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Pre- and post-fire pollutant loads in an urban fringe watershed in Southern California

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Abstract Post-fire runoff has the potential to be a large source of contaminants to downstream areas. However, the magnitude of this effect in urban fringe watersheds adjacent to large sources of airborne contaminants is not well documented. The current study investigates the impacts of wildfire on stormwater contaminant loading from the upper Arroyo Seco watershed, burned in 2009. This watershed is adjacent to the Greater Los Angeles, CA, USA area and has not burned in over 60 years. Consequently, it acts as a sink for regional urban pollutants and presents an opportunity to study the impacts of wildfire. Pre- and post-fire storm samples were collected and analyzed for basic cations, trace metals, and total suspended solids. The loss of vegetation and changes in soil properties from the fire greatly increased the magnitude of storm runoff, resulting in sediment-laden floods carrying high concentrations of particulate-bound constituents. Post-fire concentrations and loads were up to three orders of magnitude greater than pre-fire values for many trace metals, including lead and cadmium. A shift was also observed in the timing of chemical delivery, where maximum suspended sediment, trace metal, and cation concentrations coincided with, rather than preceded, peak discharge in the post-fire runoff, amplifying the fire's impacts on mass loading. The results emphasize the importance of sediment delivery as a primary mechanism for post-fire contaminant transport and suggest that traditional management practices that focus on treating only the early portion of storm runoff may be less effective following wildfire. We also advocate that watersheds impacted by regional urban pollutants have the potential to pose significant risk for downstream communities and ecosystems after fire.

Keywords Wildfire · Urban fringe · Stormwater · Los Angeles · Metals

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Introduction

Wildfires alter normal hydrologic function and behavior, ultimately increasing contaminant mobility in affected watersheds. Physical changes resulting from wildfire include acute loss of vegetation and soil organic matter, decreased soil cohesion, enhanced soil water repellency, ash layer deposition, and decreased infiltration and increased water directed to the surface and near surface pathways of burned watersheds (DeBano 2000; Robichaud 2000; Letey 2001; Jung et al. 2009). These changes greatly impact both the magnitude and timing of post-fire peak flows. Early post-fire runoff is elevated and can remain high for significant periods of time, increasing the potential for flooding several years following a wildfire (Pierson et al. 2001; Rulli and Rosso 2007; Moody et al. 2008; Moody and Martin 2009). In chaparral systems, such as those found in Southern California, increased runoff ratios have been found up to 8 years post-fire, depending on precipitation patterns, burn severity, geophysical parameters, and vegetation recovery (Scott and Meixner 2004; Kinoshita and Hogue 2011). The increase in overland flow and accelerated time to peak during post-fire storm events result in increased stream power, erosion potential, and pollutant delivery.

Wildfires are a mechanism that liberates deposited contaminants, mobilizing their transport through storm runoff. Total suspended solid (TSS) concentrations in stormwater often increase by orders of magnitude, increasing the potential mobilization and transport of particulate-bound contaminants in post-fire storm runoff (Bitner et al. 2001; Neary et al. 2005; Desilets et al. 2007; Malmon et al. 2007; Rothenburg et al. 2010; Smith et al. 2011). Increased nutrient concentrations, especially nitrate and phosphate, are commonly observed in burned systems, including Southern California's coastal mountain ranges (Riggan et al. 1985; Ranali 2004; Meixner et al. 2006; Stein et al. 2012). Trace metals released from vegetation during a fire and redeposited on soil surfaces or retained in watershed soils are subject to mobilization and transport during post-fire storms (Loring 1991; Thomson et al. 1997; Burke et al. 2010; Schiff and Tiefenthaler 2011). Wildfire's impacts on mercury transport has received some attention (Caldwell et al. 2000; Kelly et al. 2006; Burke et al. 2010; Rothenburg et al. 2010); however, fewer studies have focused on the delivery of other trace metals following fire. Studies in New Mexico's 2000 Cerro Grande Fire and Australia's 2003 bushfires in Alpine National Park reported significantly higher total concentrations of several metals, including As, Al, Ba, Cd, Cr, Fe, Mn, Pb, and Zn, in post-fire runoff (Bitner et al. 2001; Gallaher et al. 2002; Leak et al. 2003; Smith et al. 2011).

The Southern California region provides a unique opportunity to study the impacts of wildfire on urban fringe stormwater, given the close proximity between urban and natural areas and narrow airsheds (due to coastal mountain ranges) that trap air masses and facilitate high deposition rates onto the wildland areas. Winds carry pollutants from western Los Angeles sources towards the San Fernando Valley and into the eastern part of the Los Angeles Basin. Urban contaminants are deposited via both wet and dry depositions in the San Bernardino and San Gabriel Mountains, which are considered to have some of the highest deposition rates in the country (Fenn and Bytnerowicz 1997; Lu et al. 2003). Previous work in the area noted significant nutrient and other chemical loads in the storm runoff of urban fringe watersheds (Fenn and Poth 1999; Meixner et al. 2001; Fenn et al. 2003; Barco et al. 2008; Stein et al. 2012). Post-fire storm events in these contaminated, urban fringe basins have the potential to contribute significant chemical loads to downstream waterbodies, which are often already impaired and subject to management actions pursuant to TMDLs (SWRCB 2010). The two reaches of the Arroyo Seco, located downstream of the study area, are listed as impaired due to trash and coliform bacteria, while the Los Angeles River reach 2 (downstream of the Arroyo Seco confluence) listings also include ammonia, copper, lead, nutrients, oil, scum, and taste/odor (SWRCB 2010). Further downstream, water quality impairments increase to include other metals such as cadmium and zinc in the lower reaches of the Los Angeles River, as well as sediment toxicity in the Long Beach Inner Harbor (SWRCB 2010). The goal of the current study is to compare post-fire water quality with pre-fire baseline data in order to better understand the impacts of wildfire on mass loading in highly impacted, urban fringe landscapes. We ultimately hope that information from our work will provide improved guidance for post-fire watershed management practices. Our monitoring efforts focus on the mobilization and transport of trace metals throughout the first post-fire storm season after a major wildfire in the Greater Los Angeles region.

