection Agency, Water planning division. Washington, DC.

Welch, E.B., J.M. Jacoby, R.R. Horner and M.R. Seeley. 1988. Nuisance biomass levels of periphytic algae in streams. *Hydrobiologia* 157:161-168

Willett, V., J. Green, A. MacDonald, J. Baddeley, G. Cadisch, S.M.J. Francis, K.W.T. Goulding, G. Saunders, E.A. Stockdale, C.A. Watson and D.L. Jones. 2004. Impact of land use on soluble organic nitrogen in soil. *Water, Air, & Soil Pollution* 4:53-60.

Wong, K.M., E.W. Strecker and M.K. Stenstrom. 1997. GIS to Estimate Storm-water Pollutant Mass Loadings. *Journal of Environmental Engineering* August 1997:737-745.

APPENDICES

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

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

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

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

Appendix III: Description of study sites

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

Appendix IV: Algal sampling protocol

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

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

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

Appendix VI: Seasonal patterns in water quality data

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

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

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

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

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

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Review of Wildfire Effects on
Chemical Water Quality

Los Alamos
NATIONAL LABORATORY

Review of Wildfire Effects on
Chemical Water Quality

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REVIEW OF WILDFIRE EFFECTS ON CHEMICAL WATER QUALITY

by

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ABSTRACT

The Cerro Grande Fire of May 2000 burned almost 43,000 acres of forested land within the Pajarito Plateau watershed in northern New Mexico. Runoff events after the fire were monitored and sampled by Los Alamos National Laboratory. Changes in the composition of runoff water were noted when compared to runoff water composition of the previous 20 years. In order to understand the chemical water quality changes noted in runoff water after the Cerro Grande Fire, a summary of the reported effects of fire on runoff water chemistry and on soils that contribute to runoff water chemistry was compiled. The focus of this report is chemical water quality, so it does not address changes in sediment transport or water quantity associated with fires.

Within the general inorganic parameters, increases of dissolved calcium, magnesium, nitrogen, phosphorous, and potassium and pH in runoff water have been observed as a result of fire. However, the dissolved sodium, carbon, and sulfate have been observed to increase and decrease as a result of fire. Metals have been much less studied, but manganese, copper, zinc, and cesium-137 have been observed to increase as a result of fire.

INTRODUCTION

The Cerro Grande Fire of May 2000 burned almost 43,000 acres of forested land within the Pajarito Plateau watershed in northern New Mexico. Within the fire area, the burn was 34% high severity, 8% moderate severity, and 58% low severity or unburned (BAER, 2000).

Runoff events after the fire were monitored and sampled by Los Alamos National Laboratory. Changes in the composition of runoff water were noted when compared to runoff water composition of the previous 20 years. In order to understand the chemical water quality changes

noted in runoff water after the Cerro Grande Fire, it is important to understand what are the typical chemical changes associated with fire. This report is a summary of the reported effects of fire on runoff water chemistry and on soils that contribute to runoff water chemistry. The focus of this report is chemical water quality, so it does not address changes in sediment transport or water quantity associated with fires.

The table in the appendix summarizes the observations reported in publications reviewed. The information in the table is sorted by element, so that all of the observations about each element are displayed in a group. A brief synthesis of the observations for each element is included in the following text, grouped in the following categories: general inorganics, metals, and radionuclides. The bibliography contains literature identified as relevant to this subject. Not all entries were accessible for this report, so those documents summarized here are noted with an asterisk.

GENERAL INORGANICS

By far the most information available is on the general inorganics, specifically those that are plant nutrients. The effects of fire on the nutrients available for regrowth have been studied in numerous locations worldwide. The studies are largely paired watershed-type approaches, where burned watersheds are compared to unburned control watersheds. Some studies are based on comparison of pre-burn and post-burn in the same watershed.

Carbon

Carbon in the soil has been observed to increase and decrease as a result of fire. Three studies addressed carbon as a separate element, and two of the studies resulted in similar conclusions about the effect on the amount of carbon in the soil as a result of fires. Both in Australia and the State of Washington, the amount of carbon in the soils of burned areas decreased (Adams et al., 1994; Baird et al., 1999). In

Washington, the decrease in carbon in the burned soil was 10% to 30% (Baird et al., 1999). Baird et al. (1999) also noted that carbon was removed by surface erosion (280 to 640 kg/ha), which likely resulted in increased carbon in the runoff water. One study of a burned area in Zambia (Stromgaard, 1992) noted that carbon in the surface soil increased slightly. Both Stomgaard (1992) and Adams et al. (1994) observed that the changes in carbon content of the soil were limited to the surface soils.

Calcium

Calcium increases in the runoff water and sediments in the water as a result of fire. The sources of calcium are the ash and surface soil. The calcium content of runoff water was measured in Spain by Belillas and Roda (1993), in eastern Washington by Tiedemann et al. (1978), in southern California by DeBano et al. (1979a), and in Texas by Wright et al. (1976). All reported increased calcium in runoff water from burnt areas. DeBano et al. (1979a) observed an increase in calcium in runoff water from 0.52 kg/ha pre-burn to 20.04 kg/ha in the first year after the burn. However, Tiedemann et al. (1978) noted that in subsequent rain events, the calcium concentration decreased because of increased flow volume, which acted to dilute the calcium. DeBano et al. (1979a) noted the same phenomenon and recommended examining nutrient transport as a load (mass per area or flow) rather than a concentration. The hardness of water running off burnt slopes was greater than unburned slopes in Texas and calcium accounted for 57% of the hardness in a study by Wright et al. (1976).

Helvey et al. (1985) and DeBano et al. (1979a) examined the calcium content of sediments in the streams in burned areas. In Washington, Helvey et al. (1985) reported that the cation concentration (calcium, magnesium, and potassium) increased in sediments 4.5 times after a fire in Washington. Pre-fire transport of calcium was predominantly by solution and Helvey et al. (1985) attributed the post-fire

increase of calcium in sediments to increased erosion. In southern California, DeBano et al. (1979a) observed that the calcium in sediments increased from 0.52 kg/ha in unburned condition to 47.39 kg/ha after burning.

The source of calcium in the runoff water is both ash and soil. Raison et al. (1985) found that the concentration of calcium in ash was 10 to 50 times greater than the calcium concentration in the unburned litter after a fire in Australia. Calcium in ash occurs mostly in oxide and carbonate forms. The oxides are water soluble, but in Scandinavia the oxides rapidly converted to carbonate forms, which are soluble under acidic conditions only (Viro, 1974). Calcium increases in the surface soil were observed by Austin and Baisinger (1955) where the calcium level was 830% higher in the burned area than in the control in the Pacific Northwest and by Viro (1974) who found the amount of exchangeable calcium to be three times as high after the fire. The increased calcium was limited to the surface soil and was not noted in the subsoil until 20 years after the fire (Viro, 1974).

Magnesium

The concentration of magnesium has been observed to increase in soil, sediments, and runoff after fires. Three studies reported increased magnesium in runoff after fires. DeBano et al. (1979a) found that the magnesium in runoff increased from pre-fire levels of 0.07 kg/ha to 3.63 kg/ha after a fire in southern California. Tiedemann et al. (1978) noted that magnesium in the stream increased immediately after the fire, but the increased flow in subsequent runoff events decreased the magnesium concentration by dilution. Stednick et al. (1982) also found that the concentration of magnesium in a stream increased slightly after a prescribed burn in Alaska.

The magnesium concentration in sediments transported by streams also increased as a result of fire. Helvey et al. (1985) reported that the cation concentration (calcium, magnesium, and potassium) increased in sediments 4.5 times

after a fire in Washington. Pre-fire transport of calcium was predominantly by solution and Helvey et al. (1985) attributed the post-fire increase of calcium in sediments to increased erosion. DeBano et al. (1979a) observed increased magnesium in sediments from a burned area in southern California. The pre-burn magnesium concentration was 0.47 kg/ha and after the burn the amount of magnesium in the sediments was 28 kg/ha.

Magnesium is present in the ash. Raison et al. (1985) found a 10- to 35-fold increase in magnesium in ash over the unburned litter. The concentration of magnesium is also increased in the soil. Austin and Baisinger (1955) reported that the magnesium was 337% higher in the burned surface soil than in the unburned control in the Pacific Northwest. Viro (1974) reported an increase of two times as much magnesium in the surface soil after fires in Scandinavia. Likewise, Stromgaard (1992) observed an immediate increase in magnesium in surface soil. Viro (1974) noted that magnesium is easily leached into the subsoil and appreciable amounts of magnesium were found as deep as 30 cm. This finding is consistent with reported observations of Austin and Baisinger (1955) and Viro (1974) that the increased magnesium in the surface soil was relatively short-lived, returning to pre-burn levels in 2 to 6 years.

Nitrogen

Nitrogen, either in the form of nitrate or ammonia, has been observed to increase in water as a result of fire. The observations of nitrogen in soils affected by fire are more varied, the concentration of nitrogen in the soil is a function of severity and duration of the fire (DeBano et al., 1998; 1979b). Increased nitrogen in runoff was noted in the following six studies:

- Schindler et al. (1980) found the total nitrogen two times higher in water after a fire in Ontario.
- Tiedemann et al. (1978) observed that nitrate and organic nitrogen increased in stream

water after a fire in eastern Washington. The increased nitrogen was attributed to reduced demand for nitrate by vegetation. The increased organic nitrogen was attributed to organic detritus in the stream channels.

