Stormwater contaminant loading following wildfires

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Abstract

Contaminant loading associated with stormwater runoff from recently burned areas is poorly understood, despite the fact that it has the potential to affect downstream water quality. The goal of this study is to assess regional patterns of runoff and contaminant loading from wildfires in urban fringe areas of southern California. Post-fire stormwater runoff was sampled from five wildfires that each burned between 115 and 658 km^2 of natural open space between 2003 and 2009. Between two and five storm events were sampled per site over the first one to two years following the fires for basic constituents, metals, nutrients, TSS, and PAHs. Results were compared to data from 16 unburned natural areas and 6 developed sites. Mean Cu, Pb and Zn flux (kg/km^2) were between 112- and-736-fold higher from burned catchments and total phosphorous was up to 921-fold higher compared to unburned natural areas. PAH flux was four times greater from burned areas than from adjacent urban areas. Ash fallout on nearby unburned watersheds also resulted in a three-fold increase in metals and PAHs. Attenuation of elevated concentration and flux values appears to be driven mainly by rainfall magnitude. Contaminant loading from burned landscapes has the potential to be a substantial contribution to the total annual load to downstream areas in the first several years following fires.

Introduction

Periodic wildfires are a natural component of forest and scrubland ecosystems in arid and semi-arid environments such as those found in the southwestern United States, western South Africa, Chile, northern Spain and Portugal, and southwestern Australia. However, the frequency and intensity of wildfires has increased in association with human activities in and near natural forest and foothill areas (Syphard *et al.* 2007) and is expected to continue increasing in association with changes in climate patterns (Westerling *et al.* 2006). In addition to habitat destruction, wildfires have been shown to have the ability to mobilize contaminants. For example, combustion of plants and natural materials has been reported to release metals which are subsequently mobilized (Caldwell *et al.* 2000, Yamasoe *et al.* 2000, Bitner *et al.* 2001, Amirbahman *et al.* 2004, Kelly *et al.* 2006, Burke *et al.* 2010), polycyclic aromatic hydrocarbons (PAHs; Jenkins *et al.* 1996), dioxins (Nestrick and Lamparski 1983, Sheffield 1985, Gullett and Touati 2003, Meyer *et al.* 2004), and nitrogen compounds (Hegg et al 1990, Riggan *et al.* 1994, Ranali 2004, Meixner *et al.* 2006, Jung *et al.* 2009). Runoff from burned natural habitats often flows to adjacent or downstream urban areas, where the contaminants may comingle with similar urban derived pollutants and have the potential to exacerbate existing water quality issues. In southern California, catchments affected by fire often drain to water bodies that support sensitive riparian or estuarine resources that may already be stressed or impaired by urban contaminants.

Despite the potential effects on downstream water quality, routine monitoring and assessment of post-fire runoff seldom occurs. Consequently, the contribution of metals, nutrients, and organic contaminants from post-fire runoff to receiving waters

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is poorly understood, in terms of both the magnitude of potential effect and the persistence of the influence. Because of this, the relative contribution of contaminant loading from post-fire runoff compared to other sources (e.g., urban runoff or non-post-fire runoff) is also poorly understood. In addition to the direct effects of runoff from burned landscapes, the materials left behind at the burned location can be carried away from the fire in the form of smoke and ash. Subsequent atmospheric deposition can markedly increase the quantity of various constituents available to storm flows downwind of fires (Riggan *et al.* 1985). For example, Sabin *et al.* (2005) report that during the severe 2003 Southern California forest fire season, atmospheric deposition rates of Cu, Pb, and Zn went up by factors of four, eight, and six, respectively, at an unburned site in the San Fernando Valley that was approximately 30 miles from the southeastern border of the Piru/Simi Fires.

The goal of the current study is to assess regional patterns of runoff and loading of a broad suite of contaminants from wildfires in urban fringe areas of southern California. Information from five large wildfires over the six year period of 2003-2009 was used to answer three questions: 1) What is the magnitude of contaminant loading from burned areas relative to natural and urban sources? 2) How long does the fire-related contaminant loading persist? 3) What are some of the factors that may influence patterns of contaminant loading? We also provide some preliminary findings on the indirect effects on contaminant concentration in unburned urban areas that receive aerial deposition of wildfire ash.

Methods

Study Area

Post-fire stormwater runoff was sampled from five wildfire areas in southern California, which is characterized by classic Mediterranean-climate conditions of relatively mild to cool wet winters and warm to hot dry summers. Average annual rainfall is 35 cm and long-term average volumetric discharge from the Los Angeles River is approximately 4.5×10^{11} L. The study wildfires burned a minimum of 100 km^2 of natural habitats and were near or adjacent to urban areas (Table 1; Figure 1). The first of these wildfires (the Old Fire) began in October 2003, while the final wildfire (the Station Fire) started in August 2009. These fires ranged in size from 115 to 658 km^2 in natural open space areas that had <5% developed drainage areas. Prior to the wildfires, most of the burned areas were dominated by sage scrub (drought-deciduous shrubs) or chaparral (evergreen shrubs) plant communities, with two areas also having limited amounts of conifer forest.

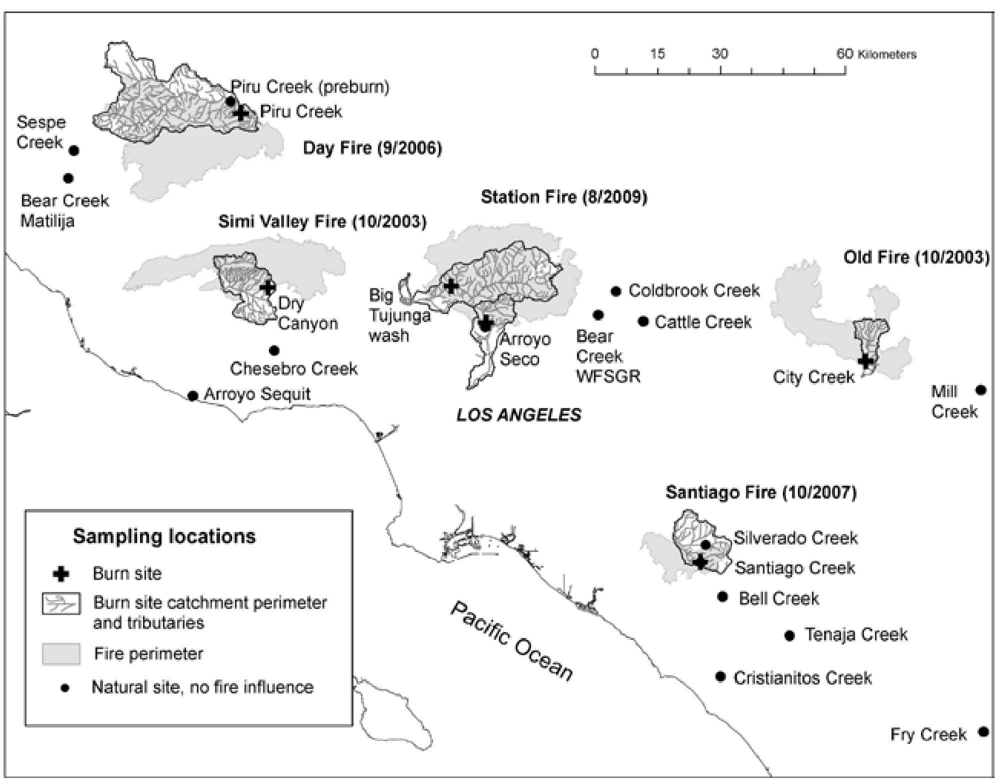

Figure 1. Sampling locations for post-fire and unburned natural sites, and burn perimeters for each of the wildfires.

Table 1. Characteristics of sampling sites for post-fire and unburned natural and urban watersheds.