Methods

Study area

The Arroyo Seco runs within a deeply carved canyon that begins near the top of the San Gabriel Mountains in the Angeles National Forest (Fig. 1). After exiting the upper basin, the Arroyo Seco is channelized and eventually converges with the Los Angeles River near downtown Los Angeles. Several reaches downstream of the Arroyo Seco's confluence with the Los Angeles River are listed as impaired for Cd, Pb, Cu, Zn, and Al pursuant to Section 303(d) of the Federal Clean Water Act (SWRCB 2010). The upper Arroyo Seco watershed, hereafter noted as the Arroyo Seco watershed, consists of approximately 41.4 km^2 of steep, mountainous terrain with elevations ranging from 431 to 1,880 m above sea level. The watershed slope and length are estimated to be 5.7 % and 17.2 km, respectively. Due to orographic effects, the average annual precipitation (840 mm/year) is relatively high compared to that of the Los Angeles Basin (375 mm/year) (LADPW 2010). The long-term (water year (WY) 1911–2010) annual stream discharge is 0.28 m^3/s, and the annual runoff coefficient is 0.22 (WY 1975–2010) (US Geological Survey (USGS) 2011). Shallow, coarse soils are found throughout the watershed, composed mostly of silty sand and gravelly silty sand, and are underlain by mainly igneous rock (Division of Mines and Geology, Department of Conservation of California 1998). Pre-fire land cover was primarily chaparral (73 %), with coniferous forests (23 %) in the uppermost part of the watershed (Homer et al. 2007). Prior to the Station Fire in 2009, the Arroyo Seco experienced two large fires which burned 57 % (1896) and 83 % (1959) of the watershed (CalFrap 2009). The Arroyo Seco was burned in its entirety during the Station Fire, at primarily moderate (64 %) severity (USDA Forest Service 2009). The remaining 8, 17, and 11 % of the watershed was burned to very low, low, and high severities, respectively (USDA Forest Service 2009).

Sample collection and analysis

Water quality sampling was conducted prior to and immediately following the Station Fire, over the rainy seasons (October through March) of both WY 2009 and 2010. Grab samples were taken during four storm events in each season (eight storms total) at primarily

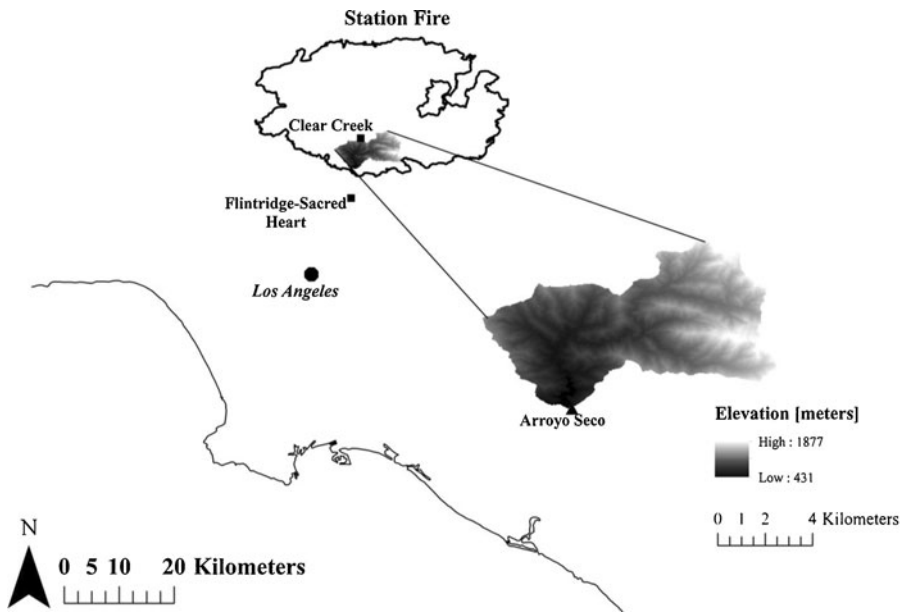

Fig. 1 Location of the Arroyo Seco watershed in relation to the Los Angeles Basin and the Station Fire boundary. The *inset* shows the relief (USGS Digital Elevation Model) of the watershed, as well as the location of the USGS stream gauge (*triangle*) and precipitation gauges (*square*) used in this study

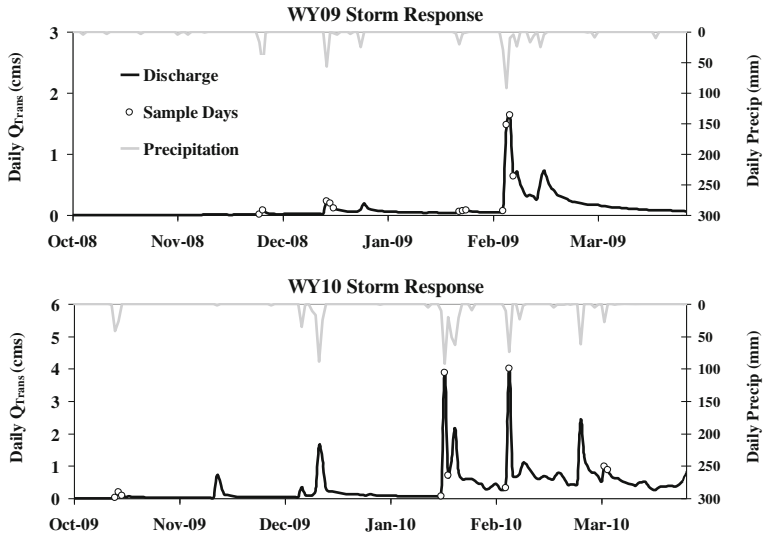

Fig. 2 Daily discharge (*bottom*, *black line*) on the left axis and daily precipitation (*top*, *gray line*) during storm seasons WY 2009 (pre-fire; *top*) and WY 2010 (post-fire; *bottom*) along with the sample dates (*open circles*) for each season. Discharge is plotted in the transformed space (Hogue et al. 2000)

2-h intervals and included at least one sample for each portion of the hydrograph (rise, peak, and recession) (Fig. 2). All samples were stored on ice in the field until they were transported back to the laboratory, where they were preserved as needed and refrigerated at 4 °C. All samples were stored for analysis within 24 h.

The sampling regimes differed slightly between the pre- and post-fire seasons due to safety restrictions and a shift in research objectives following the Station Fire. Efforts were made to sample every storm with precipitation totals >25.4 mm, and this was accomplished in WY 2009. Two early season (December) storms and one late season (March) storm of WY 2010 were not sampled (Fig. 2). However, the sample set includes the first and largest storms and spans the entire rainy season of each water year. Additional differences in the sampling between the pre- and post-fire seasons are discussed below. Sampling methodology and laboratory analysis followed protocols approved by the US Environmental Protection Agency (EPA), minimizing differences in sample results from WY 2009 and 2010.

WY 2009 (pre-fire) sampling was conducted at the watershed outlet collocated with USGS stream gauge (station #11098000) over four storm events. A total of 131 samples were collected during the WY 2009 season; 101 samples (250 ml) were collected for TSS analysis in high-density polyethylene (HDPE) bottles (triple rinsed in situ) primarily at hourly intervals. TSS was measured in all samples at University of California, Los Angeles (UCLA), using EPA Method 106.2. An additional 30 samples (120 ml) were collected for trace metal analysis using acid-washed I-Chem™ bottles (triple rinsed in situ) at 2-h intervals during the four storms. Trace metal samples were left unfiltered, acid-preserved (0.5 % HCl), and stored at 4 °C until the occurrence of the Station Fire when they were sent to Caltest Analytical Laboratory and measured for total recoverable concentrations of aluminum (Al), arsenic (As), cadmium (Cd), calcium (Ca), copper (Cu), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), potassium (K), selenium (Se), sodium (Na), and zinc (Zn) by inductively coupled plasma/mass spectrometry (ICP/MS), following EPA Method 200.8 Collision Mode.