- Stednick et al. (1982) noted increased ammonia levels in an Alaskan stream for a period of two weeks after a fire.
- Beschta (1990) reported elevated nitrogen in streams for 12 days following a fire in Oregon.
- Belillas and Roda (1993) found that the nitrate concentration in runoff from burnt slopes in Spain was higher than from un-burned slopes. Nitrate also increased in stream water from a burned catchment. The increase was noted with respect to pre-fire conditions and in comparison with a paired unburned catchment.
- Feller and Kimmins (1984) noted that clear-cutting and slash burning increased the nitrogen in streams, but could not separate the effects of logging from burning.

The changes in nitrogen content of soil after a burn have been examined in nine different studies. Three studies noted an increase of nitrogen in the burned soils (Chambers and Attiwill, 1994; DeBano et al., 1979b; and Stromgaard, 1992) and three other studies reported an increase in ammonia (DeBano et al., 1979b, 1998; Viro, 1974). Decreased nitrogen in burned soils was observed in three studies (Adams et al., 1994; Austin and Baisinger, 1955; and Baird et al., 1999). DeBano et al. (1998) state that most of the soil nitrogen is probably volatilized in high-severity fires, but large increases in ammonia can be found in the ash and underlying soils after low-severity fires.

Increased nitrogen in sediments has been noted in two studies. Helvey et al. (1985) found the total nitrogen increased by 40 times after a fire in Washington, and about 10% of the nitrogen was removed associated with sediments in streams. Thomas et al. (1999) measured the increased nitrogen in stream sediments from a eucalyptus watershed and a pine water-

shed. In the eucalyptus watershed, the nitrogen in sediments increased from an unburned level of 0.071 kg/ha to 14 to 57 kg/ha in the burned watershed. In the pine watershed, the nitrogen in sediments increased from the unburned level of 0.064 kg/ha to 17.6 to 38 kg/ha in the burned watershed. Nitrogen concentrations in plant tissue also suggest that increased nitrogen after fires is available to wetland plants in Canada (Auclair, 1977).

Potassium

Fire causes an increase in the amount of potassium in runoff water and in sediments in the water. The sources of potassium are ash and soil. Increased potassium in runoff water has been observed in eight studies:

- Belillas and Roda (1993) found that potassium was higher in overland flow water from burnt slopes in Spain.
- Schindler et al. (1980) found potassium increased in stream water in the range of 1.4 to 2.9 times in Ontario.
- DeBano et al. (1979a) observed an increase of calcium in runoff from pre-burn levels of 0.09 kg/ha to 7.67 kg/ha after fire in southern California.
- Wright (1976) noted that potassium in stream water increased 265% measured two years after fire in Minnesota.
- Tiedemann et al. (1978) found that the potassium concentration in the stream increased after a fire in eastern Washington, but decreased as the volume of flow increased. After three years, as the flow decreased, the potassium concentration increased again.
- Stednick et al. (1982) noted that the potassium concentration in an Alaskan stream increased significantly as a result of a prescribed burn.
- Beschta (1990) reported that potassium increased to a peak of 4.4 mg/L during the first major rainfall following a fire in Oregon and immediately returned to pre-fire levels of 0.6 to 1.2 mg/L.

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- Feller and Kimmins (1984) observed significant increase in potassium in a Canadian stream after logging and slash burning, but the effects of the fire cannot be separated from the logging.

One study, Belillas and Roda (1993), found a decrease of potassium in the stream water, although there had been an increase in potassium in overland flow water. The decreased stream water potassium was attributed to demand for potassium by soil biota and vegetation, particularly bracken, a species with high potassium content. Auclair (1977) examined the potassium content of vegetation tissues and noted a correlation between potassium content and fire frequency, leading to the conclusion that potassium is mobilized by burning and greater amounts are taken up by vegetation in Canada.

Increases in potassium in sediments within the runoff water were observed in southern California, Washington, and Portugal. DeBano et al. (1979a) found that the potassium in sediments from burned California slopes increased from 0.05 kg/ha in unburned conditions to 19.34 kg/ha in the first year after the burn. In Washington, Helvey et al. (1985) reported that the cation concentration (calcium, magnesium, and potassium) increased in sediments 4.5 times after a fire in Washington. Pre-fire transport of potassium was predominantly by solution and Helvey et al. (1985) attributed the post-fire increase of calcium in sediments to increased erosion. Thomas et al. (1999) reported an annual estimate of potassium in sediments from burnt eucalyptus in Portugal to increase from 0.0004 kg/ha pre-fire to 0.3 to 1.24 kg/ha after the fire.

Three studies noted increased potassium in soils after fires. In the Pacific Northwest, Austin and Baisinger (1955) reported a potassium concentration increase of 166% on burned soils that was still 112% of normal at the end of two years. DeBano et al. (1979a) noted that potassium in burned soils in southern California was higher than on unburned soil. Stromgaard (1992) also noted an increase of potassium in

soil in Zambia, but found the increase to last only 40 days. Stromgaard (1992) attributed the increased potassium to releases from the ash. One study in Scandinavia noted a decrease in potassium in the topsoil layer (Viro, 1974). The decrease of potassium in the upper soil was accompanied by an increase in potassium in the subsoil, apparently the result of potassium rapidly leaching down into the soil.

Sodium

After a fire, sodium in water increases slightly or remains the same. Three studies found increased sodium in water after burning. DeBano et al. (1979a) found that sodium in runoff increased from 0.1 kg/ha in unburned condition to 2 kg/ha after burning in southern California. Tiedemann et al. (1978) also noted that sodium increased in streams immediately after burning in eastern Washington. Stednick et al. (1982) found that sodium in stream water increased slightly after prescribed burning in Alaska. A fourth study noted increases in the concentration of sodium in stream water, but could not distinguish between the effects of logging and burning (Feller and Kimmins, 1984). However, one study by Wright et al. (1976) found that the sodium in runoff water was unchanged by burning.

Sodium in sediments carried by streams was observed to increase after a fire in southern California. Sodium in sediments increased from 0.07 kg/ha before the fire to 2.57 kg/ha after the fire. Beschta (1990) reported that 39% of sodium in the upper 14 inches of soil was removed in solution by leaching after a fire in Oregon.

Phosphorus

As a result of fire, phosphorous increases in water, sediment, and soil. Six studies reported increased phosphorus in water:
- Schindler et al. (1980) found that the total, suspended, and dissolved phosphorous increased 1.4 to 3.2 times as a result of a fire in Ontario.
- Wright (1976) observed phosphorus in-

creased in runoff 93% measured two years after a fire in Minnesota.

- Tiedemann et al. (1978) noted that both ortho-phosphorous and total phosphorous increased 2 to 3 times in burned watersheds compared to an unburned control watershed in eastern Washington.
- Stednick et al. (1982) reported that the phosphorous in water increased significantly; the average total phosphorous was 0.018 mg/L before the burn and was 0.026 mg/L after the burn.
- Beschta (1990) found that phosphorous in stream water may increase following burning, but the increases are generally small.
- Helvey et al. (1985) noted that phosphorous in streams increased 14 times, but phosphorous in water increased more than phosphorous moving in sediment.

Phosphorous in stream sediments was examined in two studies. In Portugal, Thomas et al. (1999) found that phosphorous in sediments from an unburned eucalyptus watershed was 0.0001 kg/ha, but from a burned eucalyptus watershed the amount of phosphorus in sediments was 0.17 to 0.83 kg/ha. Similarly, phosphorous in sediments from an unburned pine watershed was 0.0002 kg/ha, but from a burned pine watershed the amount of phosphorus in sediments was 0.22 to 0.41 kg/ha. DeBano et al. (1979a) found increases of phosphorous in sediments increased from 0.08 kg/ha before burning to 3.37 kg/ha after burning.

Five studies reported increases in phosphorous in soil after burning (Adams et al., 1994; Chambers and Attiwill, 1994; Austin and Baisinger, 1955; DeBano et al., 1979a; and Stromgaard, 1992). The increase in phosphorous is attributed to reduction in biological and geochemical sinks (e.g., a reduction in phosphorous fixation and precipitation) for soluble inorganic phosphorous (Adams et al., 1994). The increase in phosphorous is limited to surface soils and Stromgaard (1992) suggests that the constantly high level of phosphorous in surface soil suggests that leaching of phosphorous is limited. Auclair (1977) found a correlation between increased phosphorous content in wetland plants and the occurrence of fires, suggesting that phosphorous is mobilized by burning and taken up by plants.

Sulfur

Observations of changes in the concentration of sulfate as a result of fires are inconclusive. Sulfate concentrations have been measured in soil, runoff water, and stream water following fires. DeBano et al. (1979a) found that the sulfate concentration was higher on burnt soils than on unburned soils after a fire in chaparrel vegetation in southern California. Although Belillas and Roda (1993) noted apparent increased sulfate in runoff water from burned slopes compared to unburned slopes in Spain, they found that the increases were insignificant using the Mann-Whitney statistical test. Belillas and Roda (1993) also measured sulfate in stream water draining burned watersheds in Spain. The stream water did have minor increased sulfate in the spring after the fire.

PHYSICAL PARAMETERS

Changes in physical parameters of water and soil have been noted associated with fire. These physical parameters are pH, electrical conductivity, and cation exchange capacity.

pH: pH increases in soil and water as a result of fire. The pH of topsoil was reported to increase by 2 to 4 pH units by Austin and Baisinger (1955), Viro (1974), and Stromgaard (1992). The observed increase in pH was attributed to bases in the ash by Stromgaard (1992). The increased pH in surface soil is reported to last from five years (Stromgaard, 1992) to 50 years (Viro, 1974). The pH of the subsoil does not change as notably as the surface soil. Viro (1974) found that the average pH of the subsoil in a burned area was 0.4 pH units lower in the first 20 years after burning. However, the National Interagency Fire Center (1994) states that in typically alkaline soils of the arid and semi-arid Southwest, increases in pH are rarely observed.

