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Key Points:

- Post-fire stream water chemistry impacts were usually site, constituent, and discharge-dependent, reflecting dynamic fire-induced changes
- Despite this variability, slopes of concentration-discharge relationships often became more positive post-fire, implying altered surface or near-surface sources
- Heterogeneity in fire-generated sources and processes contributes to complexities in post-fire stream water chemistry

Supporting Information:

Supporting Information may be found in the online version of this article.

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Exploring the Complex Effects of Wildfire on Stream Water Chemistry: Insights From Concentration-Discharge Relationships

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Abstract Wildfires are a worldwide disturbance with unclear implications for stream water quality. We examined stream water chemistry responses immediately (<1 month) following a wildfire by measuring over 40 constituents in four gauged coastal watersheds that burned at low to moderate severity. Three of the four watersheds also had pre-fire concentration-discharge data for 14 constituents: suspended sediment (SS_{fine}), dissolved organic and inorganic carbon (DOC, DIC), specific UV absorbance (SUVA), major ions (Ca²⁺, K⁺, Mg²⁺, Na⁺, Cl⁻, SO₄²⁻, NO₃⁻, F⁻), and select trace elements (total dissolved Mn, Fe). In all watersheds, post-fire stream water concentrations of SS_{fine} , DOC, Ca^{2+} , Cl^- , and NO_3^- changed when compared to pre-fire data. Post-fire changes in SO_4^{2-} , K⁺, Na⁺, Mg²⁺, DIC, SUVA, and total dissolved Fe were also found for at least two of the three streams. For constituents with detectable responses to wildfire, post-fire changes in the slopes of concentration-discharge relationships commonly resulted in stronger enrichment trends or weaker dilution trends, suggesting that new contributing sources were surficial or near the surface. However, a few geogenic solutes, Ca²⁺, Mg²⁺, and DIC, displayed stronger dilution trends at nearly all sites post-fire. Moreover, fire-induced constituent concentration changes were highly discharge and site-dependent. These similarities and differences in across-site stream water chemistry responses to wildfire emphasize the need for a deeper understanding of landscape-scale changes to solute sources and pathways. Our findings also highlight the importance of being explicit about reference points for both stream discharge and pre-fire stream water chemistry in post-fire assessment of concentration changes.

Plain Language Summary Wildfires are becoming more common, yet the effects of wildfire on streams and their water quality remain unclear. Changes in stream water quality following a wildfire can have consequences for drinking water and aquatic ecosystems. We studied how stream water quality changed in four impacted watersheds following the 2020 CZU Lightning Complex Wildfire in central coastal California using measurements of stream water chemistry coupled with analysis of burned soils and ash from the same area. For sites with pre-fire data, we found that wildfire impacts on stream water quality were greatest in the most extensively burned watershed. We also found that stream water quality changes were distinct across watersheds and dependent on stream discharge. Chemical measurements of potential sources of solutes, like ash and burned soils, indicate that the variability in stream water quality was consistent with contributions from ash or other burned landscape materials. The location, composition, and amount of these wildfire-generated sources vary in space and time. This complexity can lead to some similarities as well as differences in water quality responses of different streams, like those found in our study.

1. Introduction

Wildfires are increasing in frequency and magnitude in many regions of the world due to climate change and shifts in land management practices (Abatzoglou & Williams, 2016). While wildfires are an important regulator of fire-adapted ecosystems (Bond & Keeley, 2005), key uncertainties exist in understanding how stream water chemistry and watershed function change following wildfires. Understanding wildfire impacts on stream water quality is important for effectively planning and managing wildfire-prone areas, as streams often serve as drinking water sources and provide critical ecosystem services and habitat.

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Methodology: C. Richardson, S. Wagner, R. Barton, A. Paytan, M. Redmond, M. Zimmer

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Wildfires can alter the routing and composition of water as it flows from hillslopes to downgradient streams through changes to landscape properties and processes as well as through the creation or alteration of materials, like ash, soil, and plant matter. Streams, acting as integrators of change across landscapes (Fisher & Welter, 2005), reflect the cumulative impact of wildfires on watershed hydro-biogeochemistry. The extent of this impact is contingent on how modifications to various landscape components, such as soil, vegetation, and water sources, converge with interacting physical and biogeochemical processes in both space and time following a fire.