Fire Incident	Date Started	Burn Area (km^2)	Stream Sampled	Sampling Dates	Watershed Size* (km^2)	Plant Community	Geologic Type	Most Recent Fires** (year; km^2)
Post-Fire								
Old	10/25/03	369.4	City Creek	3/3/04	51	Shrub	Igneous	2003; 4.3
								2002; 0.1
								2002; 0.1
Simi Valley	10/25/03	437.9	Dry Canyon	12/25/03	5	Shrub	Sedimentary	None
				2/26/04				
				1/7/05				
Day	9/4/06	658.4	Piru Creek	12/10/06	512	Mostly shrub; some conifer forest	Sedimentary	2002; 1.1
				12/16/06				
				1/28/07				
				2/22/07				
				4/20/07				
Santiago	10/21/07	114.9	Santiago Creek	12/8/07	17	Shrub	Sedimentary	None
				2/25/08				
Station	8/28/09	649.8	Arroyo Seco	10/13/09	42	Mostly shrub; some conifer forest	Igneous	None
				1/13/10				
				1/17/10				
				2/5/10				
				3/6/10				
Station	8/28/09	649.8	Big Tujunga Wash	10/14/09	276	Mostly shrub; some conifer forest	Igneous	None
				12/7/09				
				12/12/09				
Unburned, No Fire Influence - Natural Area								
None		0	Arroyo Seco	3/22/05	42	Forest	Igneous	None
				2/27/06				
None		0	Arroyo Sequit	12/28/04	27	Shrub	Igneous	None
				1/7/05				
				4/4/06				
None		0	Bear Creek Matilija	2/27/06	10	Forest	Sedimentary	None
None		0	Bear Creek WFSGR	4/4/06	73	Forest	Igneous	2002; 6.1
None		0	Bell Creek	1/7/05	18	Shrub	Sedimentary	None
				1/2/06				
None		0	Cattle Creek	4/27/05	53	Shrub	Igneous	2002; 7.3
				12/31/05				
None		0	Chesebro Creek	1/7/05	8	Forest	Sedimentary	None
None		0	Coldbrook	4/27/05	15	Forest	Igneous	2002; 21.7
				12/31/05				
None		0	Cristianitos Creek	1/7/05	51	Shrub	Sedimentary	2000; 1.8
None		0	Fry Creek	2/11/05	1	Forest	Igneous	None
				3/28/06				
None		0	Mill Creek	3/28/06	15	Shrub	Igneous	None
None		0	Piru Creek	2/27/06	477	Shrub	Sedimentary	2002; 1.1
None		0	Santiago Creek	2/11/05	17	Shrub	Sedimentary	None
				1/2/06				
				2/27/06				
None		0	Sespe Creek	2/27/06	128	Shrub	Sedimentary	2002; 21.7
None		0	Silverado Canyon	2/11/05	21	Shrub	Sedimentary	None
				1/2/06				
None		0	Tenaja Creek	4/28/05	42	Shrub	Igneous	None
				2/27/06				
Unburned, No Fire Influence - Urban Area								
None		0	Arroyo Seco	2/9/01	130	None	Concrete & Asphalt	
				4/6/01				
None		0	Ballona Creek	2/19/01	230	None	Concrete & Asphalt	
				4/7/01				
				11/24/01				
				5/3/03				

Table 1. Continued

Fire Incident	Date Started	Burn Area (km^2)	Stream Sampled	Sampling Dates	Watershed Size* (km^2)	Plant Community	Geologic Type	Most Recent Fires** (year; km^2)
None		0	Dominguez Channel	3/17/02	187	None	Concrete & Asphalt	
				2/2120/04				
None		0	Los Angeles River above Arroyo Seco	1/2620/01	1460	None	Concrete & Asphalt	
				2/9/01				
				2/12/01				
None		0	Los Angeles River in Long Beach	1/26/01	2161	None	Concrete & Asphalt	
				2/9/01				
				5/2/03				
None		0	Verdugo Wash	1/2620/01	65	None	Concrete & Asphalt	
				2/9/01				
				11/12/01				
Unburned, Fire Influenced Aerial Deposition - Urban Area								
Padua	10/21/03	42.3	Ballona Creek	10/31/03	230	None	Concrete & Asphalt	
Grand Prix	10/21/03	240.6		2/2/04				
Piru	10/23/03	259		2/21/04				
Verdale	10/24/03	35.1						
Simi Valley	10/25/03	437.9						
Old	10/25/03	369.4						

*Size of the watershed that had samples collected.
**Fires occurring in the last 5 years within the sampled watershed.

Igneous or sedimentary rock dominated the soil types in the study catchments. Estimated average annual discharge from the study catchments prior to the fires was on the order of 10^{10} L. Because of our focus on regional-scale fires, smaller wildfires that occurred over the same time period were not sampled.

Runoff and water quality from burned sites was compared to two types of unburned sites sampled as part of prior studies. Sixteen natural unburned sites ranging in size from 1 to 477 km^2 were located in similar geographic settings and had similar land cover (forested or scrub shrub) and geology as was present at the burned sites prior to the fires (Table 1). These sites were all >95% natural open space and had no known anthropogenic sources of contaminants other than aerial deposition (Yoon and Stein 2008).

Six urban unburned sites ranging from 65 to 2161 km^2 in the greater Los Angeles, CA area were also sampled. These sites all drained heavily urbanized areas where runoff from commercial, industrial, and residential land uses is conveyed through engineered flood control channels. Sampling sites were located at the terminal end of catchments that were greater than 65% developed land cover (Table 1).

Stormwater Sampling and Laboratory Analysis

Stormwater runoff was collected from seven streams (encompassing the five sites) that received runoff from the burned areas (Table 1; Figure 1) during the first storms following the fires. Sampling sites were selected so that they captured runoff from as much of the burned area as possible, with little to no contribution from unburned areas. Between two and five storm events were sampled per site over the first one to two years following the fires. Manual grab samples were collected when safety and accessibility permitted. Between six and ten samples were collected per storm at one to two hour intervals. Samples were collected using peristaltic pumps with Teflon® tubing and stainless steel intakes that were fixed at the bottom of the channel, pointed in the upstream direction in an area of undisturbed flow. When site accessibility and/or safety prohibited manual sampling, automatic samplers were used. Samplers were installed before the storm event and streams were auto-sampled to collect four composite samples representing different portions of the storm hydrograph. Sampling occurred from prior to the initial rise of the hydrograph to a point in time when flow decreased to 50% of the peak flow.

Precipitation and flow data were either measured on site, or obtained from the USGS (http://waterdata.

usgs.gov/ca/nwis/rt, gauge 11098000 for Arroyo Seco, and gauge 11055800 for City Creek), the Los Angeles County Department of Public Works precipitation web site (http://ladpw.org/wrd/precip/index.cfm, gauge 408 for Arroyo Seco and gauge 307 for Big Tujunga wash) or the National Weather Service San Diego Region historical precipitation website (http://newweb.wrh.noaa.gov/sgx/obs/rtp/rtpmap.php?wfo=sgx, gauge in San Bernardino for City Creek).

Collected stormwater samples were stored on ice in pre-cleaned glass bottles with Teflon-lined caps until they were shipped to the laboratory for analysis. This study took advantage of sampling efforts being done in concert with other collaborators as well as investigations under our direction; as such the constituents analyzed varied by sampling location but generally included basic constituents, metals, nutrients, TSS, PAHs and various halogens (Table 2). Laboratory analyses followed protocols approved by the US Environmental Protection Agency and Standard Methods by the American Public Health Association (Greenberg *et al.* 2000). In brief, TSS was analyzed by filtering a10- to 100-ml aliquot of stormwater through a tared 1.2 µm Whatman GF/C filter (Whatman International, Maidstone, Kent, UK). The filters plus the solids were dried at 60°C for 24 hours, cooled, and weighed. Metals samples were prepared by nitric acid digestion followed by analysis using inductively coupled plasma–mass spectroscopy. Twenty-six specific PAHs were extracted, separated, and quantified by capillary gas chromatography coupled to mass spectrometry. Analytical techniques and reporting levels were similar among sites for those constituents that were analyzed at more than one sampling location. All laboratories met data quality standards of 20% precision. Samples below the minimum detection limit (MDL) were assigned a value of 50% MDL.

Data Analysis

Change in the volume of post-fire storm runoff was assessed by comparing the runoff ratios of unburned natural, post-fire, and urban catchments. Runoff ratios were calculated as the total volume of discharge per unit area (integrated runoff depth), divided by the total precipitation for each event (total precipitation depth).