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The pH of water has also been observed to increase as a result of fires. Belillas and Roda noted a 0.2 pH unit increase in stream water from a burned area in Spain for two years after a fire. Wright et al. (1976) reported an increase in pH in runoff water from burned slopes in Texas, particularly moderate and steep slopes. Tiedemann et al. (1978) measured an increase in total alkalinity in streams from three burned watersheds in eastern Washington. The average total alkalinity increased from 0.61 mequ/L before the fire to 0.82 mequ/L after the fire. The increased pH was attributed to ash in the streams by Tiedemann et al. (1978).

Electrical Conductivity: Tiedemann et al. (1978) measured increased electrical conductivity in three streams from burned watersheds in eastern Washington. The average electrical conductivity increased from 46 µmhos/cm before the fire to 66 µmhos/cm for a short period after the fire. Tiedemann et al. (1978) attributed the increased electrical conductivity to ash in the stream. Feller and Kimmins (1984) also observed increased electrical conductivity in streams from watersheds that had been logged and burned, but could not distinguish between the effects of logging and burning.

Cation Exchange Capacity: DeBano et al. (1979a) reported that the cation exchange capacity of burned soil decreased and remained low for at least one year because the exchange sites on organic matter were destroyed by the fire.

METALS

Few studies have examined the effect of fire on metals in soil or water. Observations regarding metals in the literature examined for this review were limited to manganese, copper, and zinc.

Manganese

Manganese in soil has been observed to increase as a result of fire. Parra et al. (1996) found that total manganese and easily reducible manganese increased in both the surface soil and subsoil. The manganese increase was attributed to transportation of manganese in the form of organic complexes through the macropores of the soil. The source of manganese was reported by Parra et al. (1996) as vegetation, as manganese is concentrated in leaves, particularly of resinous plants. Chambers and Attiwill (1994) reported an increase of 279% in the concentration of water-soluble manganese after heating soil to 400°C. The amount of manganese decreased to pre-heating levels within 1 to 2 months. Chambers and Attiwill (1994) also attributed the increase in manganese to physio-chemical breakdown of manganese complexed with organic matter. Manganese concentration decreased as the microbial population increased and consequently oxidized divalent manganese to less available higher oxides. Auclair (1977) examined the manganese concentration of wetland plants in Canada and concluded that the correlation between the manganese concentration in tissue and soil parameters suggest that manganese is mobilized by burning.

Copper

Auclair (1977) examined the copper concentration of wetland plants in Canada and concluded that the correlation between the copper concentration in tissue and soil parameters suggest that copper is mobilized by burning.

Zinc

Auclair (1977) examined the zinc concentration of wetland plants in Canada and concluded that the correlation between the zinc concentration in tissue and soil parameters suggest that zinc is mobilized by burning.

RADIONUCLIDES

The 1986 accident at the Chernobyl nuclear power plant in Ukraine stirred interest in the fate of fallout radionuclides. Relevant to this review, the redistribution of fallout radionuclides, particularly cesium by forest fires, has been examined by a number of studies. Releases of

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radioactive chlorine and iodine by fire were also tested in one lab-based study.

Cesium

Cesium-137 that is present on vegetation is concentrated in surface soils as a result of fire. Paliouris et al. (1995) examined cesium-137 in a forest in Canada. Before the fire, cesium-137 was bound in organic matter on the forest floor. After a fire in the forest, cesium-137 was concentrated in the surface soil. However, Paliouris et al. (1995) examined the load of cesium-137 contained in the same pre- and post-fire area, and found the load of cesium-137 was decreased in the burned area. The decreased load was attributed to volatilization, leaching, and runoff of cesium-137. Amiro et al. (1996) did field and lab burns of various vegetation types to investigate the volatilization of radionuclides in fires. Depending on the material burned, 10% to 90% of the cesium remained in the ash and the enrichment of cesium in the ash was 4- to 20-fold. The concentration of cesium in the ash increased up to two orders of magnitude when the burn temperature reached 400°C. Amiro et al. (1996) found that the solubility of cesium decreased after burning. About 90% of the cesium on the unburned material was soluble before the burn, compared with 51% soluble from the ash after the burn.

Kashparov et al. (2000) also examined the volatilization of cesium-137 during forest fires near Chernobyl. They found that during the active phase of burning, the concentration of cesium-137 in the lower air layer was increased by several hundred times compared to background. In the smoldering phase the cesium concentration of the lower air was tens of times background, and, finally, in the post-fire phase, the cesium-137 concentration in the lower air was within several times background. Maximum deposition is predicted to be at a distance of 1500 to 2000 meters, and, at a distance of 20 km, the cesium-137 deposition can be considered insignificant (Kashparov et al., 2000). Kashparov et al. (2000) concluded that the

additional terrestrial contamination due to the resuspension of cesium-137 during forest fires is likely to be in the range of 10^{-5} to 10^{-4} of its background value.

Johansen et al. (in preparation) measured cesium-137 in sediments eroded from burned and unburned plots in southern New Mexico and northern Colorado. In southern New Mexico the cesium-137 in sediments from burned plots was 22 times greater than from paired natural plots. Similarly, in northern Colorado the cesium-137 from burned plots was four times the concentration from the unburned plot. The increased in cesium-137 in sediments was attributed to greater erosion and splash effects from rain drops in the absence of canopy, greater soil detachment and transport with decreased ground cover, and reduced infiltration.

Chlorine

Amiro et al. (1996) did field and lab burns of various vegetation types to investigate the volatilization of radionuclides in fires. Depending on the material burned, 65% to 90% of the chlorine was lost to the atmosphere in straw fires. The loss of chlorine is expected to be closer to 90% in hotter wood fires. The chlorine in the ash was 24% when the burn temperature reached 400°C. Amiro et al. (1996) found that the solubility of chlorine was unchanged after burning. About 95% of the chlorine on the unburned material was soluble before the burn, compared with 97% soluble from the ash after the burn.

Iodine

Amiro et al. (1996) did field and lab burns of various vegetation types to investigate the volatilization of radionuclides in fires. Depending on the material burned, 60% to 80% of the iodine was lost to the atmosphere in straw fires and 95% was volatilized in hotter wood fires. The concentration of iodine in the ash increased when the burn temperature reached 400°C, but decreased in fires with temperatures up to

1000°C. Amiro et al. (1996) found that the solubility of iodine increased after burning. About 10% of the iodine on the unburned material was soluble before the burn, compared with 60% soluble from the ash after the burn at 400°C. The increase in solubility is attributed to the destruction of organic materials that had originally bound the iodine (Amiro et al., 1996).

CONCLUSIONS

The majority of the literature on the effect of fire on chemical quality of water and soil has been generated by land managers seeking to understand the role of fire in ecosystems. Thus, the focus has been on quantifying the loss of nutrients from (or transport of nutrients out of) watersheds. As events occur that stimulate interest in other elements, such as radionuclide fall out after the Chernobyl accident, studies began to focus on the effects of these other elements. The fire season of 2000, burning significant portions of three nuclear facilities and thousands of acres of national forest, is likely to stimulate a fresh influx of papers on fire effects.

BIBLIOGRAPHY

Adams, M.A., J. Iser, A.D. Keleher, and D.C. Cheal. 1994. Nitrogen and phosphorus availability and the role of fire in heathlands at Wilsons Promontory. Australian Journal of Botany 42:269-281.*

Amiro, B.D., S.C. Sheppard, F.L. Johnston, W.G. Evenden, and D.R. Harris. 1996. A burning question: what happens to iodine, cesium, and chlorine in biomass fires? Science of the Total Environment 187(2):93-103.*

Anderson, S.H., compiler. 1982. Effects of the 1976 Seney National Wildlife Refuge wildfire on wildlife and wildlife habitat. U.S. Fish Wildl. Serv., Resour. Publ. 146. 28 pp.

Auclair, A.N.D. 1977. Factors affecting tissue nutrient concentrations in a Carex meadow. Oecologia (Berl.) 28:233-246.*

Austin, R.C. and D.H. Baisinger. 1955. Some effect of burning on forest soils of western Oregon and Washington. Journal of Forestry 53(4):275-280.*

Baird, M., D. Zabowski, and L. Everett. 1999. Wildfire effects on carbon and nitrogen in inland coniferous forests. Plant and Soil 209(2):233-243.*

Baker, M.B. 1990. Hydrologic and water quality effects of fire. Effects of fire management of southwestern natural resources: proceedings of the symposium, November 15-17, 1988, Tucson, AZ. Dept. of Agriculture, Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO, general technical report RM-191.

Belillas, C.M., F. Roda. 1993. The effects of fire on water quality, dissolved nutrient losses, and the export of particulate matter from dry heathland catchments. Journal of Hydrology 150:1-17.*

Beschta, R.L. 1990. Effects of fire on water quality and quantity. In: Walstad, J.D., S.R. Radosevich, and D.V. Sandberg (eds.) Natural and Prescribed Fire in Pacific Northwest Forests, Oregon State University Press, Corvallis, OR, pp. 219-232.*

Brass, J.A., V.G. Ambrosia, P.J. Riggan, and P.D. Sebesta. 1996. Consequences of fire on aquatic nitrate and phosphate dynamics in Yellowstone National Park. The ecological implications of fire in Greater Yellowstone: proceedings of the second biennial Conference on the Greater Yellowstone Ecosystem, September 19-21, 1993, Yellowstone National Park, Wyoming. Fairfield, WA: International Association of Wildland Fire, 1996. pp. 53-57.