For instance, wildfires can have wide-ranging effects on chemical and physical properties of soil. Wildfire-induced vegetation mortality can drive physical changes in soil structure and stability (Busse et al., 2010; Cerdà & Doerr, 2005; Chief et al., 2012) and lead to increases in direct precipitation from tree canopy loss that mobilizes soil-sealing microparticles (Larsen et al., 2009; Williams et al., 2019). At the same time, combusted soil organic matter has been shown to generate volatilized organic compounds that increase surface soil hydrophobicity and contribute to soil water repellency, enhancing overland flow (DeBano, 2000; Stoof et al., 2011; Woods et al., 2007).

Wildfire can also impact soil biogeochemistry. For example, fire can increase surface soil pyrogenic organic carbon content, a product of incomplete combustion of biomass at high temperatures that comprises substantial fractions of total soil organic carbon in some post-fire systems (Reisser et al., 2016). Wildfires have even been shown to impact soil mineral composition and the availability of exchangeable cations (Agbeshie et al., 2022; Certini, 2005). Moreover, fire-induced shifts in soil biology (e.g., microbial and interconnected plant communities) can play an important and interactive role in watershed biogeochemistry (Lehmann et al., 2011; Whitman, Enders, & Lehmann, 2014; Whitman, Zhu, & Lehmann, 2014).

The creation of surface materials, like ash, can likewise alter soil-water interactions and chemistry in diverse ways (Balfour et al., 2014; Woods & Balfour, 2010). At local to regional scales, ash composition can be highly variable due to differences in vegetation burned, soil type, and combustion temperatures (Bodí et al., 2014), but often is elementally dominated by Ca, K, Mg, Si, and sometimes, P, Na, S, Al, Fe, Mn, and Zn in lower proportions (Balfour & Woods, 2013; Bodí et al., 2014; Gabet & Bookter, 2011). Leaching experiments of water-soluble elements in ash thus often show high concentrations of major ions, including K⁺, Na⁺, Mg²⁺, Ca²⁺, SO₄²⁻, and Cl⁻ (Khanna et al., 1994; Khanna & Raison, 1986; Swindle et al., 2021). Moreover, ash chemistry has been shown to shift with time after hydration, indicating that endmember values may not be static (Balfour et al., 2014).

Together, these complex changes to landscape solute sources, like ash, soil, and vegetation, interact with climatic conditions, affecting stream discharge and water chemistry. For instance, stream discharge can increase after wild-fires (Benavides-Solorio & MacDonald, 2001; Jumps et al., 2022; Moody & Martin, 2001; Warrick et al., 2012) due to changes in vegetation and soil properties that affect hydrologic regimes and the partitioning of water across landscapes (Bart, 2016; Hallema et al., 2017; Havel et al., 2018; Saxe et al., 2018). However, not all fire-impacted watersheds exhibit increases in stream discharge, owing to complex interactions with landscape components (Goeking & Tarboton, 2020). Post-wildfire hydrology can also show a strong dependency on climate (Maina & Siirila-Woodburn, 2020; Murphy et al., 2015), with more recent work highlighting how wildfires can have spatially variable impacts on hydrological responses in ecoregions, like the Mediterranean, where little evidence of post-fire hydrologic change was found due to drought (Newcomer et al., 2023).

In addition to changes in stream discharge, increases in post-fire stream water suspended sediment concentrations are well documented in many burned watersheds from increases in erosion (Desilets et al., 2007; Malmon et al., 2007; Warrick et al., 2012). However, less consensus exists on the effects of wildfires on in-stream dissolved constituents (Paul et al., 2022; Smith et al., 2011). As water flows over recently burned landscapes, ash and partially combusted surface soils can contribute directly and indirectly, via leached constituents, to downgradient stream water chemistry. Similar to the chemical heterogeneity of ash and fire-affected soils, existing studies have documented a wide variety of changes in the dissolved constituents of stream water following wildfires (Raoelison et al., 2022; Smith et al., 2011).

