Dynamics of pre- and post-fire pollutant loads in an urban fringe watershed

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Abstract

This study investigates the impacts of wildfire on storm runoff chemistry in an urban fringe watershed that is highly impacted by regional atmospheric pollutants. Pre- and post-fire storm runoff was collected and analyzed for basic cations and anions, trace metals, and total suspended solids. The loss of vegetation and changes in soil properties due to fire reduced lag time and 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 sediment, trace metal, and cation concentrations coincided with peak discharge in the post-fire runoff. Our results highlight the need for treatment of sediment-bound chemicals, in order to mitigate potentially detrimental impacts on downstream water quality.

Introduction

Wildfires can contribute to contaminant loading to downstream areas. The responsible mechanisms included increased runoff associated with soil hydrophobicity, increased mobility of contaminants from soil and vegetation, and higher erosion rates (Bitner *et al.* 2001, Moody and Martin 2009, Jung *et al.* 2009, Smith *et al.* 2011). Increased nutrient concentrations, especially nitrate and phosphate, have been previously reported in post-fire runoff from Southern California's San Gabriel Mountains (Riggan *et al.* 1985, Ranali 2004, Meixner *et al.* 2006). Total suspended solid (TSS) concentrations in stormwater often increase by orders of magnitude in post-fire systems, accelerating the potential for mobilization and transport of particulate bound contaminants (Malmon *et al.* 2007, Moody and Martin 2009, Smith *et al.* 2011). Significantly higher concentrations of several metals, including As, Al, Ba, Cd, Cr, Fe, Mn, Pb, and Zn, were reported in post-fire runoff following New Mexico's 2000 Cerro Grande Fire and Australia's 2003 bushfires in Alpine National Park, (Bitner *et al.* 2001, Gallaher *et al.* 2002, Leak *et al.* 2003, Smith *et al.* 2011). However, few studies have focused on trace metal delivery following fire, particular in the urban fringe areas of southern California (Gallaher *et al.* 2002, Smith *et al.* 2011).

The recent Station fire provides an opportunity to investigate the effects of fire on stormwater loadings of metals in an urban fringe watershed. The Station fire burned for six weeks (Aug-Oct, 2009), consuming 660 km^2 of primarily Angeles National Forest in the San Gabriel Mountain Range. The burned region is immediately adjacent to dense urban areas on the east side of the Los Angeles basin. Watersheds in the front range of the San Gabriel Mountains supply

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large amounts of runoff to downstream urban water ways during winter storms, which is then directed to infiltration ponds or zones for aquifer recharge, or into flood control channels that route water through dense urban areas to coastal bays. Previous work in Southern California's front-range has revealed significant nutrient and other chemical loads in the storm runoff of local urban-fringe watersheds (Fenn and Poth 1999, Meixner *et al*. 2001, Barco et al. 2008). However, the potential for wildfire to exacerbate existing water quality problems in urban fringe watersheds has not been as well studied.

Much of the region affected by the Station Fire had not burned in over 60 years, prior to the Clean Air Act and the subsequent phase out of lead additives in gasoline, leaving a potentially large store of anthropogenic contaminants in vegetation and soil. We hypothesize that post-fire storm events in these urban-fringe basins will contribute significant chemical loads to downstream waterbodies, which are often already impaired and subject to management actions pursuant to Total Maximum Daily Loads (TMDLs) and National Pollution Discharge Elimination System (NPDES) permits. The objectives of the current study are to better understand the impacts of wildfire on mass loading in highly-impacted, urban-fringe landscapes in order to provide guidance for post-fire watershed management practices.

METHODS

Study Area

The Arroyo Seco River runs within a deeply carved canyon that begins near the top of the San Gabriel Mountains in the Angeles National Forest. After exiting the upper basin, the Arroyo Seco is channelized and eventually converges with the Los Angeles River near downtown Los Angeles. The Los Angeles River is listed as impaired for Cd, Pb, Cu, Zn, and Al pursuant to Section 303(d) of the Federal Clean Water Act. Arroyo Seco's upper basin, hereafter noted as Arroyo Seco watershed, consists of approximately 42 km^2 of steep, mountainous terrain with elevations ranging from 426 to1820 m above sea level. The watershed slope and length are estimated to be 5.7% and 17.2 km respectively. Due to orographic effects, average annual precipitation (840 mm/yr) is relatively high compared to that of the Los Angeles basin (375 mm/yr; LADPW 2011b). Long term (100 years, WY 1911-2010)