Britton, D.L. 1991. Fire and the chemistry of a south African mountain stream. Hydrobiologia 218(3):177-192.

Brown, G.W., A.R. Gahler, and R.B. Mason. 1973. Nutrient losses after clear-cut logging and slash burning in the Oregon Coast Range. Water Resources Research 7:1189-1198.

Burned Area Emergency Rehabilitation Team. 2000. Cerro Grande Burned Area Emergency Rehabilitation Plan.*

Caldwell, C.A., C.M. Canavan, and N.S. Bloom. 1998. Effects of fire on the spatial and temporal distribution of mercury in sediments of an arid-lands reservoir in south-central New Mexico. WRRI Conference Proceedings, pp. 78-83.

Chambers, D.P. and P.M. Attiwill. 1994. The ash-bed effect in eucalyptus-regnans forest: chemical, physical, and microbiological changes in soil after heating or partial sterilization. Australian Journal of Botany 42(6):739-749.*

Cheal, D. 1996. Fire succession in heathlands and implications for vegetation management. Fire and Biodiversity: The Effects and Effectiveness of Fire Management, Biodiversity Series Paper No. 8.

Christiansen, N.L. 1973. Fire and the nitrogen cycle in California chaparral. Science 181:66-68.

Crutzen, P.J. and M.O. Andreae. 1990. Biomass burning in the tropics: impact on atmospheric chemistry and biogeochemical cycles. Science 250:1669-1678.

Crutzen, P.J., I.E. Galbally, and C. Bruhl. 1984. Atmospheric effects from post-nuclear fires. Climatic Change 6:234-364.

Campbell, R.E., M.B. Baker, Jr., and P.F. Ffolliott. 1977. Wildfire effects on ponderosa pine ecosystem: an Arizona case study. Research Paper RM-191 USDA, Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO.

Davis, E.A. 1989. Prescribed fire in Arizona chaparral: effects on stream water quality. Forest Ecology and Management 26:189-206.

DeBano, L.F., P.F. Ffolliott, and M.B. Baker. 1996. Fire severity effects on water resources. In: Ffolliott, P.F., L.F. DeBano, M.B. Baker, Jr., G.J. Gottfried, G. Solis-Garza, C.B. Edminster, D.G. Neary, L.S. Allen, and R.H. Hamre, technical coordinators. Effects of fire on Madrean province ecosystems - A symposium proceedings. General Technical Report RM-289. USDA Forest Service Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO.

DeBano, L.F., D.G. Neary, and P.F. Ffolliot. 1998. Fire's Effects on Ecosystems. John Wiley and Sons, Inc., New York, 333 pp.*

DeBano, L.F., R.M. Rice, and C.E. Conrad. 1979a. Soil heating in chaparral fires effects on soil properties, plant nutrients, erosion, and runoff. Research Paper PSW-145. USDA, Forest Service, Pacific Southwest Forest and Range Experiment Station, Berkeley, CA.*

DeBano, L.F., G.E. Eberlein, P.H. Dunn. 1979b. Effects of burning on chaparral soils. I. soil nitrogen. Soil Science Society of America Journal 43:504-509.*

DeBano, L.F. and C.E. Conrad. 1976. Nutrients lost in debris and runoff from a burned chaparral watershed. In: Proceedings of the third interagency sedimentation conference, Denver, CO, March 1976. Water Resources Council 3:13-27.

DeByle, N.V. 1976. Fire, logging, and debris disposal effects on soil and water in northern coniferous forests. 1976 Proceedings XVI IUFRO World Congress, Oslo, Norway. IUFRO, 1976.

DeByle, N.V. and P.E. Packer. 1972. Plant nutrient and soil losses in overland flow from burned forest clearcuts. AWRA: National Symposium on Watersheds in Transition, Fort Collins, CO.

Emmerich, W.E. 1998. Estimating prescribed burn impacts on surface runoff and water quality in southeastern Arizona. Proceedings, AWRA specialty conference: rangeland management and water resources: May 27-29, 1998, Reno, NV. American Water Resources Association Technical Publication Series no. TPS 98-1. Herndon, VA.

Feller, M.C. 1983. Impact of prescribed fire (slash burning) on forest productivity, soil erosion, and water quality on the coast. Proceedings, Prescribed Fire-Forest Soils Symposium, Smithers, British Columbia, Canada, 2-3 Mar. 1982. Victoria, B.C.: Ministry of Forests, Information Service Branch, 1983. Land management report no. 16.

Feller, M.C. and J.P. Kimmins. 1984. Effects of clearcutting and slash burning on stream water chemistry and watershed nutrient budgets in southwestern British Columbia. Water Resources Research 20(1):29-40.*

Fuller, W.H., S. Stanton, and P.S. Burgess. 1955. Effect of burning on certain forest soils of northern Arizona. Forestry Science. 1(1):44-50.

Garger, E.K., V. Kashpur, H.G. Paretzke, and J. Tschiersch. 1998. Measurement of resuspended aerosol in the Chernobyl area. Part II. Size of resuspended particles. Radiation Environment Biophysics 36:275-283.

Gerla, P.J. and J.M. Galloway. 1998. Water quality of two streams near Yellowstone Park, Wyoming, following the 1988 Clover-Mist wildfire. Environmental Geology 36(1-2):127-136.

Gillieson, D., P. Wallbrink, and A. Cochrane. 1996. Vegetation change, erosion risk, and land management on the Nullarbor Plain, Australia. Environmental Geology 28(3):145-153.

Glunsm D.R. and D.A.A. Toews. 1989. Effect of a major wildfire on water quality in southeastern British Columbia. In: Woesserner, W.W. and D.F. Potts (eds.) Symposium Proceedings on Headwaters Hydrology.

Gosz, J.R. and C.S. White. 1985. Effects of prescribed fire on water-soluble nutrients and organics and effects of volatiles on nitrogen mineralization. Completion Report for Eisenhower Consortium for Western Environmental Forestry Research Grant #EC401, University of New Mexico.

Gottfried, G.J. and L.F. DeBano. 1990. Streamflow and water quality responses to preharvest prescribed burning in an undisturbed ponderosa pine watershed. Effects of fire management of southwestern natural resources: proceedings of the symposium, November 15-17, 1988, Tucson, AZ.: U.S. Dept. of Agriculture, Forest Service, Rocky Mountain Forest and Range Experiment Station, Fort Collins, CO, general technical report RM-191 pp. 222-228.

Grishin, A.M. and V.A.Perminov (Tomsk). 1996. Mathematical model of radionuclides transfer due to the action of wind and forest fires. III Minsk International Heat and Mass Transfer Forum -MMF-III May 20-24, 1996 - Minsk, Belarus.

Greene, S.W. 1935. Effect of annual grass fires on organic matter and other constituents of virgin longleaf pine soils. Journal of Agricultural Research 50(10):809-822.

Hall, R.G. 1994. The effects of fuel reduction burning on forest soils. In: Proceedings of conference on fire and biodiversity: The Effects and Effectiveness of Fire Management. Victorian National Parks Association, Melbourne.

Helvey, J.D., A.R. Tiedemann, and T.D. Anderson. 1985. Plant nutrient losses by soil erosion and mass movement after wildfire. Journal of Soil Water Conservation 40(1):168-173.*

Helvey, J.D. 1972. First-year effects of wildfire on water yield and stream temperature in north-central Washington. AWRA: National Symposium on Watersheds in Transition, Fort Collins, CO.

Henderson, R.A. and S.H. Statz. 1995. Bibliography of fire effects and related literature applicable to the ecosystems and species of Wisconsin. Technical Bulletin No. 187, Wisconsin Department of Natural Resources, Madison, WI.

Hoffman, R.J. and R.F. Ferreira. 1976. A reconnaissance of the effects of a forest fire on water quality in Kings Canyon National Park. U. S. Geological Survey open-file report 76-497. Prepared in cooperation with the National Park Service.

Illg, G. 1997. Forest fire, water quality, and the incident at Buffalo Creek. American Forest 103(1):33-37.

Inbar, M., L. Wittenberg, M. and Tamir. 1997. Soil erosion and forestry management after wildfire in a Mediterranean woodland, Mt. Carmel, Israel. International Journal of Wildland Fire 7(4):285-294.

Kashparov, V.A., S.M. Lundin, A.M. Kadygrib, V.P. Prostak, S.E. Levtchuk, V.I. Yoschenko, V.A. Kashpur, and N.M. Talerko. 2000. Forest fires in the territory contaminated as a result of the Chernobyl accident: radioactive aerosol resuspension and exposure of fire fighters. Journal of Environmental Radioactivity 51(3):281-298.*

Jantunen, M.J., A. Reponen, R. Mustonen, A. Itkonen, and P. Kauranen. 1992. Behavior of Chernobyl fallout radionuclides in peat combustion. Health Physics 62(3):245-249.

Johansen, M.P., T.E. Hakanson, W.F. Whicker, J.R. Simanton, and J.J. Stone. In preparation. The effects of fire on actinide mobilization by surface water erosion at Department of Energy sites.*

Johnson, C.M. and R.R. Needham. 1966. Ionic composition of Sagehen Creek, California, following an adjacent fire. Ecology 47:636-639.

Korsman, T. and U. Segerstrom. 1998. Forest fire and lake-water acidity in a northern Swedish boreal area: holocene changes in lake-water quality at Makkassjon. Journal of Ecology 86(1):113-124.

Lamont, B.B., C.L. Burrows, W. Colangelo, P.W. Swanborough, and D. Ward. 1999. Grasstrees (Xanthorrhea spp.) and the fire history of sites. Australian Bushfire Conference, Albury, July 1999.