For instance, while a recent global meta-analysis of post-fire changes in stream water quality across 121 global sites found that fire increases NO₃⁻, PO₄³⁻, total N, DOC, and suspended sediment concentrations (Hampton et al., 2022), other studies have reported contrasting findings for several of these parameters (Paul et al., 2022). Wildfire was linked to decreases in DOC concentrations in eight US watersheds studied for nearly two decades (Wei et al., 2021), and, in burned coniferous-dominated watersheds of Montana, stream water showed increases

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in NO₃⁻, Cl⁻, and SO₄², but minimal change in suspended sediment, DOC, and other nutrients (Mast & Clow, 2008). Less is known about changes in stream water concentrations of other geochemical constituents, like trace metals. A few studies have found increased concentrations of some dissolved metals (Abraham et al., 2017; Smith et al., 2011), but most work has been limited by a paucity of pre-fire and/or stream discharge data to reference. Even amongst some of the most studied post-fire stream water constituents, like DOC and NO₃⁻ (Bladon et al., 2008; Hampton et al., 2022; Rhoades et al., 2019; Uzun et al., 2020), mechanisms driving system change and across site variability remain poorly understood (Smithwick et al., 2005).

Moreover, limited knowledge exists on how hydrology and wildfire interact to drive changes in stream water constituent concentrations. Stream discharge is a widely recognized control on stream water chemistry, a finding that has grown from research on concentration-discharge (C-Q) relationships, which reflect functional linkages between watershed hydrology and biogeochemistry (Hall, 1970, 1971; Johnson et al., 1969; Musolff et al., 2015). C-Q relationships can reveal whether streams are chemostatic, when concentrations do not vary with discharge, or chemodynamic, when concentrations vary with discharge (Godsey et al., 2009). Chemodynamic solutes can trend towards enrichment, varying positively with discharge and implying near surface or surface sources, or dilution, varying negatively with discharge patterns and implying source limitation (Basu et al., 2011; Godsey et al., 2009; Murphy et al., 2018; Rose et al., 2018). As such, C-Q relationships can provide information useful for ascertaining hydrologic flow paths and solute source connectivity across landscapes (Botter et al., 2020; Knapp et al., 2022; Musolff et al., 2017; Thompson et al., 2011).

However, largely due to the limited availability of pre-fire data, little work exists on relationships between stream discharge and stream water chemistry in the context of disturbances, like wildfire. Recent work suggests that wildfire can influence C-Q behavior in unique ways (Murphy et al., 2018). In addition, existing work often overcomes pre-fire data limitations by utilizing neighboring unburned watersheds as reference points to gauge the direction and magnitude of stream water solute concentration changes after wildfires. While reference watersheds and longitudinal sampling are common workarounds, many uncertainties exist in using adjacent sites for inferring system change in stream water chemistry.

The goal of this study was to understand how wildfire alters post-fire C-Q relationships through fire-induced changes in solute availability and hydrologic connectivity. Moreover, we sought to investigate if and how C-Q patterns shift across the study watersheds (e.g., change to enrichment of solutes due to the presence of new surface and near-surface solutes, potential increases in the routing of water through surficial flow paths during rain events). We had the unique opportunity to build on pre- and post-fire C-Q data for 14 stream water constituents in three gauged coastal watersheds with low to moderate severity burns from the 2020 CZU Lightning Complex Wildfires in central California. Pre-fire data were available as these watersheds are used as local drinking water sources and hence are regularly monitored. We also collected water samples from a neighboring gauged watershed that was severely burned but had limited pre-fire data. Stream water samples were obtained throughout the first 2 years following the wildfire. We measured an additional suite of over 27 constituents that lacked pre-fire data to compare base flow and event flow means at all sites. We supported these data with measurements of water-soluble concentrations of major ions leached from ash and burned surface soils from the same water-sheds to understand how burned landscapes serve as new solute sources that can drive stream water chemistry responses following wildfires.

1.1. Study Area

The CZU Lightning Complex Wildfires were started by a series of dry lightning events and burned $350~\rm km^2$ in the Santa Cruz Mountains along the central California coast between 16 August and 22 September 2020. This study focuses on four coastal watersheds (Laguna Creek, Majors Creek, San Lorenzo River, and Scott Creek) affected by the wildfires (Figure 1). While the four watersheds are adjacent to each other, they have variable sizes, geology, and topography (Table 1). Three of these watersheds (Laguna Creek, Majors Creek, and San Lorenzo River) are used as local drinking water sources. The watersheds vary in size, from 12.9 to $352~\rm km^2$ (Table S1 in Supporting Information S1). The basin size above the point of sampling was smaller, between 9 and $276~\rm km^2$, as gauges were not co-located with river mouths (Table 1). Central coastal California has a Mediterranean climate, where rainfall occurs predominantly during the cool winter months and is out of phase with the higher evaporative demand during the warm summer months. Rainfall totals for each watershed averaged between $970~\pm~550$ and $1,160~\pm~650~\rm mm$ annually over the 2014 to 2021 water years (Table 1).