annual stream discharge is 0.28 m^3/s and the annual runoff coefficient is 0.22 (35 years, WY 1975-2010). Pre-fire land cover was primarily chaparral (73%), with coniferous forests (23%) in the uppermost part of the watershed. The Arroyo Seco was burned in its entirety during the Station Fire, at primarily moderate (64%) severity (Young 2009). The remaining 8%, 17%, and 11% of the watershed was burned to very low, low, and high severities, respectively (Young 2009).

Sample Collection and Analysis

Water quality sampling occurred during the WY2009 storm season (pre-fire), and during the WY2010 storm season (immediate post-fire). There were slight differences in the location and approach to sampling between the two years due to safety and access considerations in WY2010. A total of 131 grab samples were collected during WY2009 over four storm events. Hourly sampling was conducted at the watershed outlet (at the USGS stream gage #11098000), from the beginning of the storm until after peak flow. Samples were collected using 500 ml HDPE bottles (triple rinsed in situ) and stored on ice until transported back to the lab. A subset was reserved for TSS analysis; other samples were filtered using 0.45 μm glass fiber filters, acid-preserved (0.5% HNO_3) and refrigerated at 4°C until analysis for: Chloride (Cl), Fluoride (F), Nitrate-N (NO_3-N), Sulfate (SO_4) (EPA Method 300.0). Thirty additional samples were taken during the four WY09 storms at two hour intervals using 120 ml acid washed Ichem bottles. Samples were preserved (unfiltered) with 0.5% HCl, and stored at 4°C. Samples were then analyzed for 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 (N), Zinc (Zn) (EPA Method 200.8m).

A total of 54 grab samples were collected during the post-fire WY10 storm season, primarily at two hour intervals over four storm events. All samples were collected in HDPE bottles prepared with preservatives when appropriate. Post-fire sampling was conducted 3 km downstream from the USGS gage at the Mallard Canyon Bridge due to safety constraints. Samples were stored on ice in the field and kept at 4°C until analysis. The WY10 samples were analyzed for the above constituents using the same methods. Additionally, Total Phosphorus (T-Ph) (Method SM 4500-P E)

and Mercury (Hg) (EPA Method 245.7m) were measured post-fire. TSS was also measured in all samples using EPA Method 106.2.

Data Analysis

Fifteen minute discharge data were obtained from USGS gage #11098000. Sampling at the downstream location during WY 2010 increased the drainage area from 41.44 km^2 to 47.10 km^2 (of similar land cover type), and discharge measurements were scaled by watershed area to account for increased flow (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 and operated by the Los Angeles County Department of Public Works (LADPW 2011b). Thiessen polygons were defined using the two LA county gages Clear Creek (0.968) and Flintridge-Sacred Heart (0.032) to calculate Mean Areal Precipitation (MAP) over the watershed.

Runoff ratios were calculated for both water years and for individual storms sampled during each season. For storm event runoff ratios, 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 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 two hour increment.

The chemical load and event mean concentration (EMC) were estimated for each chemical constituent for each sampled storm using measured chemical concentrations and discharge data (scaled by area when appropriate). Chemical loads were calculated for each storm using the following integral equation:

$$F = \int_{t_0}^{t_f} C(t) \times Q(t) dt \qquad \text{Eq. 1}$$

Where F is the output stream load from the watershed, $C(t)$ is the constituent stream concentration and $Q(t)$ is the stream discharge. Concentration and discharge measurements between each sample time were estimated by linear interpolation. To facilitate comparisons between storm seasons and to other systems, mass flux was calculated as the load divided by watershed area. Event Mean Concentrations (EMCs) were calculated as the ratio of the chemical load to total storm discharge. Analysis of variance (ANOVA) was used to compare differences in chemical loads, mass flux, and EMCs between seasons with F-tests and p-values to determine significance at the 5% level.