LaPoiat, T.W. 1983. Impact of fire on recreation stream water quality and spawning habitat. Final reports. USDA, Forest Service, Forestry Sciences Laboratory, Tempe, AZ.

Lathrop, R.G. 1994. Impacts of the 1998 wildfires on the water quality of Yellowstone and Lewis Lakes, Wyoming. International Journal of Wildland Fire 4(3):169-175.

Leahy, D.M., M.C. Hansen, and M.B. Schroeder. 1993. An assessment of air quality impacts of fires associated with fire fighting operations. Journal of the Air & Waste Management Association 43(3):341-347.

Little, E.E. and R.D. Calfee. 2000. The effects of UVB radiation on the toxicity of fire-fighting chemicals. Final report. Submitted by U.S. Geological Survey, Columbia Environmental Research Center, to USDA Forest Service, Wildland Fire Chemical Systems, Missoula, MT.

Lotspeich, F.B., E.W. Mueller, and P.J. Frey. 1970. Effects of large scale forest fires on water quality in interior Alaska. Federal Water Pollution Control Administration, Alaska Water Laboratory, Pb-241922epa-660/3-75-020, 115 pp.

Lujaniene, L.G., B.I. Ogorodnikov, A.K. Budyka, V.I. Skitovich, and V. Lujanas. 1997. An investigation of changes in radionuclide carrier properties. Journal of Environmental Radioactivity 35(1):71-90.

McColl, J.G. and D.F. Grigal. 1975. Forest fire: effects on phosphorus movement to lakes. Science 188:1109-1111.

McKee, W.H., Jr. 1986. Impacts of pre-scribed burning on coastal plain soils. Proceedings of the Society of American Foresters :107-111.

Minshall, G.W. 1981. Biological, water quality, and aquatic habitat responses to wildfire in the Middle Fork of the Salmon River and its tributaries. Idaho State University, Final Report, 122 pp.

Minshall, G.W. and W. Brock. 1991. Observed and anticipated effects of forest fire on Yellowstone ecosystems. In R.B. Keiter and M.

S. Boyce, eds., Greater Yellowstone Ecosystems: Redefining America's Wilderness Heritage. Yale University Press, New Haven, CT, pp. 123-135.

Moore, D.G. and L.A. Norris. 1979. Forest chemicals in watershed management. Forest soils of the Douglas-fir region. Compiled and edited by P.E. Heilman, H.W. Anderson, and D.M. Baumgartner. Washington State University, Cooperative Extension Service, Pullman, WA, pp. 261-268.

National Interagency Fire Center. 1994. Fire effects guide. National Wildfire Coordinating Group, PMS-481.*

Neary, D.G. and J.B. Currier. 1982. Impact of wildfire and watershed restoration on water quality in South Carolina's Blue Ridge Mountains. Southern Journal of Applied Forestry 6(2):81-90.

Norris, L.A. and W.L. Webb. 1989. Effects of fire retardant on water quality. Proceedings of the Symposium on Fire and Watershed Management: October 26-28, 1988, Sacramento, CA.

Norris, L.A. and D.G. Moore. 1981. Introduced chemicals and water quality. Proceedings of the Intermountain West Watershed Management Symposium, Pullman, WA, 1980.

Paliouris, G., H.W. Taylor, R.W. Wein, J. Svoboda, and B. Mierzynski. 1995. Fire as an agent in redistributing fallout Cs-137 in the Canadian boreal forest. Science of the Total Environment 161:153-166.*

Parra, J.G., V.C. Rivero, and T.I. Lopez. 1996. Forms of Mn in soils affected by a forest fire. Science of the Total Environment 181(3):231-236.*

Pimenov, O., D.J. Sailor, R. Seffal, and G.A. Sharovarov. 1995. Radionuclide dispersion from forest fires. In: Gas-Particle Flows, D.A. Stock et al. (eds.), ASME-FED 228, pp. 155-162.

Raison, R.J., P.K. Khanna, and P.V. Woods. 1985. Transfer of elements to the atmosphere during low-intensity prescribed fires in three Australian subalpine eucalypt forests. Canadian Journal of Forest Research 15:657-664.*

Richter, D.D., C.W. Ralston, and W.R. Harms. 1982. Prescribed fire: effects on water quality and forest nutrient cycling. Science 215: 661-662.

Rinne, J.N. 1996. Short-term effects of wildfire on fishes and aquatic macroinvertebrates in the southwestern United States. North American Journal of Fisheries Management 16:653-658.

Roby, K.B. 1989. Watershed response and recovery from the Will fire: ten years of observation. In: Proceedings of the Symposium on Fire and Watershed Management: October 26-28, 1988, Sacramento, CA. Pacific Southwest Forest and Range Experiment Station general technical report PSW-109. Berkeley, CA, pp. 131-136.

Robichaud, P.R., J.L. Beyers, and D.G. Neary. 2000. Evaluating the effectiveness of postfire rehabilitation treatments. USDA Forest Service Rocky Mountain Research Station general technical report RMRS-GTR-63. Fort Collins, CO.

Schindler, D.W., R.W. Newbury, K.G. Beaty, J. Prokopowich, T. Ruszcznski, and J.A. Dulton. 1980. Effects of a windstorm and forest fire on the chemical losses from forested watersheds and on the quality of receiving streams. Canadian Journal of Fisheries and Aquatic Sciences 37(3):328.*

Scotter, G.W. 1993. Effects of forest fires on soil properties in northern Saskatchewan. Forestry Chronicles 39(4):412-421.

Simanton, J.R., G.D. Wingate, and M.A. Weltz. 1988. Runoff and sediment from a burned sagebrush community. Poster paper presented at Effects of Fire in Management of Southwestern Natural Resources, Tucson, AZ, November 14-17, 1988.

Snyder, G.G. 1975. Clearcutting and burning slash alter quality of stream water in northern Idaho. U. S. Dept. of Agriculture, Forest Service, Intermountain Forest and Range Experiment Station, Ogden, Utah, research paper INT-168.

Stark, N. 1980. Changes in soil water quality resulting from three timber cutting methods and three levels of fiber utilization. Journal of Soil and Water Conservation 35(4):183-187.

Snyder, G.G., H.F. Haupt, and G.H. Belt, Jr. 1975. Clearcutting and burning slash alter quality of stream water in northern Idaho. USDA Forest Service research paper INT-168, Ogden, UT.

Stark, N. 1976. Changes in the quality of soil water for three years following burning. Montana State University, Bozeman. Joint Water Resources Research Center report Pb-264674, Owrt Project Number A-084-Mont.

Stednick, J.D., L.N. Tripp, and R.J. McDonald 1982. Slash burning effect on soil and water chemistry in southeast Alaska. Journal of Soil and Water Conservation 37(2):126-128.*

Stromgaard, P. 1992. Immediate and long-term effects of fire and ash fertilization on a Zambian miombo woodland soil. Agriculture Ecosystems and Environment 41:19-37.*

Suman, R.F. and R.L. Carter. 1954. Burning and grazing have little effect on chemical properties of coastal plain soils. U.S. Forest Service, Southeastern Forest Experimental Station resource notes WR 77-56. 2pp.

Swanston, D.N. 1980. Influence of forest and rangeland management on anadromous fish habitat in western North America: impacts of natural events. U.S. Forest Service general technical report PNW-104. 27 pp.

Tarrant, R.F. 1956. Changes in some physical soil properties after a prescribed burn in young ponderosa pine. Journal of Forestry 54(7):439-441.

Thomas, A.D., R.P.D. Walsh, and R.A. Shakesby. 1999. Nutrient losses in eroded sediment aster fire in eucalyptus and pine forests in the wet Mediterranean environment of northern Portugal. Catena 36(4):283-302.*

Tiedemann, A.R., C.E. Conrad, J.H. Dieterich, J.W. Hornbeck, W.F. Megahan, L.A. Viereck, and D.D. Wade. 1979. Effects of fire on water: a state-of-knowledge review. U.S. Forest Service general technical report WO-10. 28 pp.

Tiedemann, A.R., J.D. Helvey, and T.D. Anderson. 1978. Stream chemistry and watershed nutrient economy following wildfire and fertilization in eastern Washington. Journal of Environmental Quality 7(4):580-588.*

Tiedemann, A.R., C.E. Conrad, J.H. Dieterich, J.W. Hornbeck, W.F. Megahan, L.A. Viereck, D.D. Wade. 1979. Effects of fire on water: a state-of-knowledge review. Prepared for the Forest Service National Fire Effects Workshop, Denver, Colo., April 10-14, 1978. Washington, D.C., Forest Service, U.S. Department of Agriculture general technical report WO-10.

Tiedemann, A.R. 1973. Stream chemistry following a forest fire and urea fertilization in north-central Washington. Pacific Northwest Forest and Range Experiment Station, Forest Service, U.S. Department of Agriculture, Portland, OR.

Townsend, S.A. and M.M. Douglas. 2000. The effect of three fire regimes on stream water quality, water yield, and export coefficients in a tropical savanna (northern Australia). Journal of Hydrology 229(3-4):118-137.

Vacca, A., S. Loddo, G. Ollesch, R. Puddu, G. Serra, D. Tomasi, and A. Aru. 2000. Measurement of runoff and soil erosion in three areas under different land use in Sardinia (Italy). Catena 40(1):69-92.

Viro, P.J. 1974. Effects of forest fire on soil. In: Kozlowski, T.T. and C.E. Ahlgren (eds.), Fire and Ecosystems. Academic Press, New York. 542 pp.*

Vitt, D.H. and S. Bayley. 1984. The vegetation and water chemistry of four oligotrophic basin mires in northwestern Ontario. Canadian Journal of Botany 62:1485-1500.