WY 2010 (post-fire) sampling was conducted at the Millard Canyon Bridge, approximately 3 km downstream of the USGS stream gauge due to safety constraints. A total of 108 samples were collected for TSS and trace metal (54 each) analysis during the post-fire WY 2010 storm season, at 2-h intervals over four storm events (Fig. 2). All samples were collected in 250 ml HDPE bottles prepared and provided by CRG Marine Laboratories. TSS samples were measured at UCLA, following EPA Method 106.2. Trace metal samples were left unfiltered and transported to CRG Marine Laboratories within 48 h, where they were analyzed for total recoverable concentrations of Al, As, Cd, Ca, Cu, Fe, Pb, Mg, Mn, Ni, K, Se, Na, and Zn by ICP/MS, following EPA Method 200.8.

Hydrologic data

Fifteen-minute discharge data were obtained at the outlet of the upper Arroyo Seco watershed (USGS station #11098000) for the entire study period. Sampling at the downstream location during WY 2010 slightly increased the drainage area from 41.4 to 47.1 km^2. USGS discharge measurements were subsequently scaled by watershed area to account for increased flow at the downstream sampling location (Galster et al. 2006).

Precipitation data were obtained from two High Sierra Electronics Model 2400 tipping bucket rain gauges located in close proximity to the Arroyo Seco operated and maintained by the Los Angeles County Department of Public Works (LADPW 2010). Theissen polygons were defined using the two LA county gauges Clear Creek and Flintridge Sacred Heart to calculate mean areal precipitation (MAP) over the watershed.

Runoff coefficients were calculated for both water years, as well as for the individual storms sampled during each season. Annual runoff coefficients were calculated as the ratio of the total annual discharge per unit area to the annual MAP. For storm event runoff coefficients, the total storm discharge per unit area was divided by the total precipitation for each event. Storm discharge was assumed to begin with the onset of precipitation and continue until either another storm began or the point during the recession when flow remained at less than five times the pre-storm value for a 2-h increment. Flood frequency analysis was undertaken using the USGS peak streamflow records from WY 1914 to 2008 and the MathWorks matrix laboratory (Matlab) program's Weibull function.

To facilitate viewing of the range of flows in the Arroyo Seco, discharge is plotted in the transformed space (similar to log) for some plots (Hogue et al. 2000). The space transformation is as follows:

$$Q_{\mathrm{Trans}} = \frac{(Q+1)^{\lambda}}{\lambda} \tag{1}$$

with λ=0.3 (Hogue et al. 2000), where Q is the discharge and Q_{Trans} is the transformed discharge.

Chemical loads were estimated for each constituent for each sampled storm using measured chemical concentrations and 15-min discharge data (scaled by area when appropriate). Loads were calculated for each storm using the following equation:

$$F = \sum C(t_i) \times Q(t_i) \tag{2}$$

where F is the output stream load from the watershed, $C(t_i)$ is the constituent stream concentration at time interval i, and $Q(t_i)$ is the instantaneous stream discharge at i. Concentration and discharge measurements between each sample time were estimated using linear interpolation.

The WY 2010 sampling location was inaccessible following the Station Fire; sampling about 2 km downstream at the JPL bridge added 5.66 km^2 to the drainage area. To facilitate comparisons between the pre- and post-fire storm seasons, output stream loads were divided by watershed area and expressed as mass flux. Event mean concentrations (EMCs) were calculated as the ratio of the chemical load to the total storm discharge to provide a flow-weighted mean of constituent concentrations during each event by dividing the mass load by storm volume.

In order to determine whether chemical concentrations in the samples exceeded water quality standards, measured chemical concentrations were compared to the acute criteria maximum concentration (CMC) for priority toxic pollutants set in the California Toxics Rule (CTR) for inland surface water (US EPA 2000). Acute CMCs are defined as the highest concentrations to which aquatic life can be exposed for a short period of time (1-h average) without deleterious effects (US EPA Clean Water Act 2002).

The EPA encourages developing site-specific translators but suggests that the conversion factors provided in the rule may be used to convert from dissolved to total recoverable criterion (US EPA 1996). Using the relationships and coefficients provided in the rule, and a hardness value of 100 mg/L, the CMC for the priority toxic pollutants measured in this study expressed in total recoverable concentration are as follows: As (360 μg/L), Cd (4.5 μg/L), Cu (14 μg/L), Pb (82 μg/L), Ni (470 μg/L), Se (20 μg/L), and Zn (120 μg/L) (US EPA 2000).

Load duration curves were created for Cd, Cu, Pb, and Zn. A flow duration curve was created using 100 years of daily discharge data and multiplied by the calculated total recoverable CMC to estimate a maximum daily load. The EMC was applied to a 24-h period to determine the daily load and plotted against

the flow duration interval of the corresponding daily storm flow for each sampled storm.

Results and discussion

Storm discharge and suspended sediment

Although the Arroyo Seco watershed experienced different precipitation patterns during the 2 years of this study, the wildfire's impacts are evident when looking at individual storm events. The total annual precipitation of 460 mm for the uncharacteristically dry WY 2009 was only half that measured in WY 2010 (920 mm), when the total annual precipitation was closer to the long-term (35-year) average of 804± 524 mm. Both the WY 2009 and 2010 annual runoff ratios of 0.12 and 0.32, respectively, were within the range of variability of the watershed's long-term (35-year) runoff coefficient of 0.22±0.14. However, comparison of individual storms with similar precipitation totals and intensities for each season indicates that the watershed's response was highly impacted by the Station Fire (Table 1). With the exception of the first post-fire storm, all of the runoff ratios of WY 2010's sampled storms exceeded those of WY 2009 by at least a factor of 2 (Table 1). While other factors such as antecedent conditions (soil moisture) likely contributed to storm response in the Arroyo Seco, the largest, late season storms of each season clearly illustrate fire-enhanced runoff. Post-fire peak flows, observed during WY 2010's January 17th storm (120 m^3/s) and February 5th storm (130 m^3/s), were 15 and 17 times that of WY 2009's largest, February 5th storm (7.65 m^3/s) and were produced with only 80 and 65 % of the precipitation, respectively (Table 1; Fig. 2). Further, flood frequency analysis conducted for pre-fire conditions in the Arroyo Seco yielded return periods of 35 and 44.6 years for the peak flows of WY 2010's January 17th and February 5th storms, respectively, while the NOAA precipitation atlas identified both rainfall events as <2-year events (Bonnin et al. 2006).