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 (USEPA 2007). Acute CMCs are defined as highest concentrations to which aquatic life can be exposed for a short period of time (1-hour average) without deleterious effects (USEPA 2007). Using the relationships and coefficients provided in the CTR, the CMC for the priority toxic pollutants measured in this study expressed in total recoverable concentration (µg/L) are as follows: As (360), Cd (4.5), Cu (14), Pb (82), Hg (2.1), Ni (470), Se (20), and Zn (120) (USEPA 2007).

RESULTS AND DISCUSSION

Storm Discharge and Sediment

Storm discharge in the Arroyo Seco increased significantly after fire. WY10 had a runoff ratio of 0.32, compared to the long term (35 years) and WY09 values of 0.22 and 0.12, respectively. With the exception of the first post-fire storm, a lower intensity rain event, runoff ratios of WY10 sampled storms exceeded those of WY09 by at least a factor of two (Table 1). Annual precipitation during WY09 (460 mm) was half that of WY10 (920 mm) and differences in the precipitation regimes may explain some of the variability in discharge (Table 1). However, post-fire peak flows observed during WY10's January 17 (1187 m^3/s) and February 5 storms (1449 m^3/s) storms were 15 and 17 times that of WY09's largest, February 5 storm (7.65 m^3/s) and were produced with only 80% and 65% of the precipitation respectively (Table 1). Flood frequency analysis conducted for pre-fire conditions yielded return periods of 35 and 45 years for the peak flows of WY10's January 17 and February 5 storms respectively, while the NOAA precipitation atlas identified both storms as <2 year events (Bonnin *et al.* 2006).

Increased post-fire storm runoff was accompanied by a corresponding increase in sediment delivery. The sediment load of the largest pre-fire storm was estimated to be 6.3 tons (t). This was doubled in the first post-fire storm, and WY10's two largest storms each carried sediment loads of

Table 1. Seasonal storm characteristics.

	Runoff Ratio	Precipitation			Discharge		
		Average (mm/15min)	Peak (mm/15min)	Total (mm)	Average (m³/s)	Peak (m³/s)	Total (m³)
WY09							
Nov 25, 2008	0.004	1.41	3.92	75.92	0.06	0.28	12.79
Dec 15, 2008	0.018	1.18	2.96	56.87	0.21	0.48	47.75
Jan 22, 2009	0.023	0.69	2.87	25.54	0.06	0.08	26.74
Feb 5, 2009	0.094	1.44	5.85	130.94	1.81	7.65	568.24
WY10							
Oct 13, 2009	0.010	1.06	2.96	68.12	0.13	0.40	30.30
Jan 17, 2010	0.250	1.79	6.96	102.98	5.25	120.63	1,187.02
Feb 5, 2010	0.371	0.99	7.59	84.82	5.39	130.82	1,450.77
Mar 6,2010	0.287	1.11	2.90	28.44	1.26	5.27	375.48

~50000 t. These estimates are supported by reports that WY10 delivered over 715,000 m³ of sediment (10x the total volume deposited in the last fifteen years) to Devil's Gate Reservoir, a flood control structure located ~3 km downstream of our sampling location (LADPW 2011a). The mean seasonal TSS concentration increased 100-fold following the fire, from 109 mg/L (1.6 - 880 mg/L) in the WY09 storm samples to 10900 mg/L (2.5 - 80500 mg/L) in the WY10 samples. While these TSS concentrations are extremely high, they are not unheard of in semi-arid, flashy systems affected by wildfire. Malmon *et al.* (2007) measured maximum TSS concentrations of 500,000 mg/L in post-fire storm runoff in the Jemez Mountains of New Mexico.
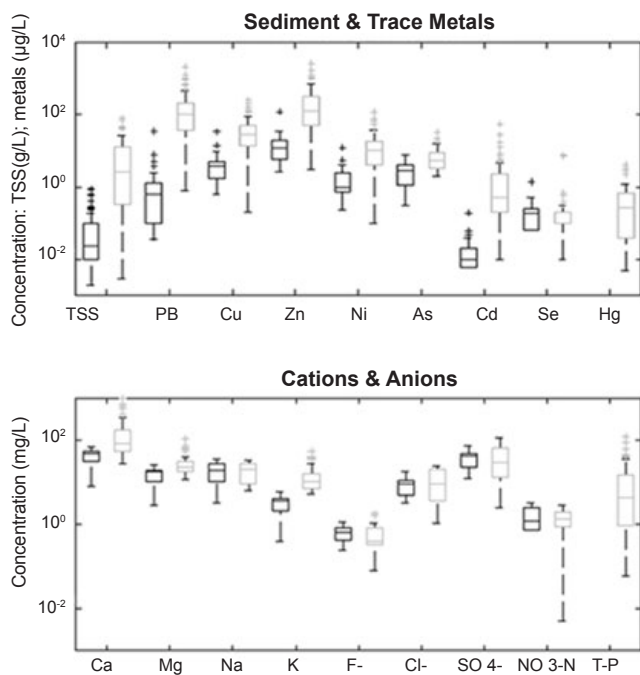
Chemical Concentrations