Wells, C.G., R.E. Campbell, L.F. DeBano, C.E. Lewis, R.L. Fredrickson, E.C. Franklin, R.C. Froelich, and P.H. Dunn. 1979. Effects of fire on soils: a state-of-knowledge review. U.S. Forest Service general technical report WO-7. 34 pp.

Wichmann. H., R. Sprenger, M. Wobst, and Bahadir. 2000. Combustion induced transport of heavy metals in the gas phase: A review. Fresenius Environmental Bulletin 9(1-2):72-125.

Weigand, S., W. Schimmack, and K. Auerswald. 1998. The enrichment of Cs-137 in the soil loss from small agricultural watersheds. Zeitschrift fur Pflanzenernahrung und Bodenkunde 161(4):479-484.

Wright, H.A., F.M. Churchill, and W.C. Stevens. 1976. Effect of prescribed burning on sediment, water yield, and water quality from bulldozed juniper lands in central Texas. Journal of Range Management 29:294-298.*

Wright, H., F.M. Churchill, and W.C. Steven. 1982. Soil loss, runoff, and water quality of seeded and unseeded steep watersheds following prescribed burning. Journal of Range Management 35(3):382-385.

Wright, H.E., Jr. 1981. The role of fire in land/water interactions. Pages 421-444 in H.A. Mooney, T.M. Bonnicksen, N.L. Christensen, J.E. Lotan, and W.A. Reiners (technical coordinators), Proceedings of the conference: fire regimes and ecosystem properties. U.S. Forest Service general technical reportWO-26.

Wright, R.F. 1976. The impact of forest fire on the nutrient influxes to small lakes in northeastern Minnesota. Ecology 57:649-663.*

APPENDIX

Author	Field Authors	Date	Type	Element	Location	Media Found	Observations
Adams	Iser, Keleher, Cheal	1994	General	C	Australia	Soil	Concentration of C greater in unburned soils than in repeatedly burned soils. Not affected at depths greater than 2 cm.
Baird	Zabowski, Everett	1999	General	C	Washington	Soil	Average C content 10% to 30% lower on burned soils than on control soils. Surface erosion removed 280 to 640 kg/ha of C.
Stromgaard		1992	General	C	Zambia	Soil	Organic carbon increased slightly in topsoils and did not change in subsoils.
Viro		1974	General	Ca	Scandinavia	Ash	Ca in ash occurs mainly as oxide and carbonate forms, with small amounts of phosphates. The oxides are water-soluble but are rapidly converted into carbonates that are soluble under acidic conditions only. Ca lost from the soil from burning were the smallest of all the cationic nutrients.
Helvey	Tiedmann, Anderson	1985	General	Ca	Washington	Sediments	Ca, Mg, K concentration increase 4.5 after fire. Fire caused change in predominant mechanism pre-fire mostly move in solution and post-fire move more with sediments.
DeBano	Rice, Conrad	1979	General	Ca	Southern California	Sediments	Ca in sediments increased from 0.52 kg/ha (unburned) to 47.39 kg/ha in the first year after a burn.
Austin	Baisinger	1955	General	Ca	Western WA & OR	Soil	Ca in burned surface soil was 830% higher than control area. After 2 years it was still 327% higher than the control.
Viro		1974	General	Ca	Scandinavia	Soil	After burning, the humus layer contained 3x as much exchangeable Ca as the control. The Ca leached slowly and only reached control level after 50 years. In the year of burning there was no increase in Ca in the mineral soil and only after 20 years was a small increase detected in the subsoil.
Stromgaard		1992	General	Ca	Zambia	Soil	Slight decline in exchangeable Ca in topsoil immediately after burning. At deeper horizons, an immediate increase in Ca, probably as a result of heat rather than leaching of bases from ash. Ca concentration decreased over time, but 5.5 years later was still higher than unburned area
Beschta		1990	General	Ca	Oregon	Soil	Metallic cations, such as Ca, are converted to oxides and remain as ash. Cumulative solution loss of 17% of the available Ca capital in the upper 14 inches of soil over 5 years.
Raison	Khanna, Woods	1985	General	Ca	Australia	Vegetation	Concentration of Ca in ash increased 10- to 50-fold over unburned litter.
Belillas	Roda	1993	General	Ca	Spain	Water	Ca was higher in overland flow water on burnt slopes than unburned slopes. The difference was significant at the 0.15 level.
DeBano	Rice, Conrad	1979	General	Ca	Southern California	Water	Ca in runoff increased from 0.41 kg/ha (pre-burn) to 20.04 kg/ha in the first year after the burn.
Tiedemann	Helvey, Anderson	1978	General	Ca	Eastern Washington	Water	Ca concentration in stream increased immediately after the fire, but in subsequent events decreased because dilution effects of increased flow.

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Author	Other Authors	Date	Type	Element	Location	Media Sampled	Observations
DeBano	Rice, Conrad	1979	General	Cation Exchange Capacity	Southern California	Soil	Cation exchange capacity of soil decreased by burning and may remain low for at least one year because exchange sites on organic matter are destroyed.
Little	Calfee	2000	General	CN		Water	Toxicity of all fire retardant chemicals containing sodium ferrocyanide significantly increased when exposed to UV. Irradiance conditions influenced free cyanide concentrations. Highest concentration of free cyanide occurred within 24 hours, and remained high up to 96 hours after exposure. Toxicity consistent with photoactivation substance is modified as a result of the energy absorbed by the parent compound that can result in a photoproduct that is more toxic than the parent compound. Humic acid concentration of the water may influence the toxicity.
Tiedemann	Helvey, Anderson	1978	General	Conductivity	Eastern Washington	Water	Average conductivity of streams in 3 watersheds increased from 46 mhos/cm pre-fire to 66 mhos/cm after the fire. Increased conductivity lasted a short period, probably result of ash in stream.
Feller	Kimmins	1984	General	Electrical Conductivity	Canada	Water	Clearcutting and slash burning appeared to increase conductivity in stream water. Cannot separate effects of clearcutting and slash burning. Effects gone in 2 years.
Wright	Churchill, Stevens	1976	General	Hardness	Texas	Water	Increases in water hardness were more pronounced on moderate and steep slopes. Ca accounted for 57% of the water hardness.
Viro		1974	General	K	Scandinavia	Ash	K in fresh ash is in oxide or carbonate form and the oxide rapidly changes to carbonate. All K compounds formed by burning are water-soluble. K in the humus layer decreased after burning, even after 50 years. K was leached into the mineral soil, generally deeper than 30 cm.
Thomas	Walsh, Shakesby	1999	General	K	Portugal	Sediment	Annual estimate of total K in sediments from burnt eucalyptus was 0.3 to 1.24 kg/ha, compared to 0.0004 kg/ha in unburned eucalyptus. The annual total K in sediments from burnt pine was 0.08 to 0.41 kg/ha, compared to 0.0005 from unburned pine. Effect lasted 2 years.
DeBano	Rice, Conrad	1979	General	K	Southern California	Sediment	K in sediments increased from 0.05 kg/ha (unburned) to 19.34 kg/ha in the first year after a burn.
Helvey	Tiedmann, Anderson	1985	General	K	Washington	Sediment	Ca, Mg, K concentration increase 4.5 after fire. Fire caused change in predominant mechanism pre-fire mostly move in solution and post-fire move more with sediments.
Austin	Baisinger	1955	General	K	Western WA & OR	Soil	K was 166% higher on burned soils, and was 112% of normal at the end of 2 years.
DeBano	Rice, Conrad	1979	General	K	Southern California	Soil	Concentration of K higher on burned soil than unburned soil.
Stromgaard		1992	General	K	Zambia	Soil	Immediate increase in K, most certainly linked to release of K in the ash. Short-lived, returned to near pre-fire levels in 40 days.

Author	Other Authors	Date	Type	Element	Location	Media Sampled	Observation
Auclair		1977	General	K	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that K is mobilized by burning.
Belillas	Roda	1993	General	K	Spain	Water	K was higher in overland flow water on burnt slopes than unburned slopes. The difference was significant at the 0.15 level.
DeBano	Rice, Conrad	1979	General	K	Southern California	Water	K in runoff increased from 0.09 kg/ha (pre-burn) to 7.67 kg/ha in the first year after the burn.
Belillas	Roda	1993	General	K	Spain	Water	Significant decrease in K in the spring after the fire was noted in stream water. Attributed to efficient K demand by the soil biota and regrowing vegetation, particularly bracken a species with high K content.
Schindler	Newbury, Beaty, Prokopowich, Ruszczynski, Dalton	1980	General	K	Ontario	Water	K concentration increased in the 1.4 to 2.9 times range. The K concentrations represent about 40% of the annual input via rain, snow, and dust.
Wright		1976	General	K	Minnesota	Water	K exports in runoff increased 265%; measured two years after the fire. One-fifth of the increase in K exports is attributed to increased runoff volume, the remainder attributed to increased concentration of K in runoff.
Tiedemann	Helvey, Anderson	1978	General	K	Eastern Washington	Water	K concentration in stream increased immediately after the fire, but in subsequent events decreased because dilution effects of increased flow. After 3 years the K concentration began to increase as flow volume decreased.
Stednick	Tripp, McDonald	1982	General	K	Alaska	Water	K concentration in stream increased significantly.
Feller	Kimmins	1984	General	K	Canada	Water	Clearcutting and slash burning appeared to increase K in stream water. K exhibited most prolonged and significant concentration increases. Cannot separate effects of clearcutting and slash burning. Effects gone in 2 years.
Beschta		1990	General	K	Oregon	Water	K concentrations increased to a peak of 4.4 mg/L during the first major rainfall after burning and immediately returned to pre-logging levels of 0.6 to 1.2 mg/L. Metallic cations, such as K, are converted to oxides and remain as ash. Cumulative solution loss of 14% of available K capital from top 14 inches of soil in 5 years.
Viro		1974	General	Mg	Scandinavia	Ash	Mg in ash occurs mainly as oxide and carbonate forms, with small amounts of phosphates. The oxides are water-soluble but are rapidly converted into carbonates that are soluble under acidic conditions only. Mg leaches into the subsoil; appreciable amounts of Mg were found as deep as 30 cm in the mineral soil.
Raison	Khanna, Woods	1985	General	Mg	Australia	Ash	Concentration of Mg in ash increased 10- to 35-fold over unburned litter.
Helvey	Tiedmann, Anderson	1985	General	Mg	Washington	Sediment	Ca, Mg, K concentration increase 4.5 times after fire. Fire caused change in predominant mechanism pre-fire mostly lost in solution and post-fire more lost in sediments.