The increase in post-fire storm runoff was accompanied by a corresponding increase in suspended sediment. The median TSS concentration of all of the WY 2009 storm samples was 23.3 mg/L (ranging from 1.6 to 880 mg/L), while the median TSS concentration of the WY 2010 storm samples increased over 10-fold to 259 mg/L (ranging from 2.5 to 80,500 mg/L) (Table 2; Fig. 3). While the observed post-fire TSS concentrations are extremely high, they are not unheard of in semiarid, flashy systems affected by wildfire. Researchers in the Jemez Mountains of New Mexico measured maximum TSS concentrations of 500,000 mg/L in post-fire storm runoff (Malmon et al. 2007). Additionally, the suspended sediment load of the largest pre-fire storm (February 5, 2009) of 6.27 t was doubled in the first post-fire storm (October 13, 2009), and WY 2010's two largest storms (January 17, 2010 and February 5, 2010) each carried suspended sediment loads of approximately 50,000 tonnes. Similarly, LADPW reports over 715,000 m^3 of

Table 1 Storm characteristics for each studied storm, including runoff ratio, precipitation, and discharge parameters (average, peak, and total)

	Runoff	Precipitation			Discharge		
	Ratio	Average (mm/15 min)	Peak (mm/15 min)	Total (mm)	Average (cms)	Peak (cms)	Total m^3
WY09							
Nov 25, 2008	0.004	1.41	3.92	75.9	0.06	0.28	12.8
Dec 15, 2008	0.018	1.18	2.96	56.9	0.21	0.48	47.8
Jan 22, 2009	0.023	0.69	2.87	25.5	0.06	0.08	26.7
Feb 5, 2009	0.094	1.44	5.85	131	1.81	7.65	568
WY10							
Oct 13, 2009	0.010	1.06	2.96	68.1	0.13	0.40	30.3
Jan 17, 2010	0.250	1.79	6.96	103	5.25	121	1190
Feb 5, 2010	0.371	0.99	7.59	84.8	5.39	131	1450
Mar 6, 2010	0.287	1.11	2.90	28.4	1.26	5.27	375

Table 2 Maximum concentration, EMC, and mass flux for each storm and averaged over each season for TSS, Cu, Pb, and Zn

	WY09			WY10		
	Max conc.	EMC	Mass flux	Max conc.	EMC	Mass flux
TSS	(mg/l)	(mg/l)	(kg/km^2)	(mg/l)	(mg/l)	(kg/km^2)
Storm 1	157	25.8	2.47	6380	517	299
Storm 2	NA	NA	NA	80600	47500	1170000
Storm 3	51.6	25.4	5.60	71800	46200	1230000
Storm 4	882	16.3	151	47900	11600	40200
Season Avg	363.39	22.5	53.2	51700	26400	611000
Cu	(μg/l)	(μg /l)	(g/km^2)	(μg /l)	(μg /l)	(g/km^2)
Storm 1	6.60	4.35	0.42	90.8	20.8	12.0
Storm 2	4.00	2.64	2.57	207	169	4170
Storm 3	2.30	1.44	0.32	256	114	3030
Storm 4	34.0	5.22	48.5	36.5	22.6	78.6
Season Avg	11.7	3.41	13.0	148	81.5	1820
Pb	(μg /l)	(μg /l)	(g/km^2)	(μg /l)	(μg /l)	(g/km^2)
Storm 1	1.10	0.69	0.07	954	78.8	45.4
Storm 2	1.70	0.70	0.69	2080	1230	30400
Storm 3	0.11	0.10	0.02	1290	831	22100
Storm 4	35.0	0.93	8.64	277	81.3	282
Season Avg	9.48	0.61	2.35	1150	555	13200
Zn	(μg /l)	(μg /l)	(g/km^2)	(μg /l)	(μg /l)	(g/km^2)
Storm 1	34.0	13.8	1.32	606	82.8	47.8
Storm 2	26.0	17.3	16.9	2540	1480	36500
Storm 3	15.0	5.97	1.31	1670	956	25400
Storm 4	120	5.07	47.2	601	178	618
Season Avg	48.8	10.5	16.7	1360	674	15700

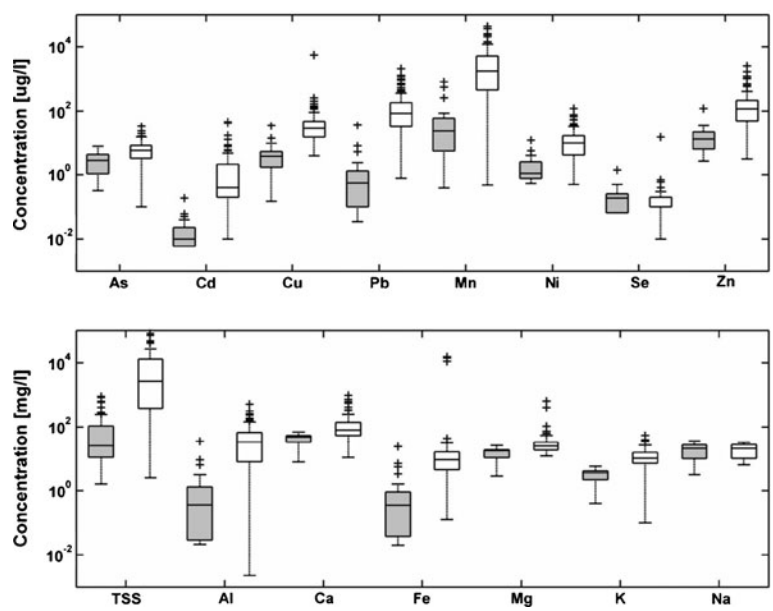

Fig. 3 Tukey's box plots of the overall constituent concentrations for both the pre-fire year, WY 2009 (*gray fill*), and post-fire year, WY 2010 (*no fill*). The *top* and *bottom edges* of each box represent the 75th and 25th percentiles, respectively, and the *line* bisecting the box represents the median

sediment (approximately 1,900,000 tonnes) deposited into Devil's Gate Reservoir during the 2009–2010 storm season, a flood control structure located on the Arroyo Seco ~6 km downstream of USGS stream gauge #11098000 (LADPW 2011). The sediment loads in Devil's Gate were ten times the total volume deposited in the reservoir since its last cleanout in 1994 (LADPW 2011). The Arroyo Seco had experienced at least two major floods since 1994 (El Niño years 1998 and 2005 yielded peak flows of 124 and 100 m^3/s, respectively), indicating that the sediment delivery to Devil's Gate Reservoir was primarily a result of wildfire-induced conditions, including debris flows and enhanced bed scour and bank erosion, rather than flooding alone (LADPW 2011; USGS 2011).