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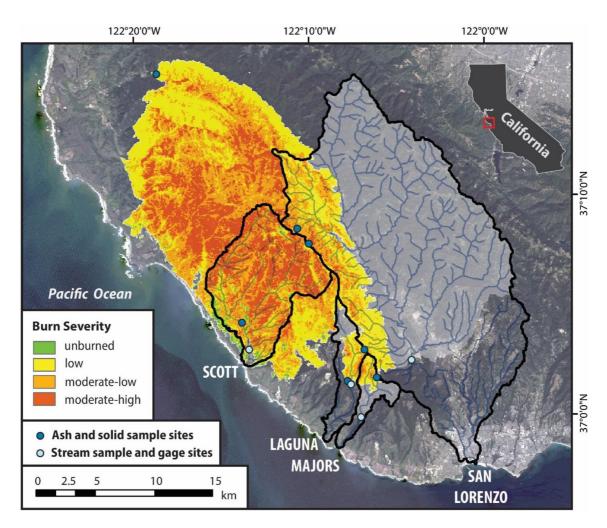


Figure 1. Study area overview showing the 2020 CZU Lightning Complex Wildfire perimeter and burn area with severity indicated by color (with unburned areas within the burn perimeter shown in green). Bold black lines depict watershed boundaries. Light blue circular markers show the stream water sampling and gauge site locations, and teal circular markers show ash and solid sample collection sites. Shaded areas depict the portion of the watershed representing the drainage basin above the point of sampling.

The Majors Creek and San Lorenzo River watersheds are dominated (62%–86%) by sedimentary formations, with the remaining fraction consisting of igneous or metamorphic bedrock and surficial sediments (Table 1). These sedimentary formations are primarily comprised of sandstone, mudstone, and shale, while igneous components are mostly low-permeability granodiorite, quartz diorite, and granite. In the Laguna Creek Watershed, schist (48%) and igneous (40%) formations account for roughly half of the system's bedrock. The Scott Creek Watershed is composed primarily of sandstone (55%) and igneous (42%) bedrock.

Land cover across all watersheds is relatively consistent, with evergreen and mixed forests covering 80%–86% of the basins (Table 1). Forests are mainly comprised of Coast redwood (*Sequoia sempervirens*) and Douglas fir (*Pseudotsuga menziesii*), with other non-coniferous species, such as Red alder (*Alnus rubra*), Tanoak (*Notholithocarpus densiflorus*), Bay laurel (*Umbellularia californica*), and Bigleaf maple (*Acer macrophyllum*).

Wildfire characteristics were not consistent across the watersheds (Table 1). The Scott Creek Watershed was severely impacted by the wildfire, with nearly 98% of the watershed burned at mostly moderate-low to moderate-high severity. The Laguna Creek, Majors Creek, and San Lorenzo River watersheds experienced low severity burns that affected between 16% and 32% of the total catchment area (Table S1 in Supporting Information S1). However, given that samples were collected upstream of the river mouth, we calculate the burn extents for the watersheds upstream of the gauge (20%–60%), reflecting the proportion of the drainage area impacted as relevant to our study.

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Table 1
Watershed Sizes, Geology, Land Use, and Burn Characteristics Above the Point of Sampling

	Laguna	Majors	San Lorenzo	Scott
General characteristics				
Watershed area (km²)	9.0	9.9	276	73.5
Avg. Slope (%)	24.4	21.4	33.3	35.1
Water year average rainfall (2014–2021) (mm)	$1,160 \pm 650$	$1,040 \pm 570$	$1,020 \pm 570$	970 ± 550
Geology				
Sandstone and other (shale, siltstone, mudstone) (%)	12	62	86	55
Igneous (quartz diorite, etc.) (%)	40	37	8	42
Surficial sediments (%)	0	<1	2	3
Schist (%)	48	1	3	<1
Burn characteristics				
Burn area (%)	60	37	20	98
Low severity (%)	38	23	12	12
Moderate-low severity (%)	20	12	7	45
Moderate-high severity (%)	2	2	1	42
Land use				
Forest (evergreen, mixed)	84	86	80	83
Shrub	5	6	17	2
Developed	11	8	2	15