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Author	Other Authors	Date	Type	Element	Location	Media Sampled	Observations
DeBano	Rice, Conrad	1979	General	Mg	Southern California	Sediment	Mg in sediments increased from 0.47 kg/ha (unburned) to 28 kg/ha in the first year after a burn.
Austin	Baisinger	1955	General	Mg	Western WA & OR	Soil	Mg in burned surface soil was 337% higher than in unburned control. At the end of 2 years had returned to pre-burn concentrations.
Viro		1974	General	Mg	Scandinavia	Soil	After burning, the humus layer contained 2x as much exchangeable Mg as the control, but 6 years later the amounts were equal. In the year of burning there was a small decrease in Mg in the mineral soil.
Stromgaard		1992	General	Mg	Zambia	Soil	Immediate increase in Mg followed by a slow depletion of the soil store of Mg.
Beschta		1990	General	Mg	Oregon	Soil	Metallic cations, such as Mg, are converted to oxides and remain as ash. Cumulative solution loss of 13% of the available Mg capital in the upper 14 inches of soil over 5 years.
DeBano	Rice, Conrad	1979	General	Mg	Southern California	Water	Mg in runoff increased from 0.07 kg/ha (pre-burn) to 3.63 kg/ha in the first year after the burn
Tiedemann	Helvey, Anderson	1978	General	Mg	Eastern Washington	Water	Mg concentration in stream increased immediately after the fire, but in subsequent events decreased because dilution effects of increased flow.
Stednick	Tripp, McDonald	1982	General	Mg	Alaska	Water	Mg concentration in stream slightly increased.
Helvey	Tiedmann, Anderson	1985	General	N	Washington	Sediment	Total N (in kg/ha) increased 40 times after the fire, soil carried 10% of N lost.
Thomas	Walsh, Shakesby	1999	General	N	Portugal	Sediment	Annual estimate of total N in sediments from burnt eucalyptus was 14 to 57 kg/ha, compared to 0.071 kg/ha in unburned eucalyptus. The annual total N in sediments from burnt pine was 17.6 to 38 kg/ha, compared to 0.064 from unburned pine. Effect lasted 2 to 3 years.
Adams	Iser, Keleher, Cheal	1994	General	N	Australia	Soil	Concentration of N and potentially mineralizable N greater in unburned soils than in repeatedly burned soils. Not affected at depths greater than 2 cm.
Chambers	Attiwill	1994	General	N	Australia	Soil	At temperatures above 400jC concentrations of inorganic N were about twice the control. Concentration of N decreased in surface soils to pre-heating level in 16 months.
DeBano	Dunn, Eberlein	1979	General	N	Southern California	Soil	Intense burn on dry soil increased ammonia in mineral soil, while decreasing it in litter. Less ammonia produced in moist soil. Amount of NO3-N was decreased in litter, but unchanged in underlying soil. Destroyed amino acids are likely source of ammonia. Total N loss depends on burn intensity 80% of total N in litter and upper 2 cm of soil destroyed when max temp in litter reached 825jC; 40% at 600jC, and 20% at 486jC.
Austin	Baisinger	1955	General	N	Western WA & OR	Soil	Reduction of 67% of N in soil after burning. After 2 years the N was only 75% of unburned control average.

Author	Other Authors	Date	1998	Element	Location	Media Studied	Observations
DeBano	Rice, Conrad	1979	General	N	Southern California	Soil	Concentration of N higher on burned soil than unburned soil. However, the N in amount per unit area probably decreases compared to the N in the pre-fire unburned biomass.
Baird	Zabowski, Everett	1999	General	N	Washington	Soil	Average N content 13% to 46% lower on burned soils than on control soils. Surface erosion removed 14 to 22 kg/ha of N.
Viro		1974	General	N	Scandinavia	Soil	As a result of burning, the amount of ammonia in the humus layer was increased 5-fold at the time of burning. The ammonia level decreased by half during the year of burning. Overall, it was decreased in the first 3 years after burning. Ammonia increased 12 years after burning, but a normal level was not reached until 50 years after burning. There was an increase in the level of nitrate nitrogen in the humus layer for at least 6 years after burning. The decrease in ammonia and concomitant increase in nitrate are attributed to the increased nitrification of ammonia owing to the drop in acidity.
DeBano	Neary, Ffolliott	1998	General	N	General	Soil	The concentrations of NH4-N can increase, decrease, or remain the same depending on the severity and duration of a fire. Most of the soil N is probably volatilized in high-severity fires. However, large amount of NH4-N can be found in the ash and underlying soil after low-severity fires.
Stromgaard		1992	General	N	Zambia	Soil	Immediate increase in N in topsoil, but no increase in subsoil. At a depth of 15 cm a loss of N was observed. N levels declined to pre-burn level in 3.5 years.
Auclair		1977	general	N	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that N is mobilized by burning.
Schindler	Newbury, Beaty, Prokopowich, Ruszczynski, Dalton	1980	General	N	Ontario	Water	Total N 2 times higher. More dissolved than particulate.
Tiedemann	Helvey, Anderson	1978	General	N	Eastern Washington	Water	NO3-N increased in streams in burnt watersheds. Increase the result of reduced demand for NO3-N by vegetation and increased nitrification. Increased nitrification is thought to be the more important mechanism. Organic N also increased, probably due to leaching and detachment of organic detritus accumulated in stream channels. Increased flows would affect larger areas of detritus accumulation.
Stednick	Tripp, McDonald	1982	General	N	Alaska	Water	No significant changes in nitrogen concentrations in streams after burning. Ammonium-nitrate concentrations increased for two weeks after the fire. Organic detritus in stream probably responsible for organic N increase.
Beschta		1990	General	N	Oregon	Water	Elevated ammonia-nitrogen concentrations occurred in stream flow for a period of 12 days after burning. Most studies show essentially no change or small increase in nitrate-nitrogen concentrations.

Author	Other Authors	Date	Type	Element	Location	Media Sampled	Observation
Belillas	Roda	1993	General	N	Spain	Water	NO3 was higher in overland flow water on burnt slopes than unburned slopes. The difference was significant at the 0.15 level.
Belillas	Roda	1993	General	N	Spain	Water	NO3 increased in stream water from burned catchment both in comparing pre- and post-burn in the same catchment and with a paired unburned catchment. Increases remained for at least 2 years after the fire.
Feller	Kimmins	1984	General	N	Canada	Water	Clearcutting and slash burning appeared to increase NO3 in stream water. Cannot separate effects of clearcutting and slash burning. Effects gone in 2 years.
DeBano	Rice, Conrad	1979	General	Na	Southern California	Sediment	Loss of Na in sediments increased from 0.07 kg/ha (unburned) to 2.57 kg/ha in the first year after a burn.
DeBano	Rice, Conrad	1979	General	Na	Southern California	Water	Loss of Na in runoff increased from 0.1 kg/ha (pre-burn) to 2 kg/ha in the first year after the burn.
Tiedemann	Helvey, Anderson	1978	General	Na	Eastern Washington	Water	Na concentration in stream increased immediately after the fire, but in subsequent events decreased because dilution effects of increased flow. After 3 years the Na concentration began to increase as flows decreased.
Stednick	Tripp, McDonald	1982	General	Na	Alaska	Water	Na concentration in stream slightly increased.
Wright	Churchill, Stevens	1976	General	Na	Texas	Water	Remained low in runoff water, not affected by burning.
Feller	Kimmins	1984	General	Na	Canada	Water	Clearcutting and slash burning appeared to increase Na in stream water. Cannot separate effects of clearcutting and slash burning. Effects gone in 2 years.
Beschta		1990	General	Na	Oregon	Water	Cumulative movement of Na in solution was 39% of the available Na capital in the upper 14 inches of soil over 5 years.
Viro		1974	General	P	Scandinavia	Ash	P in ash is largely as water-soluble alkali phosphates. P in humus layer decreased after burning. The amount of P in the humus decreased by about 75% and began to rise again 12 years after burning. The P was likely mostly precipitated in the surface layers of the mineral soil as magnesium phosphate.
Viro		1974	General	P	Scandinavia	Ash	The amount of easily soluble P in the humus layer was increased 2x by burning. Increased P was found in the soil to a depth of 30 cm in the first year after burning.
Raison	Khanna, Woods	1985	General	P	Australia	Ash	Concentration of P in ash increased 10-fold over unburned litter.
Helvey	Tiedmann, Anderson	1985	General	P	Washington	Sediment	P moving in solution was much greater than P moving with sediment. Total P losses increased 14 times.
Thomas	Walsh, Shakesby	1999	General	P	Portugal	Sediments	Annual estimate of total P lost in sediments from burnt eucalyptus was 0.17 to 0.83 kg/ha, compared to 0.0001 kg/ha in unburned eucalyptus. The annual total P lost in sediments from burnt pine was 0.22 to 0.41 kg/ha, compared to 0.0002 from unburned pine. Effect lasted 1 year.