Chemical concentrations

Storm water chemistry in the Arroyo Seco varied greatly between different chemical constituent groups (trace metals and cations), reflecting differences in storm transport both prior to and following the Station Fire. Tukey's schematic box plots are used to present data distributions for all sampled constituents and show the median and 25th and 75th percentiles of chemical concentrations observed over all sampled storms of each WY 2009 and 2010 rainy seasons (Fig. 3). The increase in the median concentration of all samples from WY 2009 to 2010 was over two orders of magnitude in Pb and Cd; over one order of magnitude in Al and Mn, and Zn; and ninefold, sixfold, and fourfold in Cu, Ni, and Fe, respectively. A slight increase (less than twofold) was observed in the median As concentrations of the post-fire samples, while little change was noted in the Se concentrations. Other local studies have noted that As and Se are geologically sourced and tend to be enriched in local streams even under non-burn conditions (Yoon and Stein 2008). The trace metal enhancement is consistent with observations in the storm runoff of other semiarid, burned systems, which authors have attributed to increased sediment delivery and release from vegetative storage (Gallaher et al. 2002; Leak et al. 2003; Smith et al. 2011). The greatest increases were seen in trace metals identified as priority toxic pollutants in the CTR, including Pb, C, Zn, and Cu. Although the Arroyo Seco is essentially undeveloped, concentrations of these constituents were higher than those observed in the Los Angeles River during storm events and are in the range of those measured in channels draining highways, industrial areas, and mining operations (Thomson et al. 1997; US EPA 2000; Blake et al. 2003; Tiefenthaler et al. 2008; Joshia and Balasubramanian 2010). Based on the limited studies of trace metals following wildfire, this behavior is not unique to our system; however, the Pb concentrations measured in the Arroyo Seco were higher than those observed in other post-fire studies (Gallaher et al. 2002; Leak et al. 2003; Smith et al. 2011). We hypothesize that this is due to the study area's proximity to the Los Angeles Basin and the accumulation of anthropogenic Pb in the San Gabriel Range over the 60 years prior to the Station Fire.

Cation concentrations were also enriched in the post-fire samples though not nearly to the extent of most trace metals (Fig. 3). The median post-fire Mg, Ca, and K concentrations measured were two, three, and four times the pre-fire values, respectively. Other studies have noted elevated concentrations of these elements in post-fire storm runoff, attributed to leaching of ash and partially burned litter on the forest floor, as well as surface soil erosion (DeBano et al. 1979; Bitner et al. 2001; Ranali 2004). Prior to the Station Fire, all of these metals appear to have been primarily contributed by geologic weathering and transported in baseflow, as they tended to be diluted at high flows. The observed increase in the WY 2010 cation concentrations suggests both increased availability and alterations in the dominant transport mechanism of these constituents. Na was the only cation whose concentrations showed virtually no change from pre- to post-fire seasons (Fig. 3); Na was not likely to have been released from vegetation during the fire. Rainwater and bedrock geology are likely the primary contributors of Na to local stream systems (Barco et al. 2008; Jung et al. 2009).

Intra-storm behavior

Physical changes resulting from the Station Fire significantly altered both the magnitude and timing of trace metal concentrations in the Arroyo Seco storm runoff (Fig. 4). Prior to the fire, flushing was observed in most constituents throughout the entire rainy season, regardless of storm size. A typical first flush pattern was observed in WY 2009's November 25th (first) storm, where the highest concentrations of Pb, Zn, as well as TSS, occurred during the rising limb of the hydrograph, immediately following peak precipitation (Fig. 4). Cd concentrations peaked even earlier, immediately following the first pulse in precipitation, while

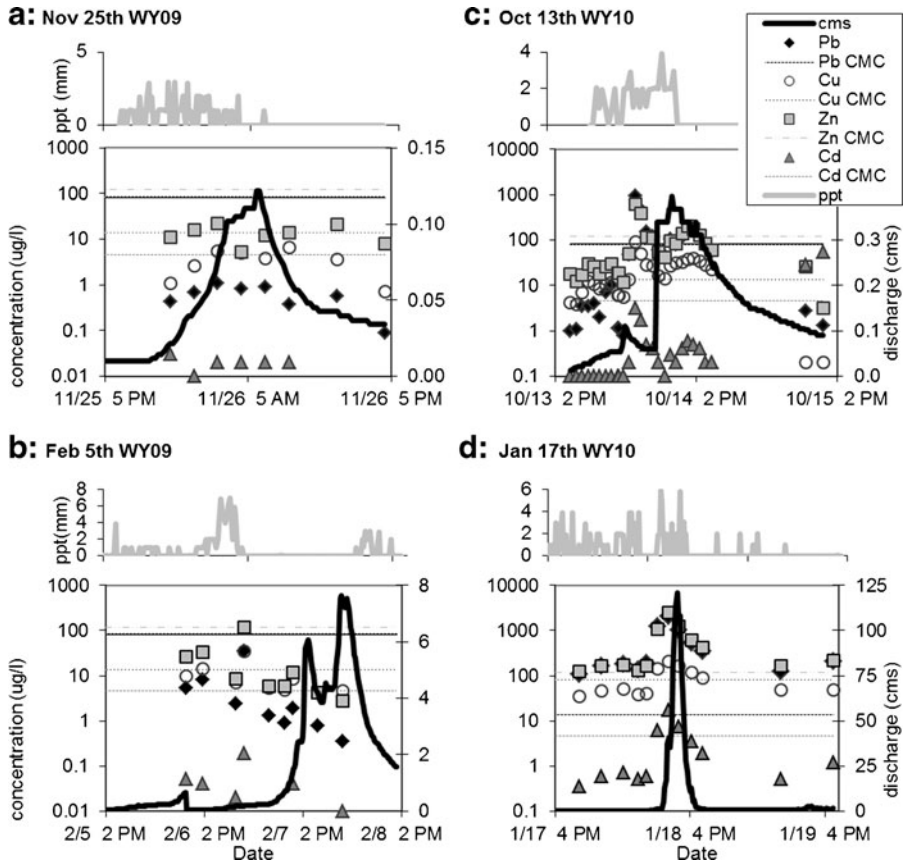

Fig. 4 Precipitation (*light gray line*, *top subplot*), transformed discharge (*black line*, *bottom subplot*, *right axis*), TSS (*gray cross*), trace metal concentrations and water quality criterion (*bottom subplot*, *left axis*) for two storms sampled during WY 2009 (*left*) and WY 2010 (*right*). Trace metals shown include Pb (*black diamonds*), Cu (*open circles*), Zn (*light gray boxes*), and Cd (*dark gray triangles*). Criterion are shown for Pb (*black dashed line*), Cu (*black dotted line*), Zn (*light gray dashed line box*), and Cd (*dark gray dashed line*) calculated using the variables provided in the CTR

Cu exhibited its highest concentration on the hydrograph's falling limb. In WY 2009's February 5th (largest) storm, the maximum trace metal (and TSS) concentrations occurred during the first rise in flow in every case, well before peak discharge. Following the fire, a similar behavior was observed during WY 2010's first storm, a low-intensity rainfall event that occurred on October 13. However, a shift in behavior was observed in WY 2010's January 17th storm and for the remainder of the post-fire season. Here, the highest trace metal concentrations coincided with peak discharge in every case (Fig. 4). Cd, Cu, Pb, and Zn exceeded the estimated CMCs during every sampled storm, with the exception of Cd in the final storm of WY 2010. The pre-fire storm data demonstrate that a relatively large storm was required to mobilize contaminants from Arroyo Seco prior to the Station Fire. While the post-fire data show that even small, low-intensity events could significantly elevate trace metal concentrations, in larger storms at peak discharge, these metal concentrations could exceed water quality criterion by as much as 20-fold.