Stormwater chemistry in the Arroyo Seco varied greatly between different constituent groups (trace metals, cations, and anions) reflecting differences in hydrologic transport before and after the Station Fire. Both the magnitude and variability of the trace metal concentrations increased following the Station Fire (Figure 1). A significant increase was observed in all measured trace metal concentrations except for As and Se. Increases in median concentrations from WY09 to WY10 were over two orders of magnitude for Pb and Cd; over one order of magnitude for Al, Mn, and Zn; and nine, six, and four-fold for Cu, Ni, and Fe, respectively. A slight increase (< two-fold) 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 semi-arid, 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.* 2010). The greatest increases were seen in trace metals identified as priority toxic pollutants in the CTR, including Pb, Cd, 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, Blake *et al.* 2003, Tiefenthaler *et al.* 2008, Žák *et al.* 2009, 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 are significantly higher than other post-fire studies (Gallaher *et al.* 2002, Leak *et al.* 2003, Smith *et al.* 2010). We hypothesize that this is due to the watershed's proximity to the Los Angeles basin and accumulation of anthropogenic Pb over the 60 years prior to the Station Fire.

Cation concentrations were enriched in the post-fire samples though not nearly to the extent of most of the trace metals; however, enrichment was not accompanied by increased variability. The median post-fire Mg, Ca, and K concentrations

Figure 1. Tukey boxplots of the overall constituent concentrations from both WY09 (black) and WY10 (grey). The top and bottom edge of each box represents the 75th and 25th percentile, respectively, and the line bisecting the box represents the median.

increased by two, three, and four times 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 and increased surface soil erosion (Debano 1979, Bitner *et al.* 2001, Ranali 2004). Prior to the Station Fire, all of these metals appear to have been geologically sourced and transported in baseflow, as they were diluted at high flows. The observed increase in the WY10 cation concentrations suggests both increased availability and alterations in the dominant transport mechanism of these constituents. Na is only the cation whose concentrations showed virtually no change from the pre to post fire periods, and other studies have noted that bedrock geology and rainwater are the major contributors of Na to local stream systems (Barco *et al.* 2008, Jung *et al.* 2009).

Anionic concentrations were the reverse of cationic concentrations. Median post-fire concentrations remained within the pre-fire range but showed greater variability overall. As noted earlier, only the dissolved fraction was measured for Cl, F, NO_3-N, and SO_4 in the WY09 samples. Due to budget constraints, only total concentrations were measured in the WY10 samples. This could be a

factor in the increased variability post-fire, at least at the high end of the spectrum. Concentrations in the lower range more likely reflect altered flowpaths and perhaps volatilization from surface soil and litter (NO_3 volatilization temp is 200ºC). The slight decrease observed in post-fire F and SO_4 concentrations may also suggest altered flowpaths, where a system characterized by long recessional flows prior to the fire is now dominated by overland flow (Jung *et al.* 2009). Because anion concentrations did not change significantly, even with a 100-fold increase in TSS concentrations post-fire, sediment does not appear to be a controlling factor in the transport of these constituents. Observed anions are likely dissolved in baseflow or rainwater, or in the case of nitrates flushed from the upper few cm of the soil surface via interflow (Barco *et al.* 2008, Wessel 2009).