Author	(Other) Authors	Date	Type	Element	Location	Media Studied	Observations
DeBano	Rice, Conrad	1979	General	P	Southern California	Sediments	Loss of P in sediments increased from 0.08 kg/ha (unburned) to 3.37 kg/ha in the first year after a burn.
Adams	Iser, Keleher, Cheal	1994	General	P	Australia	Soil	Concentrations of available P were usually greater in soils from repeatedly burnt soils than unburned soil. Suggests increase in inorganic forms over organic forms. Increase in P attributed to reduction in biological and geochemical (e.g., a reduction in P fixation and precipitation) sinks for soluble inorganic P. Not affected at depths greater than 2 cm.
Chambers	Attiwill	1994	General	P	Australia	Soil	Heating mineralized most of the labile organic P resulting in large and sustained increases in available P and bicarbonate P(i). May be the result of release of P during formation of hematite.
Austin	Baisinger	1955	General	P	Western WA & OR	Soil	Available P was 2x as high on burned than on unburned soil. Returned to unburned levels within 2 years.
DeBano	Rice, Conrad	1979	General	P	Southern California	Soil	Concentration of P higher on burned soil than unburned soil.
Stromgaard		1992	General	P	Zambia	Soil	Increase in available P down to 25 cm occurred immediately after burning. One month later increased P was down 40 cm. pH changed very little at deeper levels, so increase of P is not attributed to increased solubility of iron and aluminum phosphate. Constantly high level of available P suggests that leaching of P is limited.
Auclair		1977	general	P	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that P is mobilized by burning.
Schindler	Newbury, Beaty, Prokopowich, Ruszczynski, Dalton	1980	General	P	Ontario	Water	Total, suspended, and dissolved P increased 1.4 to 3.2 times post-fire. This represents about 40% of the annual input via rain, snow, and dust.
Wright		1976	General	P	Minnesota	Water	P exports in runoff increased 93%; measured two years after the fire. Two-thirds of the increase in P exports is attributed to increased runoff volume, the remainder attributed to increased concentration of P in runoff.
Tiedemann	Helvey, Anderson	1978	General	P	Eastern Washington	Water	Both ortho-P and total-P in streams were 2 to 3x higher in burned watersheds than in unburned watershed.
Stednick	Tripp, McDonald	1982	General	P	Alaska	Water	Burning increased organic P concentrations in surface waters significantly. Average total P increased from 0.018 to 0.026 mg/L.
Beschta		1990	General	P	Oregon	Water	Phosphorus export in stream water may increase following burning, but losses are generally small.
Austin	Baisinger	1955	General	pH	Western WA & OR	Soil	Top 0.5 inch of soil became quite alkaline, with an average pH of 7.6. The control spot average pH was 4.5. After 2 years, the average pH in the burned area was 5.7.
DeBano	Rice, Conrad	1979	General	pH	Southern California	Soil	pH increases slightly.

Author	Other Authors	Date	Type	Element	Location	Media Sampled	Observations
Viro		1974	General	pH	Scandinavia	Soil	The pH of the humus layer was increased by 2 to 3 pH units in burned areas. In the subsoil the pH changes were small, but in the first 20 years after burning the average pH was 0.4 pH units lower on burned sites than on unburned sites. A difference of 0.2 pH units persisted for 50 years.
Stromgaard		1992	General	pH	Zambia	Soil	Immediately following burning, soil pH rose by 2 to 4 pH units; likely caused by bases in the ash. pH returned to pre-burning levels 5 years later.
Belillas	Roda	1993	General	pH	Spain	Water	Minor decrease in pH (0.2 pH units) for two years after the fire were noted in stream water.
Wright	Churchill, Stevens	1976	General	pH	Texas	Water	pH in runoff water from moderate and steep slopes increased slightly.
Feller	Kimmins	1984	General	pH	Canada	Water	Clearcutting and slash burning appeared to increase pH in stream water. Cannot separate effects of clearcutting and slash burning. Effects gone in 2 years.
National Wildfire Coordinating Group		1994	General	pH	Various	Soil	Rarely do arid or semiarid soils, which are typically alkaline, exhibit increased pH after burning. Those that do are near neutral initially, may increase a few tenths of a pH unit, then return to pre-burn levels within a year or two after burning.
DeBano	Rice, Conrad	1979	General	SO4	Southern California	Soil	Concentration of SO4 higher on burned soil than unburned soil.
Belillas	Roda	1993	General	SO4	Spain	Water	SO4 was higher in overland flow water on burnt slopes than unburned slopes. The difference was not significant using the Mann-Whitney test (P> 0.05).
Belillas	Roda	1993	General	SO4	Spain	Water	Minor decrease in SO4 in the spring after the fire was noted in stream water.
Tiedemann	Helvey, Anderson	1978	General	Total Alkalinity	Eastern Washington	Water	Average total alkalinity in streams in 3 watershed increased from 0.61 mequ/L pre-fire to 0.82 mequiv/L after the fire. Increased total alkalinity lasted a short period, probably a result of ash in the stream.
Auclair		1977	Metals	Cu	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that Cu is mobilized by burning.
Parra	Rivero, Lopez	1996	Metal	Mn	Spain	Soil	After fire, total Mn increases in both upper and lower soil horizons, possibly due to transportation in the form of organic complexes through the macropores of the soil. Easily reducible Mn increased in burned soil. Mn increases likely due to vegetation, Mn concentrated in leaves particularly resinous.
Chambers	Attiwill	1994	Metals	Mn	Australia	Soil	Increase of 279% in concentration of water-soluble Mn after heating to 400¡C. Decreased to pre-heating levels within 1 to 2 months. Increase in Mn attributed to physio-chemical breakdown of Mn complexed with organic matter. Ensuing reduction in concentration of water soluble Mn most likely due to rapid increase in the microbial population and consequent oxidation of divalent Mn to less available higher oxides.

Author	Other Author	Date	Type	Element	Location	Media Sampled	Generalization
Auclair		1977	Metals	Mn	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that Mn is mobilized by burning.
Beschta		1990	Metals	Mn	Oregon	Water	Elevated Mn concentrations occurred in stream flow for a period of 12 days after burning.
Auclair		1977	Metals	Zn	Canada	Vegetation	Correlation between concentration in tissue and soil parameters suggests that Zn is mobilized by burning.
Amiro	Sheppard, Johnston, Evenden, Harris	1996	Radionuclides	Cl	Lab	Ash	65% to 90% of Cl lost to atmosphere in straw fires. Loss of Cl to atmosphere in hotter wood fires expected to be closer to 90%. At 400¡C only 24% of the Cl was recovered in the ash. The Cl was 95% soluble from the ash, essentially the same as solubility in unburned material (97%).
Pallouris	Taylor, Wein, Svoboda, Mierzynski	1995	Rad	Cs	Canada	Soil	Pre-fire Cs-137 bound in organic matter on forest floor. After fire, Cs-137 concentrated in surface soils. Lower Cs-137 load in burned areas. Loss of Cs-137 to volatilization, leaching, and runoff.
Amiro	Sheppard, Johnston, Evenden, Harris	1996	Radionuclides	Cs	Lab	Ash	10% to 90% of the Cs remained in the ash. Concentration of Cs in the ash increased up to 2 orders of magnitude at 400¡C burn. Cs enrichment in the ash was 4- to 20-fold in the field burns. 51% of the Cs was soluble after the 400¡C burn, a decrease from 90% soluble in unburned material.
Kashparov	Lundin, Kadygrib, Protsak, Levtchuk, Yoschenko, Kashpur, Talerko	2000	Radionuclides	Cs	Ukraine	Air	Resuspension of Cs-137 during forest fires will add about 10^{-7} to 10^{-5} of its background value. During active burning phase the concentration of Cs-137 in the lower air layer in the immediate zones increases by several hundred times compared to background levels. During smoldering phase Cs-137 concentration is tens of times increased and in the post-fire period it is several times higher.
Johansen	Hakonson, Whicker, Simanton, Stone	2000	Radionuclides	Cs	New Mexico	Sediments	Burned plots at WIPP yielded 22 times greater Cs-137 than paired natural plots. Increased loss of Cs-137 attributed to greater erosion and splash effects from raindrops without canopy cover, greater soil detachment and transport from less groundcover, and reduced infiltration.
Johansen	Hakonson, Whicker, Simanton, Stone	2000	Radionuclides	Cs	Colorado	Sediments	Burned plots at RFETS yielded 4 times greater Cs-137 than paired natural plots. Increased loss of Cs-137 attributed to greater erosion and splash effects from raindrops without canopy cover, greater soil detachment and transport from less groundcover, and reduced infiltration.
Amiro	Sheppard, Johnston, Evenden, Harris	1996	Radionuclides	I	Lab	Ash	60% to 80% lost to atmosphere from straw burns; 95% lost to atmosphere in hotter wood burns. Concentration of I in the ash increased in fires up to 400¡C and then decreased although some I was detectable in 1000¡C burn. Solubility of I in ash increased from 10% soluble in unburned material to 60% soluble in material burned at 400¡C. Increase in solubility attributed to destruction of organic materials that had originally bound the I.

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