Contaminant levels in runoff from the burned areas were compared to constituent levels in runoff from 16 unburned natural areas (Yoon and Stein 2008) and 6 developed catchments not influenced by wildfire (Stein *et al.* 2007). Event flow-weighted mean concentrations (EMC), mass loadings, and flux rates were calculated for each site. The event EMC was calculated for individual storms according to Equation 1:

$$EMC = \frac{\sum_{i=1}^{n} C_i \bullet F_i}{\sum_{i=1}^{n} F_i} \qquad \text{Eq. 1}$$

where: *EMC* was flow-weighted mean concentration for a particular storm; C_i was individual runoff sample concentration of *i*th sample; F_i was instantaneous flow at the time of *i*th sample; *n* was number of samples per event.

Table 2. Method detection limits for the various constituents measured at each sampling location. N/A indicates that the constituent was not analyzed for that location.

Constituent	Arroyo Seco	Big Tujunga Wash	City Creek	Dry Canyon	Santiago Creek	Piru Creek	Ballona Creek
Total metals (µg/L)							
Cu	0.40	0.40	N/A	0.1	0.03 – 0.40	N/A	0.08 – 2.0
Pb	0.05	0.05	N/A	0.1	0.03 – 0.05	N/A	0.03 – 0.5
Ni	0.20	0.20	N/A	0.1	0.03 – 0.20	N/A	0.04 – 5.0
Zn	0.10	0.10	N/A	0.1	0.03 – 0.10	N/A	0.1 – 5.0
PAHs (ng/L)	1 – 1000	1 – 10	N/A	1	1	N/A	1 – 5
Nutrients (mg/L)							
Nitrate	0.01 – 0.04	0.01	N/A	0.02	0.01 – 0.02	0.01	0.01 – 0.05
Total phosphorus	0.02 – 1.60	0.02 – 0.80	N/A	0.02	0.02	N/A	0.01
Sulfate	0.01 – 0.10	0.01	0.01	N/A	0.01	0.01	N/A
TSS (mg/L)	N/A	0.5	N/A	0.1	0.1 – 4.0	N/A	0.1 – 5.0

Event mass loadings were calculated as the product of the EMC and the storm volume during the sampling period. Flux estimates facilitated loading comparisons among catchments of varying sizes. Flux was calculated as the ratio of the mass loading per storm (kg) and contributing catchment area (km^2). In all cases, non-detects were assigned values of one-half the minimum detection limits.

Differences among the groups were investigated using a one-way ANOVA (Sokal and Rohlf 1995) on rank transformed data, with a significance level of $p < 0.05$. An ANOVA on ranks was used because the assumptions of equal variance were not always met, and this procedure has been shown to be more powerful than the Kruskal-Wallis non-parametric one-way ANOVA (Key and Benson 2004). When a significant difference was determined, a Ryan-Einot-Gabriel-Welsch multiple comparison test was used to identify which groups differed. For those analytes that were only measured in two groups (post-fire runoff and either unburned natural or urban areas), a t-test was used with the ranked data.

Controlling mechanisms on the magnitude of constituents in post-fire runoff were investigating by analyzing the influence of underlying geology, stream slope, catchment size, and burn severity. Geology data for southern California were obtained from the USGS mineral resources on-line spatial database (http://tin.er.usgs.gov/geology/state/state.php?state=CA). Differences in flux values between igneous and sedimentary rocks (the two geologic types that dominated the catchments within the sampled watersheds) were examined using student's t-test. The burn severity estimates were developed using methods based on Key and Benson (2004), using information from the Moderate Resolution Imaging Spectroradiometer (MODIS) website (http://modis.gsfc.nasa.gov/). Differences among the groups were investigated using an ANCOVA (Sokal and Rohlf 1995) on ranked data with event rainfall as a covariate. In all cases we used a significance level of $p < 0.05$.

The persistence and/or attenuation of contaminant levels in post-fire runoff were evaluated based on variations in contaminant flux relative to the cumulative rainfall since each fire. Cumulative rainfall was used instead of time-since-end-of-burn because we hypothesize that reductions in contaminants are likely due to the washoff-effect from subsequent rain events. Contaminant flux was also investigated in relation to rainfall amounts during each individual storm. For these analyses, data from all study sites were pooled and analyzed using Pearson correlation analysis with log-transformed chemistry data.

Potential indirect effects of fire on contaminant loading were evaluated by comparing pre- and post-fire EMC data in runoff from the unburned Ballona Creek watershed, which received ash fallout from six of the concurrent wildfires in southern California in October 2003 (Figure 2). The Ballona Creek watershed is located in western Los Angeles County, approximately 20 km from the nearest wildfire. The sampling point drains 230 km^2 and is approximately 85% developed, representing a typical urbanized watershed for southern California (Ackerman *et al.* 2005). Pre-fire stormwater runoff chemistry data were available from four rain events measured during a previous study, while three post-fire sampling events were captured, beginning in October 2003. Flow data for Ballona Creek was obtained from the US Army Corps of Engineers website (http://www.spl.usace.army.mil/cgi-bin/cgiwrap/zinger/slLatestBasin.cgi?lacda+stage). Background contaminant levels in Ballona Creek were estimated as the upper 95% prediction level of the pre-fire log-transformed EMCs. Contaminant concentrations in the post-fire samples were considered enriched (i.e., greater than typical concentrations in this stream) if their log-transformed EMCs exceeded these background levels.

Results

Relative Magnitude of Contaminant Loading

Average runoff ratios and runoff per unit area were comparable between burned and unburned natural areas (Table 3). Peak flows from burned catchments were "flashier" (rapid rise and decline in the hydrographs) than in natural unburned areas, and had hydrographs that were comparable to urban catchments (Figure 3).

Mean Cu, Pb and Zn flux and concentration were significantly higher from burned catchments than unburned natural areas ($p < 0.0001$ for Cu, Pb and Zn), with differences ranging from a 112-fold increase for Cu to a 736-fold increase for Pb (Figure 4). The total PAH mean flux from burned areas was four times greater than from urban areas, although the differences were not significant (PAHs were not measured in unburned natural areas). Total phosphorous concentrations from burned areas were enriched by 921-fold relative to unburned natural areas (*p*

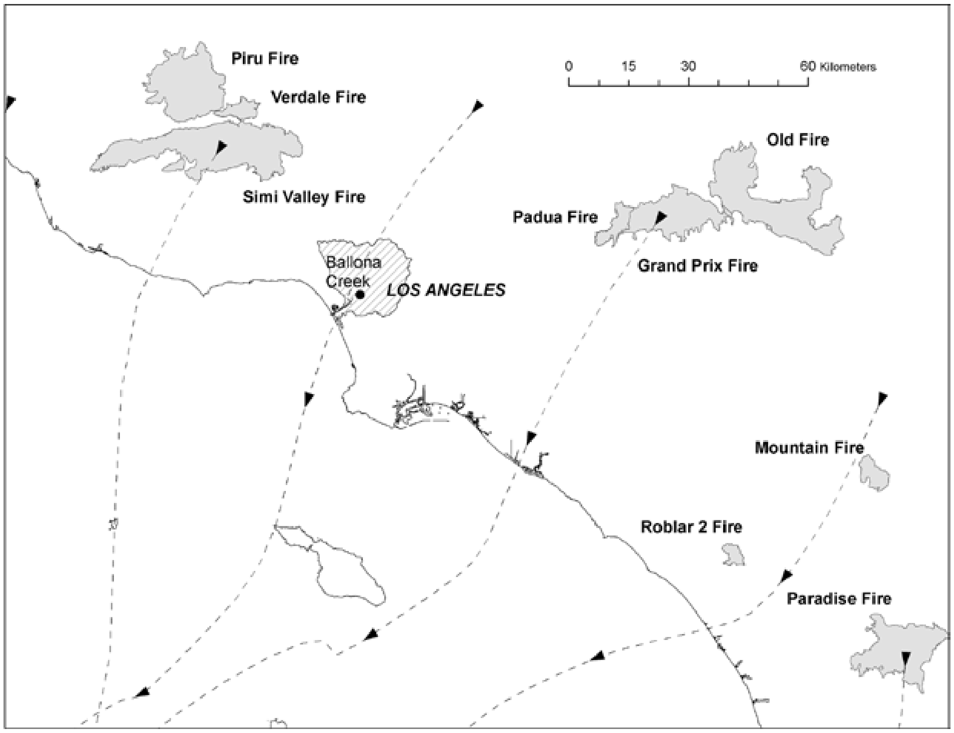

Figure 2. Wildfires in the greater Los Angeles area in October 2003, which may have contributed to the ash fallout effecting runoff water quality in the Ballona Creek watershed. The wind trajectory lines are from October 26, with the arrows separated by 6 hours

<0.0025). We expected nitrate+nitrite enrichment to be lower as it is typically found predominantly in the dissolved phase. This was the case; nevertheless, nitrate+nitrite concentrations were still two- to four-fold higher for burned areas compared to unburned natural areas ($p < 0.0007$; Figure 5).