Note. Whole watershed characteristics are shown in Table S1 of Supporting Information S1. Igneous rocks found in these watersheds are all low conductivity, aside from some Mesozoic/Paleozoic marble, which makes up less than 0.8% of the watersheds. The San Lorenzo Watershed also contains a small amount of basalt accounting for roughly 0.3% of the entire watershed's bedrock geology.

2. Materials and Methods

2.1. Field Sampling

We sampled each of the four streams (Laguna Creek, Majors Creek, Scott Creek, and San Lorenzo River) over two water years, starting in October 2020 following the wildfire, which burned during August 2020. No rain events occurred prior to our sampling. During the first water year (WY 2021), 11 samples were collected at each site, with eight collected during rain events and the remaining three during baseflow, aside from Scott Creek (Figure 2). At Scott Creek, the first event flow sample was missed, and two other event flow samples could not be collected at the main river site due to widespread flooding; as a result, only five event flow samples were collected at this site for WY 2021. Baseflow samples during WY 2021 were collected before the start of the rainy season (October), in between rain events during the mid-rainy season (December), and following the rainy season (April). During the second water year (WY 2022), four samples were collected in total at three of the four sites (Laguna Creek, Majors Creek, and Scott Creek), with three during rain events and the remaining one during baseflow before the wet winter season (October) (Figure 2). Not all WY 2022 samples were processed due to time and funding limitations; of the WY 2022 samples collected, we analyzed for suspended sediment and DOC concentrations for all four events and cation concentrations for only the first three field events. In the context of hydroclimatic variability, water years 2021 and 2022 were below normal. Event samples were collected during separate rain events. We targeted peak flow periods for sampling due to the logistical constraints of sampling at higher frequencies across multiple watersheds simultaneously. These post-fire stream water samples were complemented by measurements from other public agencies, as discussed in Section 2.3 (see Tables S3 and S4 in Supporting Information S1 for sample count summaries).

All stream water samples were collected as 4 L grab samples from flowing portions of the channel by standing at the stream bank and, when possible, at the center of the stream. Samples were kept on ice and filtered within 2–4 hr of collection through pre-combusted 0.7 μ m GF/F filters followed by a 0.2 μ m nylon membrane filter. Samples for dissolved inorganic carbon (DIC) were not filtered and immediately poured into 125 ml borosilicate

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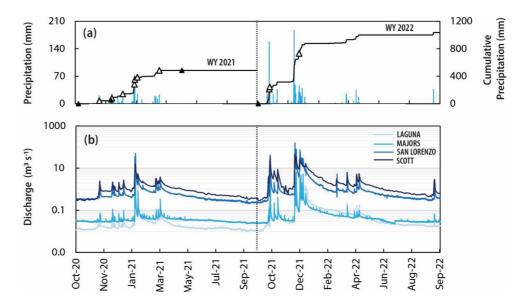


Figure 2. (a) Daily and cumulative precipitation totals from Ben Lomond Rain Station (#32058), and (b) hydrographs for each stream sampled during WY 2021 and WY 2022. Triangular markers represent sampling events, with solid black triangles indicating baseflow samples and white triangles indicating event flow samples. The County of Santa Cruz sampling events are not depicted as samples were collected at different frequencies depending on solute. Total sample numbers for each constituent during post-fire periods are available in Table S4 of Supporting Information S1.

bottles with Si-free greased glass stoppers and poisoned with ${\rm HgCl_2}$ to inhibit biological activity. Dissolved trace element samples were filtered and acidified to a pH below 2 with triple distilled trace clean ${\rm HNO_3}$. Suspended sediment data was collected bankside via surface dip sampling due to the nature of high-flow event sampling and the risk of landslides and debris flows that required minimizing time at each site (Edwards et al., 1999). Estimates may be considered a minimum if we only captured fine suspended sediment, and, as such, we denote these suspended sediment measurements as ${\rm SS_{fine}}$ to differentiate from total suspended sediment, similar to Jumps et al. (2022).