The pre-fire cation data support work previously conducted in the Arroyo Seco, showing some dilution during high flows, while the post-fire data show a shift in behavior (Barco et al. 2008; Wessel 2009). Most cations and concentrations remained essentially constant throughout the WY 2009 early season storms, exemplified in the November 25th (first WY 2009 storm) pollutograph (Fig. 5). Little change and minimal dilution was observed in cation concentrations during the February 5th (largest) storm of WY 2009. This storm also produced the lowest cation concentrations of the entire WY 2009 storm season, with the exception of K (Fig. 5). Following the fire, in WY 2010's October 13th (first) storm, the flushing behavior seen in the trace metals was observed in most cations. In the WY 2010 January 17th storm, most of the maximum cation concentrations occurred prior to peak flow, suggesting a shift in suspended sediment facilitated transport (Fig. 5). Ca and Mg concentrations increased 12-fold and 5-fold, respectively, from pre-storm concentrations during this event. In the case of Na, initial flushing behavior was not observed, as it was diluted during peak flow in the

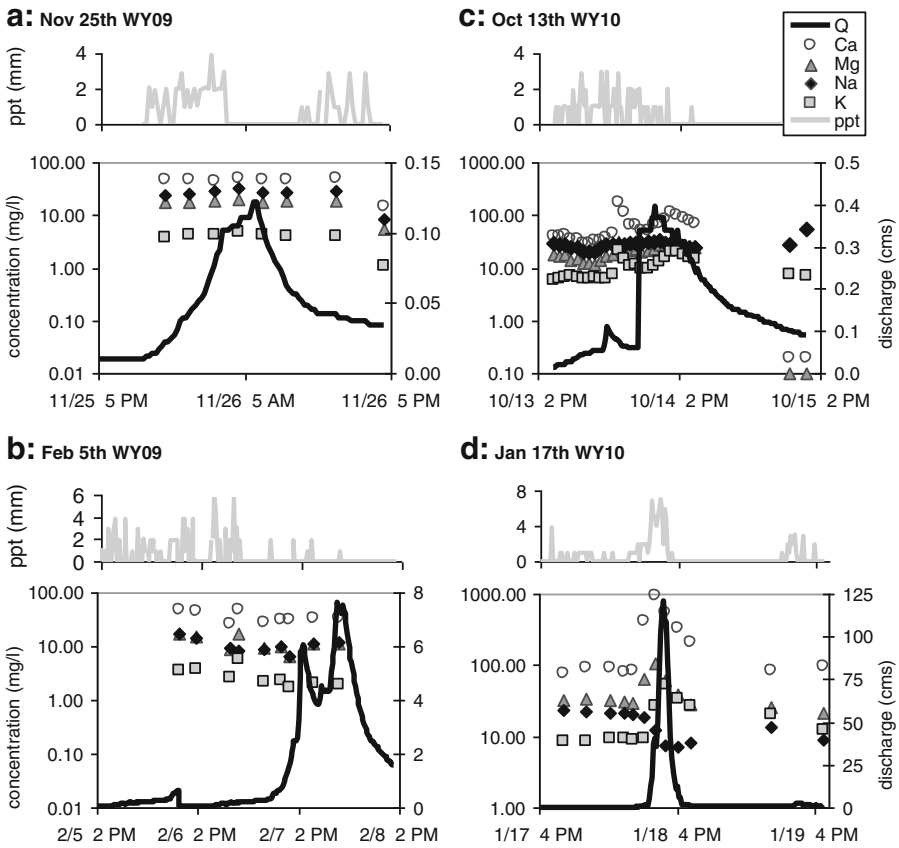

Fig. 5 Precipitation (*light gray line*, *top subplot*), transformed discharge (*black line*, *bottom subplot*, *right axis*), and the cation concentrations (*bottom subplot*, *left axis*) for two of the four storms sampled during WY 2009 (*left*) and WY 2010 (*right*). The metals shown include Ca (*open circles*), K (*light gray boxes*), Mg (*dark gray triangles*), and Na (*black diamond*)

January 17th storm and for the remainder of WY 2010 sampling.

Seasonal distributions

EMC distributions demonstrate the Station Fire's combined impacts on storm discharge, and the timing of chemical delivery affected seasonal patterns in the Arroyo Seco. Prior to the fire, most constituents (As, Cd, Fe, Mn, Ni, Na, Se, and Zn) showed the highest EMC early in the WY 2009 rainy season (November 25th and December 15th storms) (Fig. 6). This resembles other local urban fringe systems where early season storms flushed out constituents accumulated on the watershed's surface over the dry season (Yoon and Stein 2008). Discharge had a greater impact than seasonal flushing on Cu and Pb, which exhibited the highest EMCs in the WY 2009 February 5th (largest) storm, and on Ca, K, and Mg, whose highest EMCs occurred during WY 2009 January 22nd (smallest) storm (Fig. 6). It is also noteworthy that the EMCs of all constituents measured throughout WY 2009 remained relatively constant and rarely varied by more than a factor of 2 (Fig. 6). Conversely, many of the post-fire trace metal and cation EMCs varied by over one order of magnitude, and seasonal distributions closely resembled the distribution of the WY 2010 storm discharge, indicating that individual storm discharge had a stronger influence than early season flushing for most of the constituents (Fig. 6). We hypothesize that early storms do not flush accumulated materials from the watershed and that loading to the system continues throughout the year dependent on individual storm rainfall. As observed in the pollutographs, maximum trace metal and cation concentrations corresponded to peak discharge, rather than preceding it (as in WY 2009). This, combined with the increased post-fire peak flows, greatly affected both the magnitude and distribution of the trace metal and cation WY 2010 EMCs. For most trace metals and cations, the increased post-fire concentrations were accentuated when weighted by flow. Increases of at least one and up to three orders of magnitude from the pre-fire year were