Persistence of Elevated Contaminant Levels

Contaminant flux values were positively correlated with event rainfall for metals, nutrients, and total PAHs (Figure 6). Total suspended solids were not significantly correlated with event rainfall; however, TSS was analyzed in fewer storm events and did not include the largest storms sampled. There did not appear to be a consistent relationship between flux and cumulative rainfall, therefore no threshold in cumulative rainfall was identified which coincided with a reduction in contaminant flux. Examining the data by location did not improve the interpretation of how long contaminant levels persist.

Other factors that were evaluated that may influence the magnitude or persistence of contaminant loading included underlying geology, burn severity, catchment size, and steepness. Of these factors, only geology showed some relationship to the effect of fire on contaminant loading. Runoff from burned areas underlain by sedimentary rock resulted in TSS flux values that averaged 2,540 times that of fires in catchments underlain by igneous ($p = 0.01$; Figure 7). However, unlike TSS, there were no differences in concentrations or flux of metals, nutrients, or PAHs based on the underlying geology.

Indirect Effects

Indirect effects were observed in the urban catchment that was not burned but received smoke and ash fallout from regional fires. Concentrations of metals and PAHs in Ballona Creek were greatest in the runoff during the storm event immediately following the wildfires (Figure 8). The first post-fire EMCs of Cu, Pb, Ni, Zn and total PAHs were each three times the mean of the pre-fire values, with Cu, Pb and Zn exceeding the upper 95% prediction interval of the pre-fire EMCs. The concentrations of metals in Ballona Creek decreased to background levels after the first post-fire storm event following the regional wildfires. Post-fire total PAHs also decreased after the first storm event following the fires, but post-fire concentrations did not exceed the background levels.

Discussion

Burned natural areas exhibit contaminant loading properties similar to those of urban landscapes. In particular, PAH, metals and nutrient concentrations

Table 3. Runoff ratios for post-fire and unburned natural and urban watersheds.

Site	Storm Date	Watershed Size (km^2)	Event Rainfall (mm)	Flow (m^3)	Runoff Ratio
Post-Fire					
Santiago	12/8/07	17	34.5	4919	0.008
Santiago	2/25/08	17	10.7	8645	0.048
Dry Canyon	12/25/03	5	41.1	6228	0.032
Dry Canyon	2/26/04	5	54.9	220750	0.838
Dry Canyon	1/7/05	5	25.1	12916	0.107
Arroyo Seco	10/13/09	42	71.1	23568	0.008
Arroyo Seco	1/13/10	42	5.1	934	0.004
Arroyo Seco	1/17/10	42	105.7	1114109	0.254
Arroyo Seco	2/5/10	42	82.3	1072469	0.314
Arroyo Seco	3/6/10	42	28.4	142379	0.121
Big Tujunga Wash	10/14/09	61	25.4	28764	0.019
Big Tujunga Wash	12/7/09	61	32	7276	0.004
Big Tujunga Wash	12/12/09	61	54.9	38578	0.011
Piru	12/9/06	512	11.2	9689	0.002
Piru	12/16/06	512	1.3	7136	0.011
Piru	1/27/07	512	48.8	207551	0.008
Piru	2/22/07	512	3.3	22019	0.013
Piru	4/20/07	512	8.9	37055	0.008
City Creek	2/25/04	51	20.6	112096	0.107
City Creek	3/1/04	51	27.7	84598	0.06
RANGE		5 - 512	1.3 - 105.7	934 - 1,114,109	0.002 - 0.838
Unburned, No Fire Influence - Natural Area					
Arroyo Seco	3/22/05	42	28.7	17774	0.015
Arroyo Seco	2/27/06	42	85.3	339155	0.095
Arroyo Sequit	12/28/04	27	49.3	4228	0.003
Arroyo Sequit	1/7/05	27	55.4	18646	0.012
Arroyo Sequit	4/4/06	27	53.6	319212	0.221
Bear Creek Matilija	2/27/06	10	147.8	148985	0.101
Bear Creek WFSGR	4/4/06	73	124	1051321	0.116
Bell Creek	1/7/05	18	35.3	33863	0.053
Bell Creek	1/2/06	18	41.4	20145	0.027
Cattle Creek EFSGR	4/27/05	53	27.4	133684	0.092
Cattle Creek EFSGR	12/31/05	53	11.4	1253	0.002
Chesebro Creek	1/7/05	8	50.8	9234	0.023
Coldbrook NFSGR	4/27/05	3	28.7	27996	0.325
Coldbrook NFSGR	12/31/05	3	172	72372	0.14
Cristianitos Creek	1/7/05	51	35.6	147840	0.082
Fry Creek	2/11/05	1	57.2	4664	0.082
Fry Creek	3/28/06	1	45.7	3176	0.069
Mill Creek	3/28/06	15	63.5	18914	0.02
Piru Creek	2/27/06	477	79.8	816515	0.021
Santiago Creek	2/11/05	17	64.5	341851	0.312
Santiago Creek	1/2/06	17	52.6	5167	0.006
Santiago Creek	3/10/06	17	20.6	14927	0.043
Sespe Creek	2/27/06	128	143	1265404	0.069
Silverado Creek	2/11/05	21	67.8	436975	0.307
Silverado Creek	1/2/06	21	47.2	12355	0.012
Tenaja Creek	4/28/05	42	23.4	42158	0.043
Tenaja Creek	2/27/06	42	8.1	165795	0.486
RANGE		1 - 477	8.1 - 172.0	1253 - 1,265,404	0.002 - 0.486

Table 3. Continued

Site	Storm Date	Watershed Size (km^2)	Event Rainfall (mm)	Flow (m^3)	Runoff Ratio
Unburned, No Fire Influence - Urban Area					
LA River above Arroyo Seco	1/26/01	1460	18	1670884	0.063
LA River above Arroyo Seco	2/9/01	1460	14.2	725320	0.035
LA River above Arroyo Seco	2/12/01	1460	96.8	3833944	0.027
LA River at Wardlow	1/26/01	2161	18	592634	0.015
LA River at Wardlow	2/9/01	2161	14.2	34539	0.001
LA River at Wardlow	5/2/03	2161	35.6	14355784	0.187
LA River at Wardlow	2/2/04	2161	11.4	2277114	0.092
Verdugo Wash	1/26/01	65	18	808137	0.689
Verdugo Wash	2/9/01	65	14.2	449744	0.487
Verdugo Wash	11/12/01	65	96.8	1233626	0.196
Arroyo Seco	2/9/01	130	35.6	63664	0.014
Arroyo Seco	4/7/01	130	17.8	225511	0.097
Ballona Creek	2/18/01	338	15	548709	0.108
Ballona Creek	4/7/01	338	12.4	821612	0.195
Ballona Creek	11/24/01	338	15.2	1147447	0.223
Ballona Creek	5/2/03	338	20.3	1331529	0.194
Dominguez Channel	3/17/02	187	2.8	85858	0.164
Dominguez Channel	2/21/04	187	15.2	740174	0.26
RANGE		65 - 2,161	2.8 - 96.8	34,539 - 14,355,784	0.001 - 0.689
AVERAGE		845	26.2	1,719,235	0.169

were comparable to those from fully developed catchments. We are aware of only one previous study that documented metals enrichment in post-fire runoff, and none that monitored PAHs following fires. Gallaher and Koch (2004) documented Cu, Pb, and Zn concentrations in post-fire runoff following the Cerro Grande fire in New Mexico that were similar to the ranges observed in this study (4 - 290 µg/L total Cu, 0.4 - 860 µg/L total Pb, 14 - 1380 µg/L total Zn). However, concentrations from the Cerro Grande fire were not compared to corresponding data from unburned natural and urban catchments. Of particular note from this study is that the concentrations and fluxes we measured are typically several hundred times higher from burned areas than natural background levels, particularly during large rain events. These concentrations are 60 to 200% higher than levels considered toxic under the California Toxics Rule (promulgated by the California State Water Resources Control Board), suggesting that levels have the potential to contribute to toxic effects in downstream aquatic organisms. Numerous previous studies have documented increases in nutrient concentrations by up to several 100-fold following fires (Earl and Blinn 2003, Bladon *et al.* 2008, Smith *et al.* 2011) as observed in this study.