Intra-Storm Behavior

The Station Fire greatly impacted both the magnitude and timing of trace metal concentrations in Arroyo Seco's storm runoff (Figure 2). A typical first flush pattern was observed in WY09's November 25 storm, where the highest concentrations of Pb, Zn, as well as TSS (not shown), occurred during the rising limb of the hydrograph, immediately following peak precipitation (Figure 2). Cd peaked earlier than Pb, immediately following the first pulse in precipitation, while Cu's highest concentration occurred on the hydrograph's falling limb. In WY09's February 5 (largest) storm, maximum trace metal (and TSS) concentrations occurred during the first rise in flow, well before peak discharge. A similar pattern was seen in WY10's October 13 (first) storm, a low intensity rain event. A shift occurred in WY10's January 17 storm, which held for the remainder of the post-fire season, where maximum trace metal concentrations coincided with peak discharge in every case (Figure 2). Following the fire, Cd, Cu, Pb, and Zn exceeded estimated CMCs during every storm with the exception of Cd in WY10's final storm. Our observations demonstrate that a relatively large storm was required to mobilize contaminants from Arroyo Seco prior to the Station Fire. Following wildfire, even small, low intensity events significantly elevated trace metal concentrations and, in larger storms at peak discharge, contaminants exceed water quality criterion by as much as 20 times.
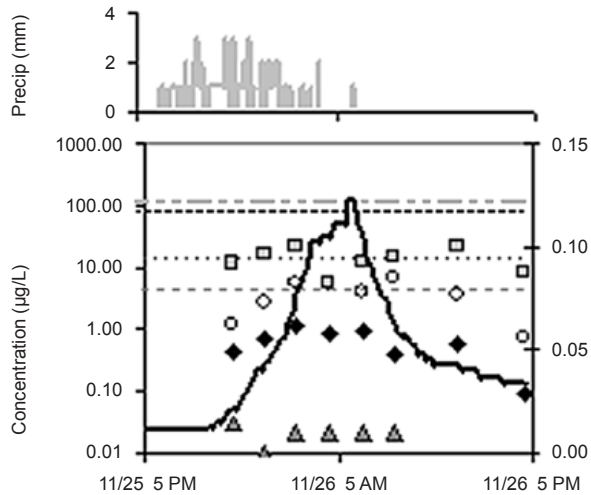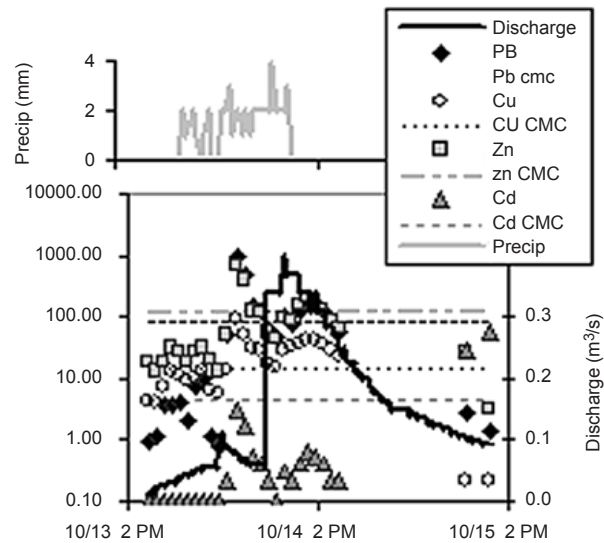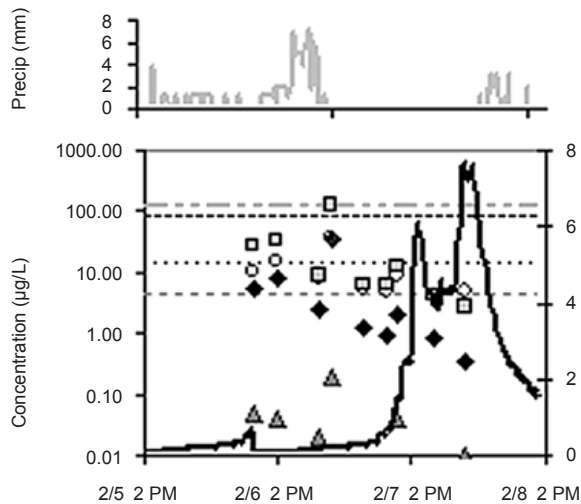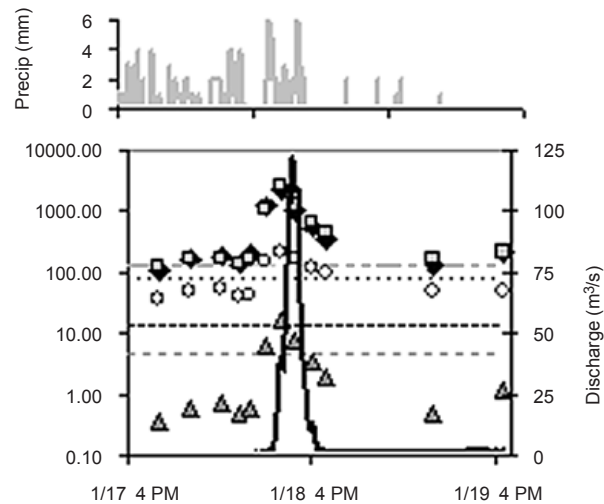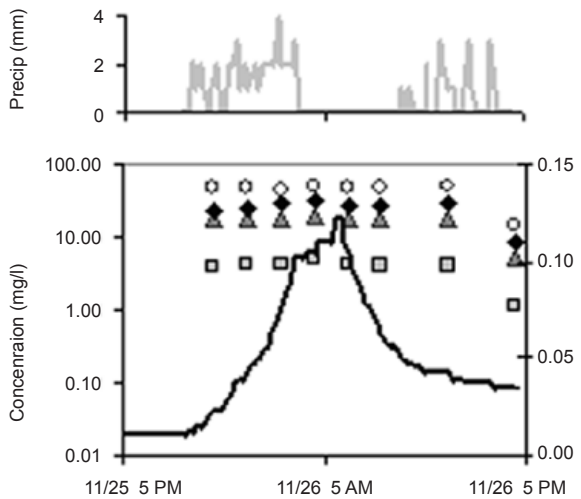
Figure 2. Precipitation (light grey line, top subplot), transformed discharge (black line, bottom subplot, right axis), trace metal concentrations and water quality criterion (bottom subplot, left axis) for two storms sampled in both WY09 (left) and WY10 (right). Trace metals shown include Pb (black diamond), Cu (open circle), Zn (light grey box), and Cd (dark grey triangle). Criterion are shown for Pb (black dashed line), Cu (black dotted line), Zn (light dashed line box), and Cd (dark grey dashed line) calculated using the variables provided in the CTR. CMC = Criteria Maximum Concentration.