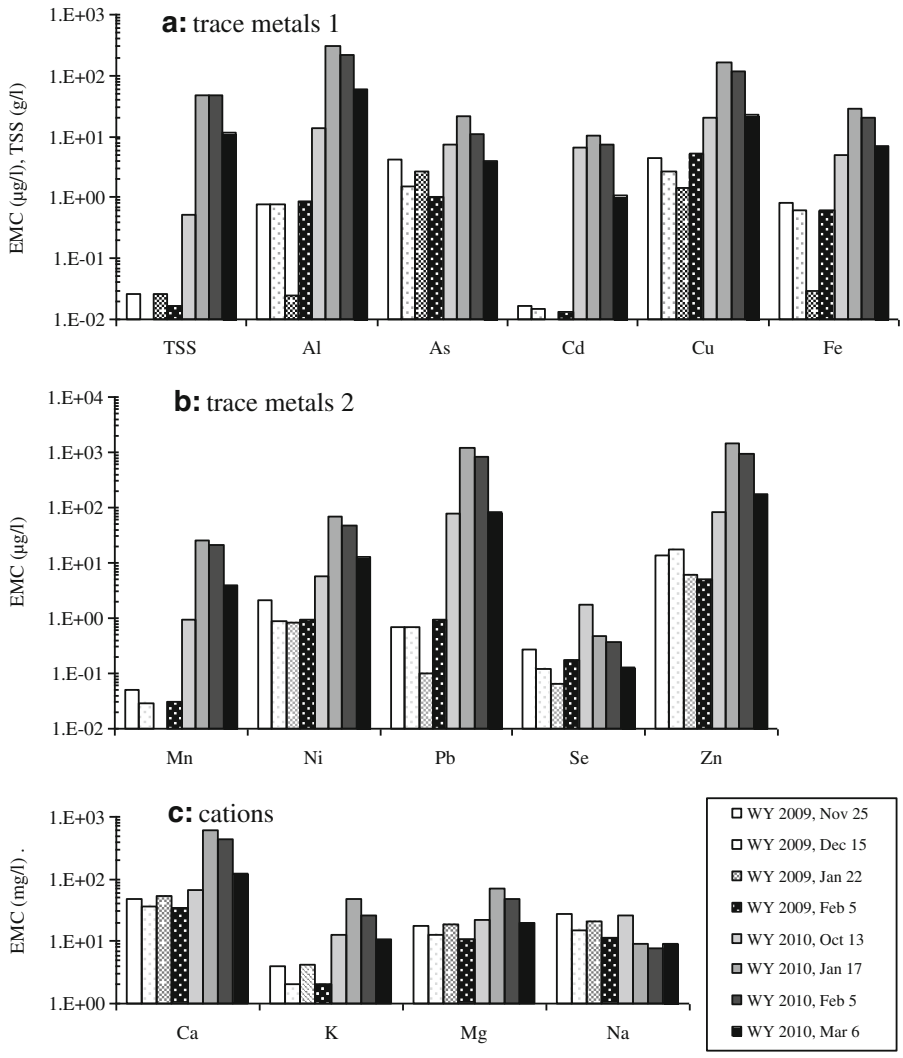

Fig. 6 EMC values for trace metals (*top* and *middle*) and cations (*bottom*) for each storm of WY 2009 (*dotted bars*) and WY 2010 (*filled bars*). The EMC units are as follows: TSS is presented in grams per liter, trace metals are in micrograms per liter, and cations are in milligrams per liter

observed in the trace metals, with the exception of Se which followed the flushing pattern observed in WY 2009 (Fig. 6). Unlike Ca, K, and Mg, the pre-fire seasonal distribution of Na did not appear to be greatly impacted by the Station Fire, where the highest EMCs of both WY 2009 and 2010 occurred in the first storm of the season. Additionally, Na was the only measured constituent to show a decrease in EMC following the fire (Fig. 6).

In both WY 2009 and 2010, the seasonal load distribution of most of the measured constituents reflected the distribution of total storm discharge throughout each season; however, differences in the magnitude of the mass flux between the WY 2009 and 2010 storms demonstrate the wildfire's impact on suspended sediment and chemical loads (Table 2). Increased suspended sediment delivery in the post-fire storms is accompanied by significantly enhanced trace metal flux (Fig. 6). One (As and Cu), two (Al, Fe, Ni, and Zn), and three (Cd, Mn, and Pb) orders of magnitude increases were observed in the trace metal fluxes of the largest pre-fire (February 5th) and post-fire (January 17th) storms. During the January 17th storm of WY 2010, fluxes of the US EPA criteria pollutants Cd, Cu, Pb, and Zn were calculated to be 0.25, 4.07, 30.5, and 36.5 kg/km^2, respectively; values that are in the range of those observed in watersheds draining highly contaminated mining areas (Žák et al. 2009). Ca, K, and Mg fluxes were also all over one order of magnitude greater in the WY 2010 January 17th storm than in the largest storm sampled during WY 2009.

Hydrochemical loading

Load duration curves created for the metals that exceeded CMC estimates (Cd, Cu, Pb, and Zn) show that it was unlikely that water quality thresholds would be exceeded for any constituent other than Cu in typical storms in the Arroyo Seco watershed prior to the Station Fire (Fig. 7). The Arroyo Seco discharges into the Los Angeles River which is listed as impaired for Cd, Pb, Cu, Zn, and Al pursuant to Section 303(d) of the Federal Clean Water Act. Barco et al. (2008) has shown the importance of considering urban fringe watersheds, such as the Arroyo Seco, as an upstream source of chemical contaminants to downstream waters. This is particularly true following wildfire when pollutants previously stored in a watershed's vegetation and soil may be more readily transported to downstream waters.

Correlations between constituent concentrations and instantaneous discharge, TSS, and total dissolved solids (TDS) help to elucidate fire-induced changes in hydrochemical dynamics in the Arroyo Seco (Fig. 8). Also displayed are correlation coefficients for the linear relationships between the previously mentioned constituents (Fig. 8). The trace metals, exemplified by Pb, are well correlated with TSS in both the pre- and post-fire samples. Others have noted strong correlations between trace metals and TSS and have utilized these relationships to approximate metal transport as a function of sediment delivery (Thomson et al. 1997; Joshia and Balasubramanian 2010). Our data suggest that these methods would be applicable in a burned system. Trace metal concentrations and discharge relationships shifted from a slightly negative to positive following the fire, while a negative relationship with and little correlation to TDS was observed in both the pre- and post-fire samples (Fig. 8). Like the trace