In the years following fires, contaminant loading from burned landscapes has the potential to be a substantial contribution to the total annual load to downstream areas. To provide context we compared mass loadings from storms measured as part of this study to estimated annual loads for wet and dry years from a regionally calibrated stormwater runoff model based on the Rational Method (Ackerman and Schiff 2003). The most direct comparison is between the Arroyo Seco and Tujunga watersheds (which burned during the Station Fire) and the larger Los Angeles River watershed to which both these subwatersheds drain. Based on mean loads, we estimate that a single post-fire storm can produce between 5 and 40% of the total annual load of metals and between 7 and 35% of the total annual load of PAHs for the entire Los Angeles River watershed (depending on the total annual rainfall). We do not have the ability to directly relate increased flux from burned areas to increases in total contaminant load at downstream areas due to confounding factors such as spatially variable rainfall, role of interception by debris basins, and additional downstream sources. Nevertheless, the relative magnitude of loads from burned areas suggest that post-fire runoff is a significant source of contaminants to downstream areas and is worthy of management attention.

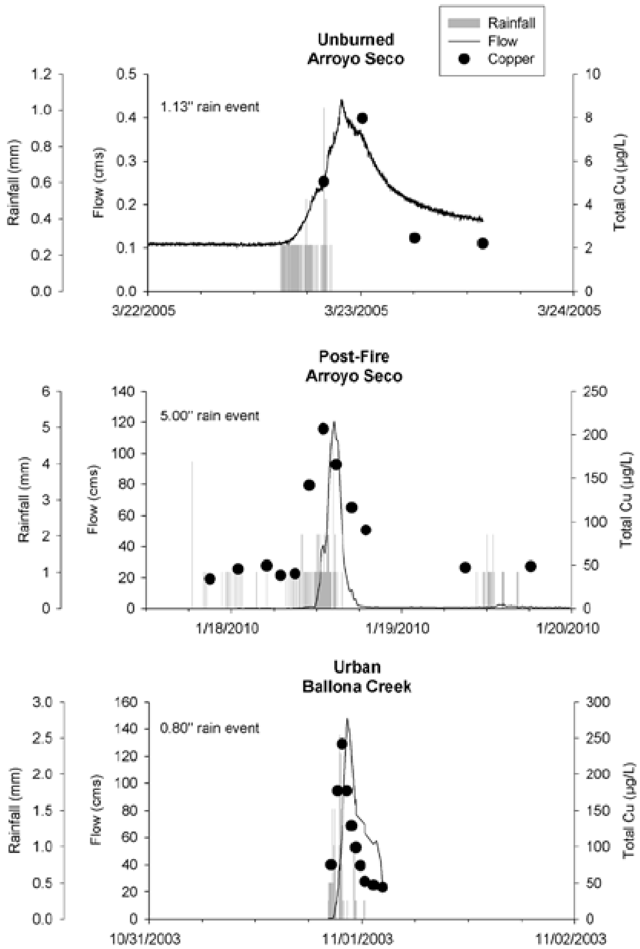

Figure 3. Hydrographs and pollutant mobilization at unburned natural, post-fire, and urban catchments. The examples provided here are representative of differences in hydrographs observed between treatment groups at all study locations. The Arroyo Seco and Ballona Creek catchment areas are 42 and 230 km^2 at their respective sampling locations.

Although TSS and phosphorous flux values were more than four times higher in post-fire runoff than in natural unburned areas, the differences were not significant, likely due to the high variability associated with post-fire conditions. Variability in sediment flux is reflected by values that ranged from 10 to 500,000 kg/km^2. These values bracket the sediment flux values observed in previous studies. For example, Kunze and Stednick (2006) reported sediment flux of 95,000 kg/km^2 following the Bobcat fires in Colorado. Moody and Martin (2001) summarized sediment flux ranging from 41,000 to 146,000 kg/km^2 from burned sites in Colorado and Australia, and Petticrew *et al.* (2006) reported average flux of 12,000 kg/km^2 from burned sites in British Columbia. Site-specific results were often less variable. For example, at the Simi Valley site we monitored paired catchments and consistently observed a greater than 1,000-fold increase in sediment flux from burned catchments relative to unburned catchments of similar size and land cover. Measurements over multiple storms from the Santiago and Tujunga sites exhibited a five- to seven-fold increase in sediment flux relative to unburned natural areas. Other authors have reported a 6- to10-fold increase in sediment yield following medium to large scale fires (Key and Benson 2004, Gallaher and Koch 2004, Earl and Blinn 2003, Bladon *et al.* 2008, Smith *et al.* 2011, Kunze and Stednick 2006, Moody and Martin 2001, Petticrew *et al.* 2006, Ice *et al.* 2004, Warrick and Rubin 2007, Silins *et al.* 2009).

Anecdotal observations at individual study sites suggest that sediment and contaminant flux returns to near baseline levels within several years following fires, with the majority of attenuation occurring in the first two years, depending on rainfall. For example, following the Santiago Fire, metals and TSS concentration and flux increased by 10-fold over measured pre-fire levels, but returned to baseline levels by the first storm of the subsequent season. Similar results were observed for the paired catchments measured in the Simi Fire burned areas. Studies from US Forest Service's San Dimas experiment forest in southern California show that nearly all (85%) of the total sediment delivered to the debris basins following fires came in the first year after the fire (Wohlgemuth *et al.* 2008). Similarly, Robichaud *et al.* (2009) reported substantial reduction in sediment yield in the first three years following the 2000 Bitterroot Valley wildfires fires in Montana. Gallaher and Koch (2004) reported that by the end of the third rainy season after the Cerro Grande (New Mexico) fire, concentrations of metals in suspended sediment carried by runoff from burned areas typically fell to near pre-fire background levels. The decreases in concentrations appear to be related to a flushing of ash and burned soils from the landscape by runoff events.

Despite these site-specific patterns, when looking at the results of all five fires, no statistically consistent patterns emerged as either a function of time or cumulative precipitation following the fire. Instead flux and concentration were more dependent on total event rainfall and intensity, which may have an overriding effect on the amount of material mobilized from the contributing drainage area and delivered to the stream. Wohlgemuth *et al.* (2008) also observed that consistent attenuation timeframes