Pre-fire cation and anion results supported previous work conducted in the Arroyo Seco, noting ions to be diluted and NO_3 concentrated during high flows (Barco *et al.* 2008). However, these patterns do not hold following fire. Most cation and anion concentrations remained essentially constant throughout WY09's November 25 (first) storm (Figure 3). In WY09's February 5 storm, precipitation was sufficient to concentrate the cations (except Na) and dilute the anions (except NO_3)

(Figure 3). However, this storm produced the lowest cation and anion concentrations of the entire WY09 season (except of K and NO_3). Following the fire, in WY10's October 13 storm, the flushing behavior seen in the trace metals was also observed in cations (except Na) as well as NO_3 and T-P, while anion concentrations peaked with discharge (Figure 3). In WY10's January 17 storm, cation concentrations increased up to five fold and, like the trace metals, maximum post-fire concentrations occurred just
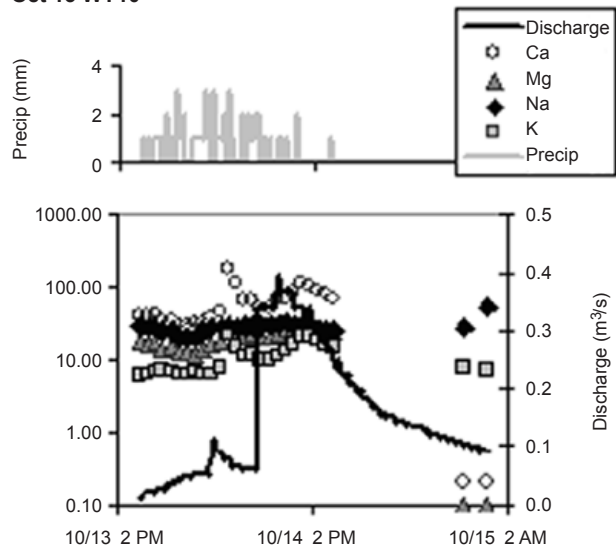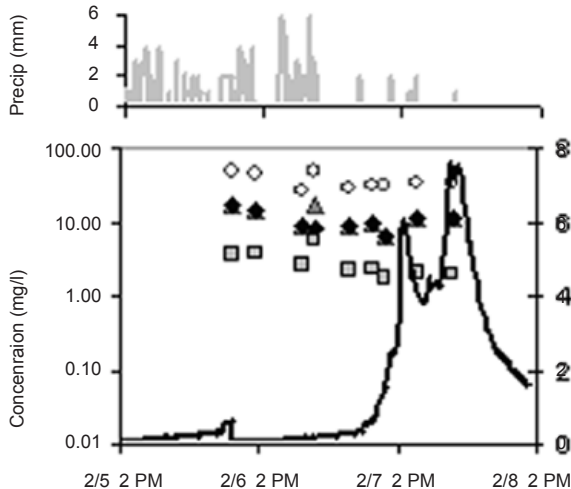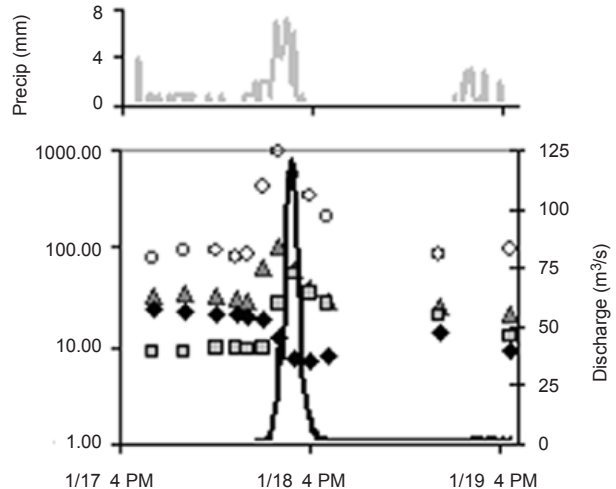
Figure 3. Precipitation (bold grey line, top subplots); transformed discharge (bold black line, right axis); and Ca, K, Mg, and Na concentrations (circle, square, triangle, and diamond, respectively; left axis) for 2 of the 4 storms sampled in WY09 (left), and 2 of the 4 storms sampled in WY10 (right).

prior to peak flow (Figure 3). The anions were diluted at peak flow in the January 17 storm and for the remainder of WY10. After the flushing of the first post-fire storm, the dilution behavior observed prior to the Station Fire was accentuated as overland flow became the dominant component in the large post-fire runoff.

Seasonal Distributions

While load distributions reflect total storm discharge during both periods, EMC distributions highlight the fire's impact on seasonal patterns (Figure 4). Prior to the fire, most constituents