2.2. Analysis of Stream Water Chemistry

Stream water samples were analyzed for a suite of constituents. SS_{fine} concentrations were measured at the University of California (UC) Santa Cruz as dry weight differences on pre-weighed, combusted GF/F filters; precision for this method based on duplicate analysis for most samples was below 10%. Major cations (Ca²⁺, K⁺, Mg²⁺, Na+) were determined on a Thermo iCap 7400 ICP-OES at UC Santa Cruz; cation concentrations were analyzed with an internal standard and certified reference material (NIST 1643f), with a run precision and accuracy below 2% and 4%, respectively. Particulate organic carbon and nitrogen (POC and PON) concentrations were calculated using SS_{fine} and C:N molar ratios determined via CN Elemental Analyzer at the UCSC Stable Isotope Lab. Trace element samples (total dissolved Mn, Fe, Li, Al, V, Cr, Co, Ni, Cu, Zn, As, Rb, Sr, Cd, Ag, Cs, Ba, Pb, U, Be, Gd, Se, and Ti) were analyzed on a Thermo X-Series 2 ICP-MS at the University of Georgia's Center for Applied Isotope Studies and run with an internal standard. Samples were run in triplicate, and the relative sample standard deviation (RSD) for all trace elements was generally better than 5%. Major anion (Cl⁻, SO₄²⁻, and F⁻) samples were also run on a Dionex DX500 at the University of Georgia's Center for Applied Isotope Studies, with an average RSD of 7.7% across ions. Nutrient (NH₄⁺, NO₃⁻ + NO₂⁻, NO₂⁻, PO₄³⁻, SiO₄⁴⁻) concentrations were analyzed on a Lachat Quickchem 8000 Flow Injection Analyzer at San Jose State University's Moss Landing Marine Laboratory. NO₃⁻ + NO₂⁻ concentrations are referred to as NO₃⁻ throughout as NO₂⁻ concentrations were negligible. Nutrient precision and accuracy were below 5%. DIC samples were analyzed on a UIC Coulometer at UC Santa Cruz, with a precision of 2.2% and an accuracy of 1.5%. Total dissolved N and DOC samples were run on a Shimadzu TOC-V-CSH analyzer at Rensselaer Polytechnic Institute, with an average RSD below 1.5% for both constituents. DON was calculated as the difference between TDN and dissolved inorganic N. Absorbance of light at 254 nm was measured for all samples on a Thermo Genesys 10S UV-Visible Spectrophotometer at UC Santa

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Cruz. These values were normalized to DOC concentration to obtain mass-specific UV absorbance (SUVA), with a duplicate precision below 2%.

2.3. Other Sources of Pre- and Post-Fire Stream Water Chemistry Data

Nearly all pre-fire data were obtained from the City of Santa Cruz (CSC; see Table S3 in Supporting Information S1 for data availability, Tables S4 and S5 in Supporting Information S1 for sample details), and all post-fire data used to complement our sampling efforts was also from CSC. For pre-fire data, records generally start in 2004 for SS_{fine} and 2014 for other constituents. CSC data for suspended sediment was collected with roughly the same bankside grab sample technique and drying method; hence, we classify these samples as SS_{fine} as well. All DIC data for CSC samples were calculated in CO2SYS using total alkalinity, temperature, conductivity, and pH data (van Heuven et al., 2011).

Additional pre-fire data for the San Lorenzo River was acquired from the County of Santa Cruz for Cl⁻ (n = 52), DIC (n = 20), NO₃⁻ (n = 54), and SO₄²⁻ (n = 52), as well as the U.S. Geological Survey (USGS) for total suspended sediment (n = 221; see Table S3 in Supporting Information S1 for data availability). USGS measured TSS via a depth-integrated sampler at a downstream site on the San Lorenzo River (USGS Station 11161000) along with clay and sand fractions (Swarzenski et al., 2022). To correct these data to upstream values at our sampling location, we leveraged points in time when samples were collected within 1–3 hr of one another at both sites. This allowed us to regress paired measurements of clay/sand fractions along with TSS concentrations at the downstream site with respect to SS_{fine} data at our upstream site. We considered correcting the downstream data set to upstream SS_{fine} using both TSS (n = 12, $y = 1.66x^{0.74}$, $R^2 = 0.93$) and clay size fractions of TSS (n = 12, $y = 1.34x^{0.82}$, $R^2 = 0.89$; Figure S1 in Supporting Information S1). Due to potential sampling biases in our post-fire data set and the CSC pre-fire data, which may favor the collection of smaller size classes of suspended sediment, we opted to use the clay fraction correction.