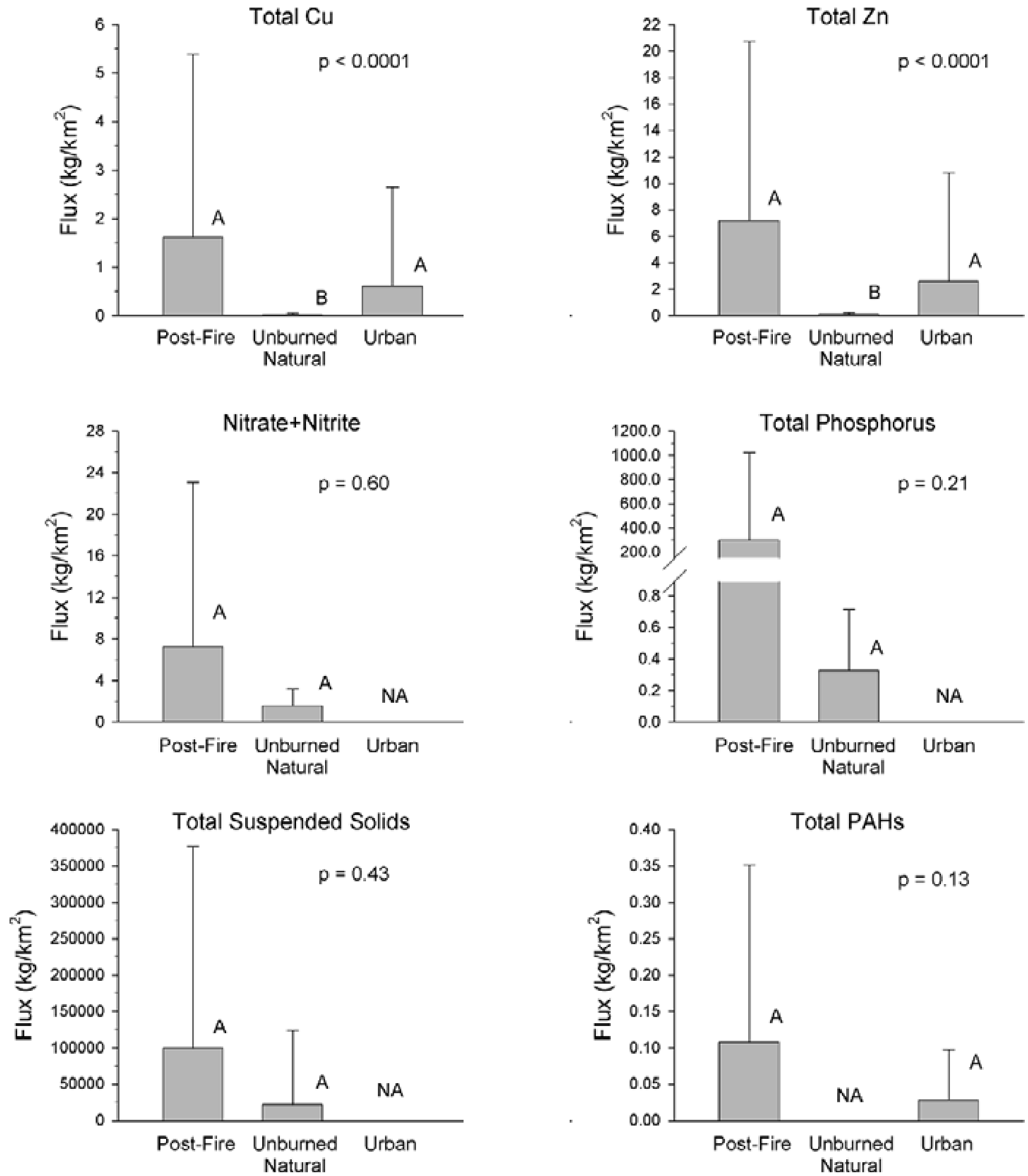

Figure 4. Contaminant flux among regional sources. The bars represent the mean flux + standard deviation of individual storms. The letters indicate statistical similarities ($p \leq 0.05$). NA = not analyzed.

are difficult to predict and that catchment response in southern California is perhaps more related to the regional factors of topography, soils, and rainfall than to fire characteristics. Robichaud *et al.* (2009) also reported a significant linear relationship between 10-minute rainfall intensity and sediment flux as the predominant predictive factor in attenuation of post-fire sediment yields over time.

The difficulty in predicting persistence of elevated contaminant levels may be a function of the time-variable mechanisms of response following fires. Immediately following fire, contaminant delivery to streams is a function of reduced rainfall interception associated with loss of vegetated cover, increased runoff, and increased water repellency due to chemical changes in soil properties (Wiilliard *et al.* 2005, Debano 2000). This is often associated with higher erosion, rill and gully formation and sediment washoff (Cannon *et al.* 2001). These effects have been shown to decrease markedly in the first 1 to 3 years following fires depending on site-specific conditions and rainfall (Moody and Martin 2001, Ice *et al.* 2004, Robichaud *et al.* 2009, Dodds *et al.* 1996, Gray and Dighton 2006). As the catchment begins to recover, these factors likely decrease in importance

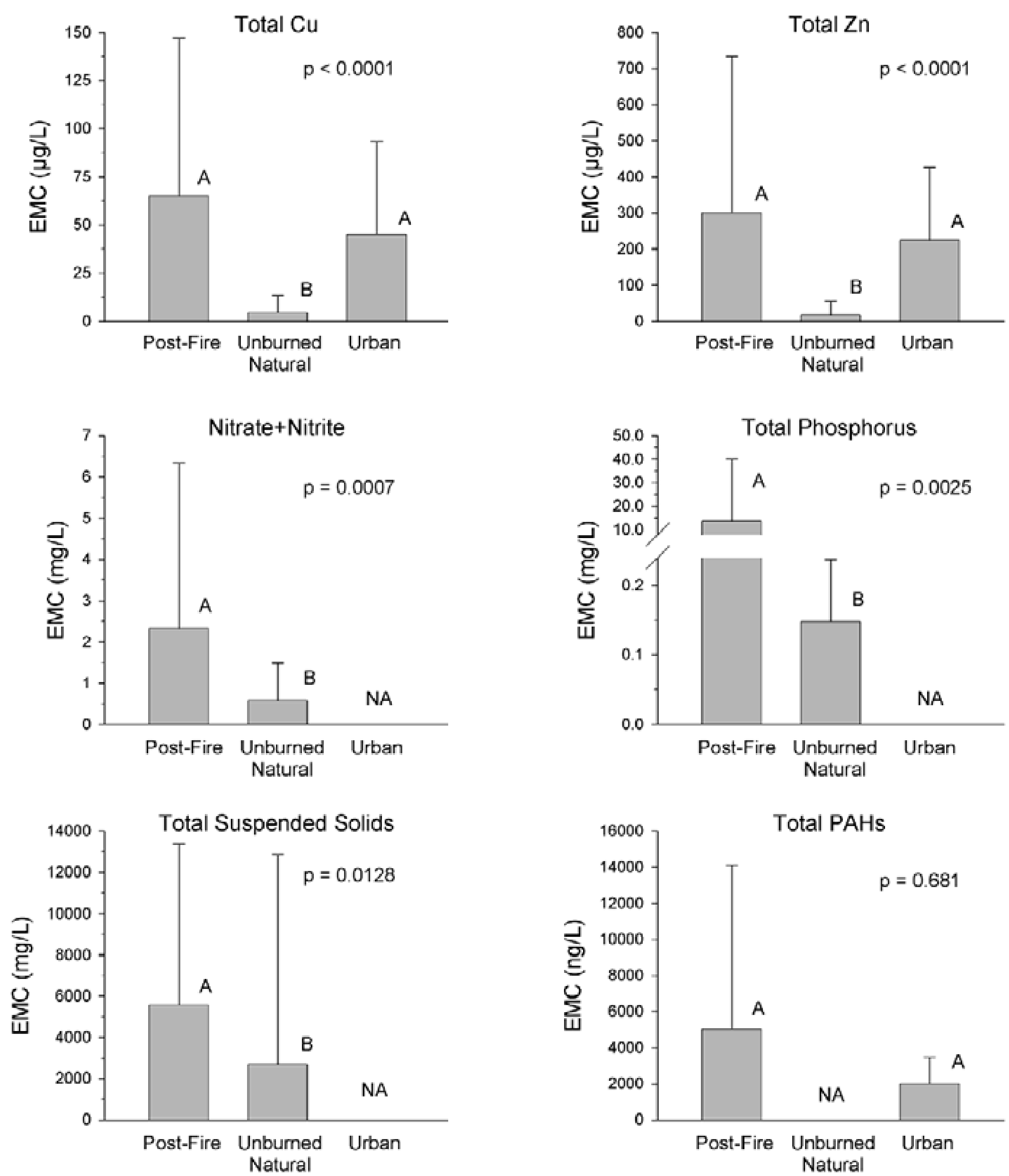

Figure 5. Contaminant concentrations among regional sources. The bars represent the mean + standard deviation of individual storm EMCs. The letters indicate statistical similarities ($p \leq 0.05$). NA = not analyzed.

and are surpassed by residual effects of fine particle and ash delivery to the streams. Ash monitoring following the 2007 southern California wildfires showed significantly elevated levels of metals (hundreds of parts per million) and other contaminants in ash that persisted at least a year following fire (Plumlee *et al.* 2007). This ash may adhere to soil and organic matter and persist in streams and adjacent drainage areas for years, depending on rainfall patterns. Elevated fine sediment levels that persist for several years following reduction in the overall sediment yield suggest continued leaching of materials from burned watersheds (Gallaher and Koch 2004). This pattern was also observed in runoff from the Santiago Fire where the relative proportion of particle-bound to dissolved metals remained high for three years, despite reductions in overall metal flux. While the data on persistence patterns is inconsistent from site to site, it does suggest that sampling from burned catchments should extend beyond the first several years and/or 75 cm of cumulative rainfall in the southern California region.