showed the highest EMC early in WY09 (November 25 and December 8 storms), resembling other local urban-fringe systems where early season storms flush constituents accumulated over the dry season (Yoon and Stein 2008). Storm discharge had a greater impact on Cu and Pb, which exhibited the highest EMCs in WY09's February 5 (largest) storm, and on Ca, K, and Mg's whose highest EMCs occurred during WY09's January 9 (smallest) storm. However, all of the WY09 EMCs remained relatively constant and rarely varied by more than a factor of two (Figure 4). The anion EMC distribution showed little change following the Station Fire. Despite the
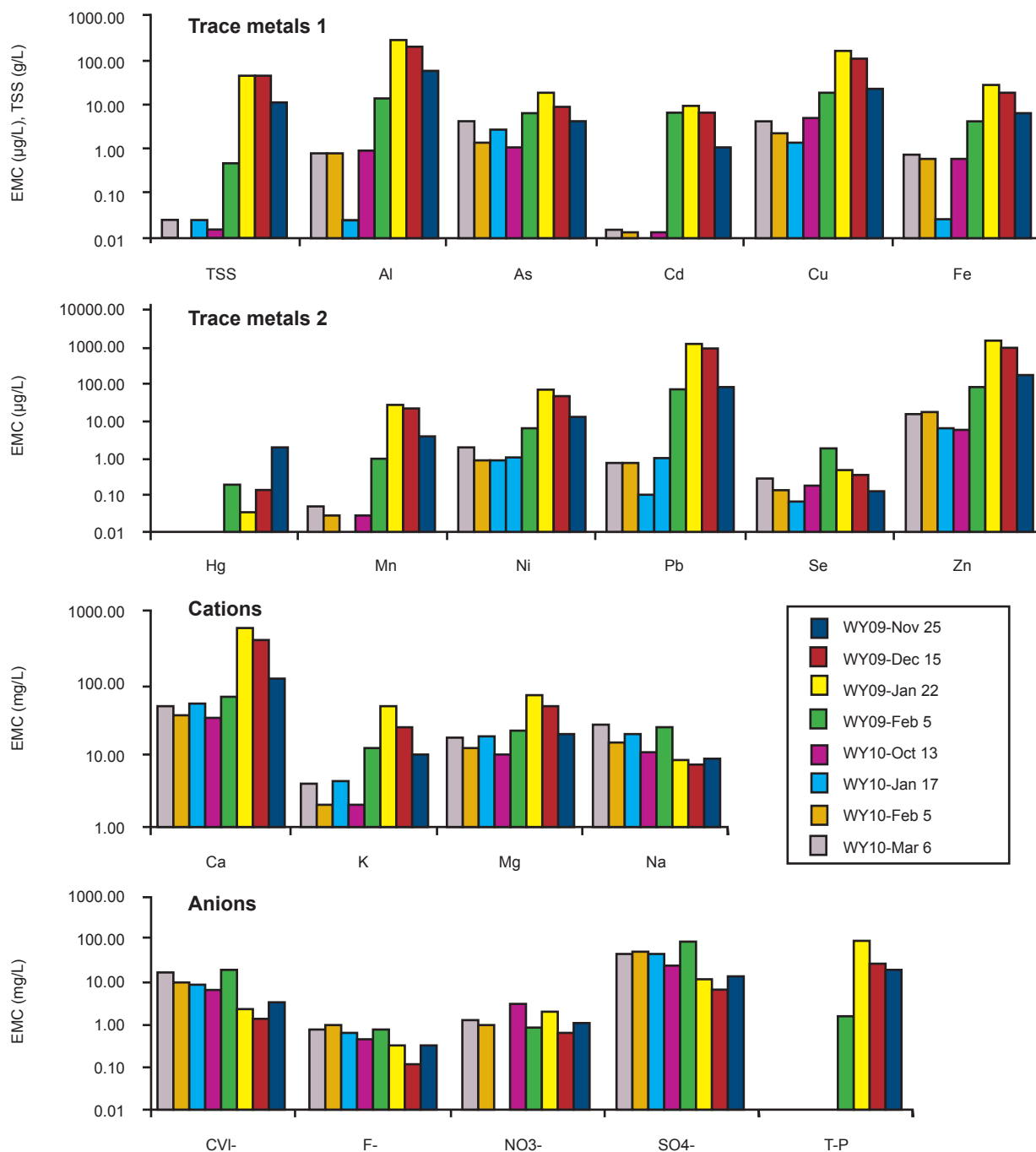
Figure 4. EMC values for trace metals, cations, and anions for each storm sampled in WY09 and WY10.

increased post-fire runoff, anion EMCs and fluxes did not increase by more than two-fold, and all values returned to below WY09 February 5 storm values by the third post-fire storm. This is even true for NO_3, which is noteworthy, because previous work in the San Gabriel Mountains has shown that NO_3 is not flushed from these systems by the end of the winter rainy season (Fenn and Poth 1999, Meixner *et al.* 2006, Barco *et al.* 2008).

Most post-fire trace metal and cation EMCs varied by one order of magnitude and, similar to mass flux, seasonal distributions closely resembled the distribution of WY10's storm discharge (Figure 4). Because maximum post-fire trace metal and cation concentrations corresponded to, rather than preceded, peak discharge (as in WY09), increased post-fire concentrations were accentuated when weighted by flow. One (As, Ca, Cu, K, Mg), two

(Al, Fe, Ni, Zn) and three (Cd, Mn, Pb) order of magnitude increases were observed in fluxes between the largest pre (February 5) and post-fire (January 17) storms.

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