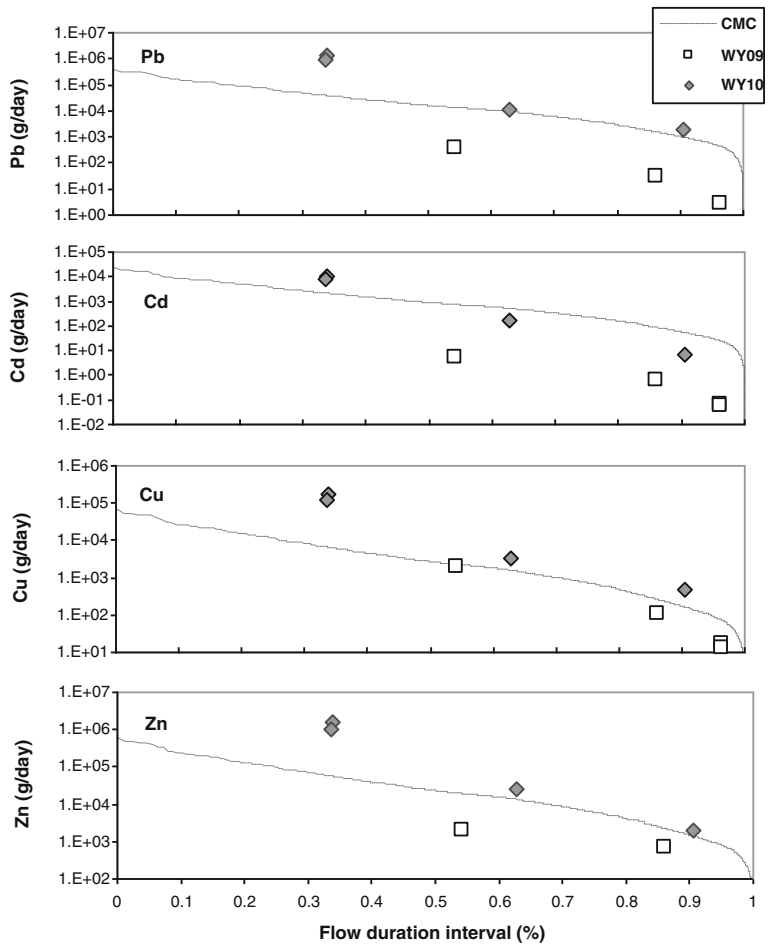

Fig. 7 Load duration curves for Pb, Cd, Cu, and Zn relative to the CMC (*dashed line*). The EMC of each storm from WY 2009 (*hollow squares*) and WY 2010 (*solid diamonds*) are plotted against the flow duration interval found by matching the daily flow from each storm to its corresponding rank

metals, most of the cation concentrations (exemplified by Ca) shifted from a slightly negative to a strong positive relationship with discharge. This and the strong post-fire correlation of Ca to TSS demonstrate an alteration in the transport of this constituent (Fig. 8), with a shift from dissolved to suspended load due to increased suspended sediment in these storms. Typically, the system is characterized by long recessional flow with the opportunity to transport the dissolved constituents. Post-fire response times, however, were observed to be quicker and "flashy." In the case of Na concentrations, the positive correlation to TDS that was observed prior to the fire was enhanced in the post-fire samples (Fig. 8).

Conclusions

The Station Fire resulted in enhanced runoff, elevated peak flows, and increases in suspended sediment and chemical concentrations in the Arroyo Seco. While only the largest pre-fire storm was able to mobilize contaminants in the basin, even small post-fire storms yielded concentrations that exceeded water quality criterion. The greatest changes were observed in trace metals, where concentrations of most constituents increased significantly following the Station Fire. Urban pollutants, such as Cd and Pb, exhibited concentrations in the range of those observed in channels draining highways, industrial areas, and mining operations. Timing of chemical delivery shifted from the initial rise in flow to peak discharge in post-fire storms, which contributed to significant increases in storm EMCs and loads. For pre-fire conditions in the Arroyo Seco, variables such as seasonal timing and antecedent conditions appeared to be major factors in determining runoff chemistry for most measured constituents. However, following the Station Fire, peak discharge and especially sediment transport were the controlling factors in pollutant delivery, particularly for potentially toxic metals. Our results have significant implications for storm water management. Current treatments focus

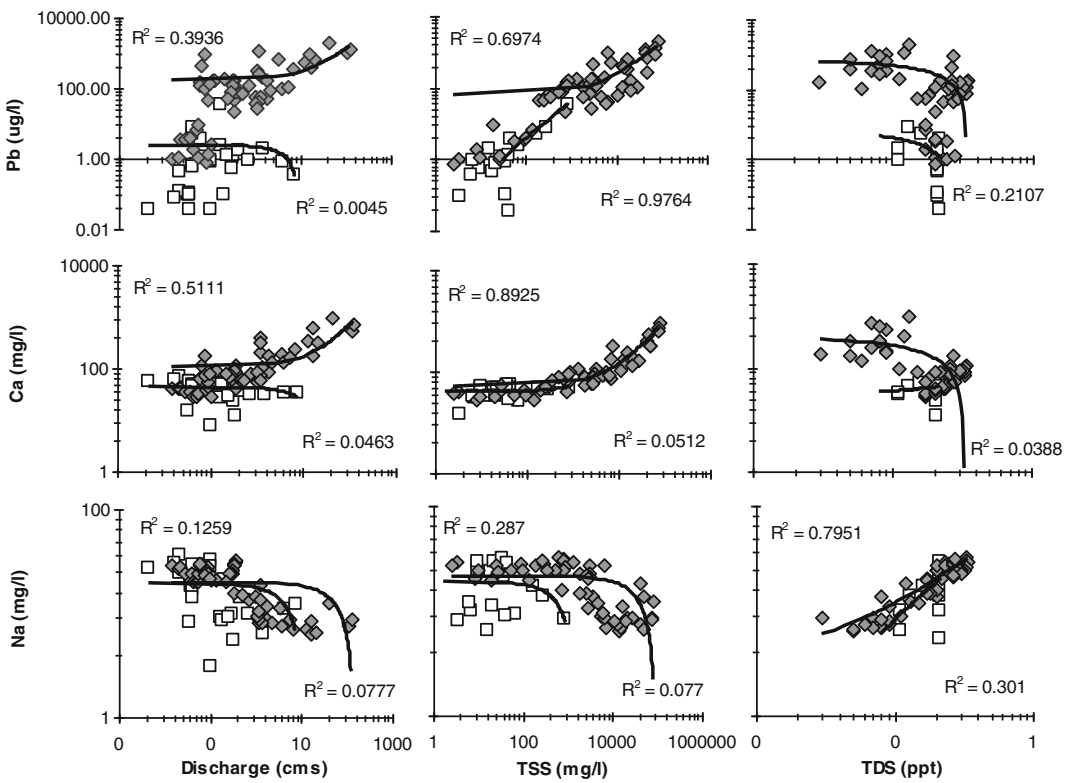

Fig. 8 Constituent concentrations from each sample taken over WY 2009 (*open squares*) and WY 2010 (*solid diamonds*) plotted against instantaneous discharge (*left*), TSS (*center*), and TDS (*right*). R^2 values are shown for the WY 2009 (*lower right*) and WY 2010 (*upper left*) samples

primarily on the early portion of storm water runoff to reduce mass loading of pollutants. However, new management strategies and treatment methods are needed for post-fire systems. The use of flood control structures that retain sediment are likely the most effective (and available) means to mitigate detrimental impacts to downstream water quality. However, we advocate that, in the future, the chemistry of captured sediment must be considered prior to disposal, especially in watersheds located near large urban centers.

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