Aerial deposition can be a substantial source of contaminant loading following fires. Unlike direct runoff, aerial deposition can affect both burned and

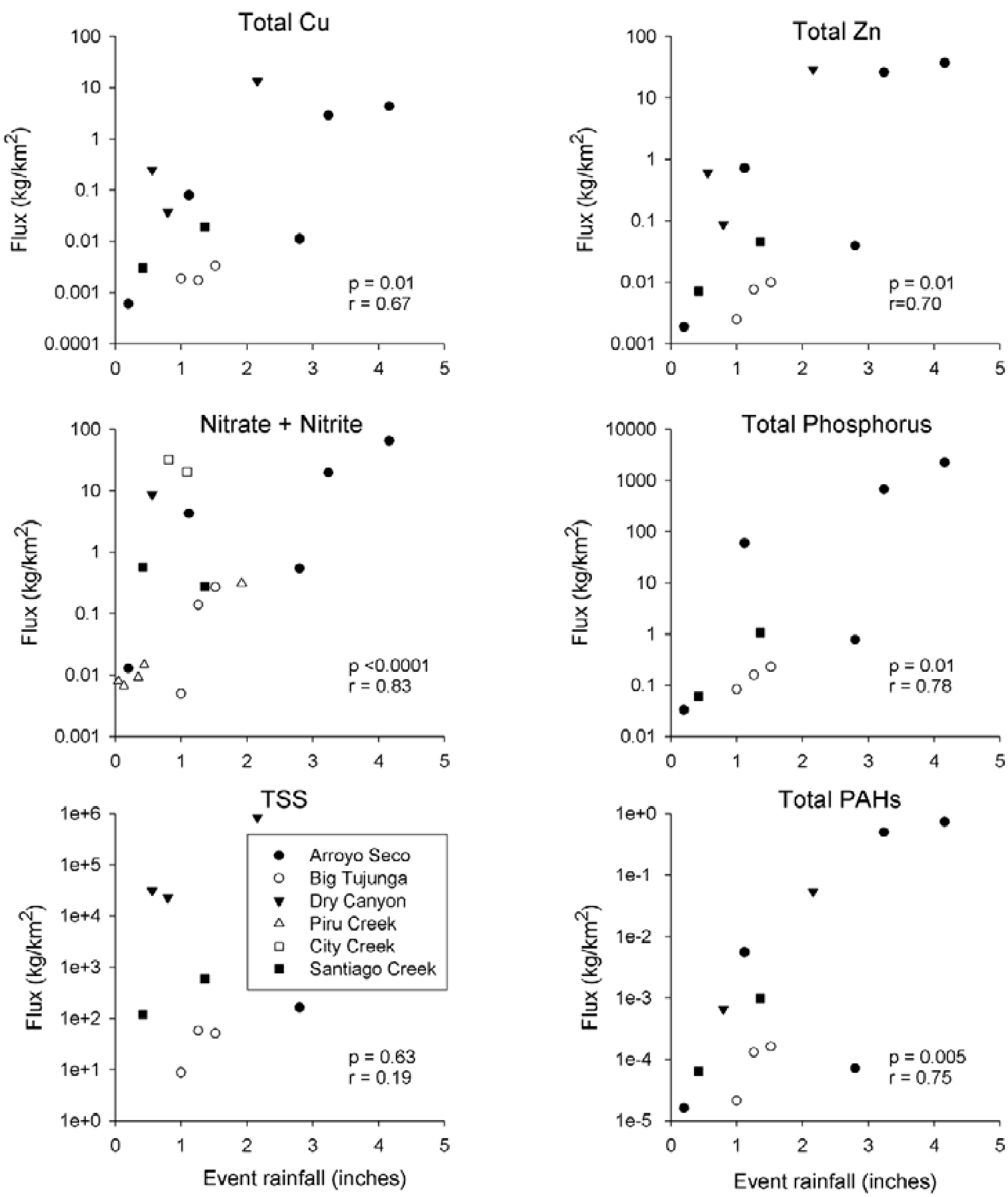

Figure 6. Relationship between contaminant flux and event rainfall for the burned catchments.

unburned catchments depending on prevailing wind patterns. Results from the Ballona Creek watershed indicate that peak stormwater concentrations of metals and PAHs following ash fallout from the 2003 wildfire season were approximately triple those seen in "typical" urban stormflow. From a mass perspective, we estimate that approximately 10% of the total annual load of metals and PAHs in 2003 may have come from these storms, based on regional urban stormwater loading estimates from Stein *et al.* (2007). PAHs were comprised of primarily high molecular weight compounds, which are indicative of combustion by-products. Earlier work in southern California also documented distinct increases in dry aerial deposition rates of nine trace metals along the section of the southern California coast covered by a forest fire smoke following the 1975 Angeles National Forest Fires (just north of Los Angeles); that study reported dry deposition rates of 4, 10, and 18 µg/week for Cu, Pb, and Zn, respectively (Young and Jan 1977). Gerla and Galloway (1998) also reported a doubling of nitrate concentrations in the unburned Crow Creek watershed associated with ash fallout that persisted for a year following the 1998

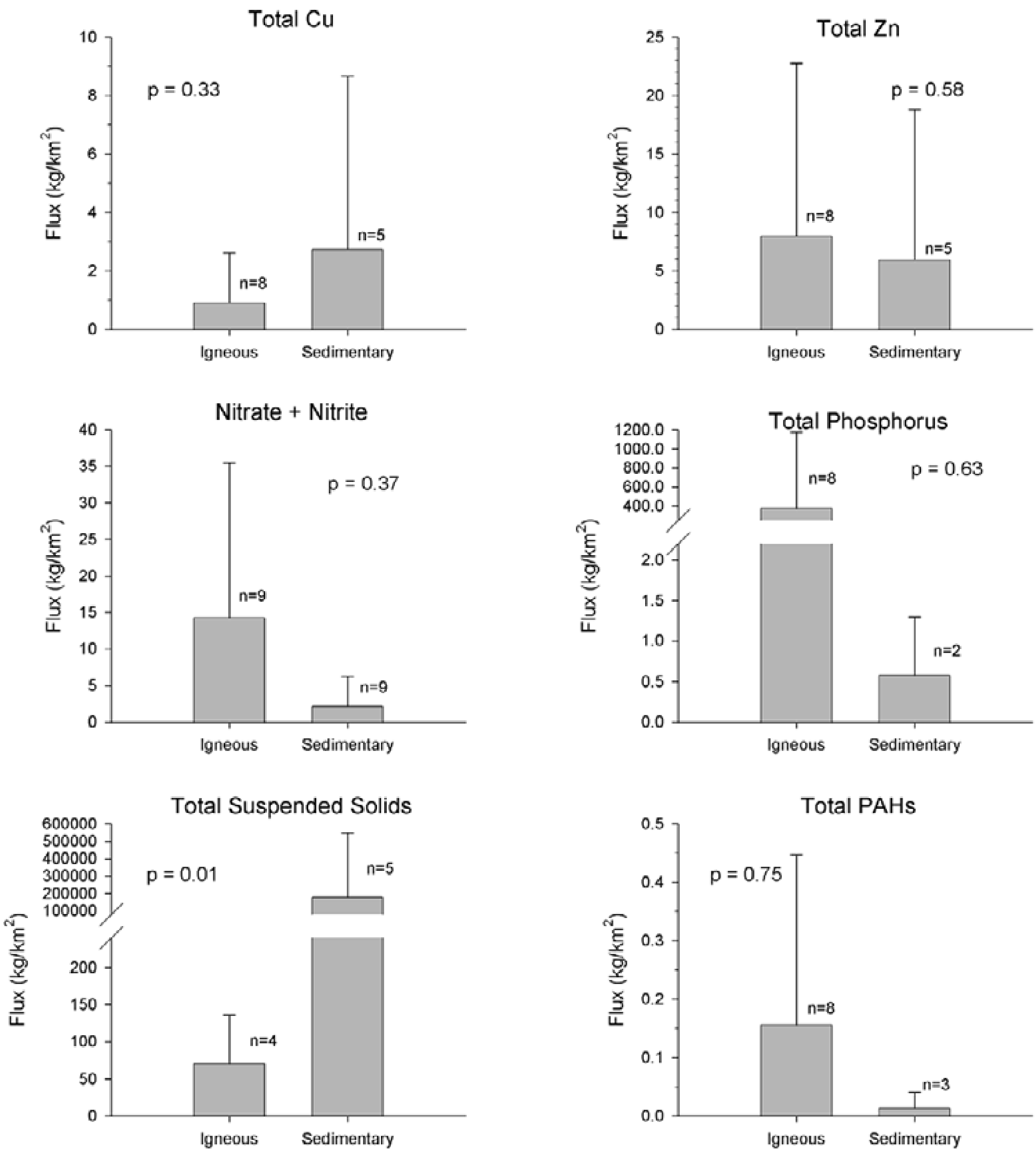

Figure 7. Differences in contaminant flux by underlying geology. The bars represent the mean flux + standard deviation of burn sites.

Yellowstone wildfires. Unlike the regional patterns of elevated contaminant levels from directly burned catchments, concentrations in the Ballona Creek watershed were only high for the first storm event. The substantial amount of impervious cover in this watershed likely resulted in near complete washoff during the first storm. The indirect effects observed in the Ballona Creek watershed probably represent a worst-case scenario. Prevailing wind patterns delivered ash from several large fires directly over the Ballona Creek watershed (Figure 2) and the first storm event occurred while the regional wildfires were still burning (helping to extinguish the flames); thereby maximizing opportunities for aerial scavenging and deposition. The presence of ash in urban areas may not be as dramatic for the first post-fire storm event under different circumstances, where there are days or weeks between wildfire and storms and an opportunity for wind to dissipate the deposited ash. Nevertheless, these results indicated that water quality managers in areas not receiving direct runoff from burned areas may need to consider the effect of wildfire as a potential source of contaminants affecting water quality.

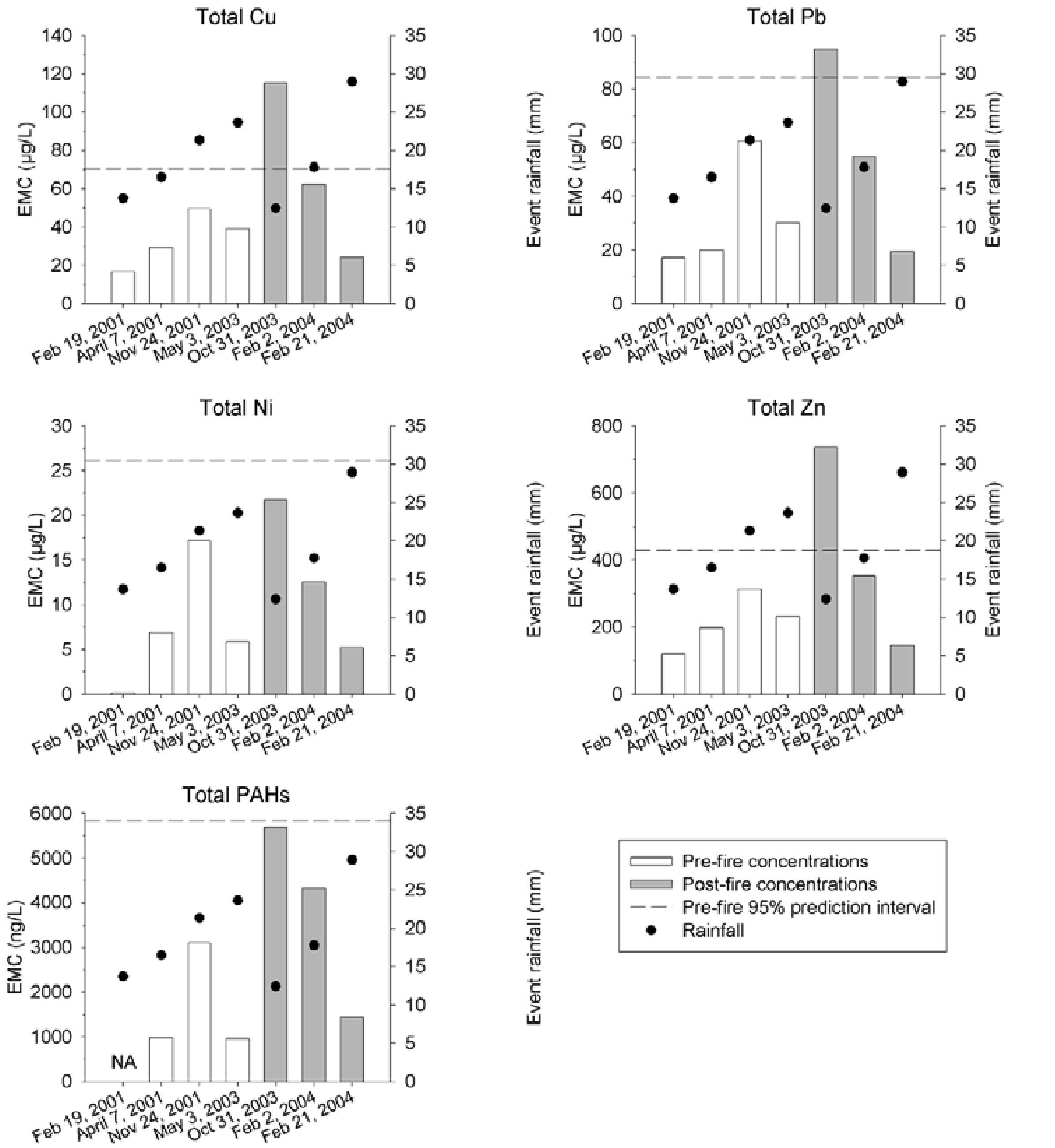

Figure 8. Event mean concentrations in Ballona Creek urban storm water runoff, before and after the October 2003 regional wildfires. NA = not analyzed.

We advocate that future studies of post-fire stormwater quality should focus on understanding additional sources and factors that may influence the magnitude and persistence of post-fire contaminant effects and on the effect of fire on biological end-points. This study did not address potential effects of commonly used flame retardants, which have been shown to have potentially toxic effects on instream biota (Little and Calfee 2002). Post-fire response may include installation of management measures aimed at reducing erosion and downstream delivery of sediment and contaminants. None of the fires we studied made extensive use of these measures; however, when properly installed such measures have the ability to capture up to two-thirds of excess sediment Kunze and Stednick (2006). From an effects perspective, our analysis focused on measures of total metals because the majority of metals occur in the particulate phase (particularly following fires). However, the dissolved fraction of metals is more bioavailable and may be a better indicator of potential toxic effects. Future studies aimed at understanding the distribution of particulate to dissolved metals over time, particularly in the three to five years following fires would aid in evaluation of potential toxic effects to instream biota and downstream sensitive species.

Finally, since many water quality regulations and monitoring programs are increasingly focused on biological endpoints, such as benthic macroinvertebrates, understanding the effect of post-fire runoff on these communities should be a priority. Past research following fires in the Gila River Watershed in Arizona suggest that the density of macroinvertabrates is substantially lower in streams receiving ash input, but that macroinvertebrate densities return to prefire conditions within one year (Earl and Blinn 2003). However, a literature review by Minshall (2003) found that direct effects of fire are generally minor or indiscernible. In contrast, indirect effects, resulting primarily from increased rates of runoff and channel alteration, have the greatest impacts on macroinvertebrate community metrics and foodweb responses. Minshall (2003) also found that post-fire effects are variable in time and space, but in smaller size streams that are otherwise undisturbed, changes generally are restricted to the first 5 to 10 years following fire. However, affects may be more important in streams already affected by other stressors. More focused monitoring of both the chemical and biological effects of post-fire runoff will help managers better target their actions to address potential deleterious effects associated with contaminants in post-fire runoff.

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