For each watershed with CSC pre-fire data, we expanded the SS_{fine} measurements by utilizing turbidity data collected more frequently. To do this, we regressed turbidity data with paired measurements of SS_{fine} at each location (Laguna, $y = 0.95x^{0.93}$, $R^2 = 0.92$; Majors, $y = 0.52x^{1.09}$, $R^2 = 0.98$; San Lorenzo, $y = 0.96x^{1.05}$, $R^2 = 0.98$; Figure S2 in Supporting Information S1).

Finally, at Scott Creek, the NOAA National Marine Fisheries Service collected high-frequency pre-fire and post-fire turbidity data roughly 1.5 km downstream of the sampling location in a lagoon using a Eureka Manta Multi-Probe (see Table S3 in Supporting Information S1 for data availability). We used the lagoon turbidity time series data to compare pre- and post-fire periods as the upstream river site lacked pre-fire stream water chemistry data

2.4. Precipitation and Discharge Data

Spatially integrated precipitation totals were calculated for each watershed in Google Earth Engine. Precipitation data at the watershed scale are from the PRISM Climate Group using spatially-integrated monthly time-series data at a resolution of 4638.3 m (Daly et al., 2008). Discharge data for Majors Creek and Laguna Creek were accessed via the CSC, which maintains gauges at both sampling sites (see Table S3 in Supporting Information S1 for data availability). The San Lorenzo River has a gauge operated by USGS co-located with our sampling site location (USGS Station 11160500) (see Table S3 in Supporting Information S1 for data availability). Scott Creek discharge data was compiled from pre-fire water level and rating curve records from NOAA National Marine Fisheries Service. Post-fire records at Scott Creek were collected by NOAA in WY 21 and by us in WY 22. Due to gaps in records, we backfilled missing daily water level data at this site by building regressions between existing Scott Creek daily water level data (W_{SC}) and daily San Lorenzo River discharge (Q_{SR}): WY 2019 (n = 364), $log(W_{SC}) = 0.17(log(Q_{SR}) - 0.09)$, $R^2 = 0.73$; WY 2020 (n = 232), $log(W_{SC}) = 0.19(log(Q_{SR}) - 0.10)$, $R^2 = 0.80$; WY 2021 (n = 58), $log(W_{SC}) = 0.21(log(Q_{SR}) - 0.64)$, $R^2 = 0.95$; WY 2022 (n = 154), $log(W_{SC}) = 0.26(log(Q_{SR}) - 0.12)$, $R^2 = 0.85$.

2.5. Spatial Data

Difference normalized burn ratio (dNBR) maps were generated using Landsat 8 C2 L2 imagery courtesy of the USGS in TerrSet 2020. The pre-fire image was collected on 3 April 2020, and the post-fire image was collected on 21 March 2021. Images were corrected for hillside illumination with NBR and dNBR calculated

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subsequently. Burn severity classifications were based on dNBR range suggestions from Key and Benson (2006) as follows: -0.1 to 0.099, unburned; 0.1 to 0.269, low severity; 0.27 to 0.439, moderate-low severity; 0.44 to 0.659, moderate-high severity; and 0.660 to 1.300, high severity.

Land use data are from the 2019 National Land Cover Database (Dewitz, 2021). Forest percentages used in this study are the sum of "Evergreen Forest" and "Mixed Forest." Classification definitions are available online from the NLCD database. Geology data are from a digitized geologic map of Santa Cruz County based on Brabb et al. (1997).

2.6. Pre- and Post-Fire Statistical Comparisons

For constituents with no pre-fire data, which prevented pre- and post-fire comparisons, we averaged WY 2021 and WY 2022 base and event flow concentrations from our samples (not including the CSC data). Base flow samples were defined as below the 50th flow percentile for each site, but more commonly below the 25th percentile. Event flow samples were always collected after rainfall, with all samples above the 50th flow percentile, but typically and more commonly, above the 75th percentile. We used Mann-Whitney Rank Sum Tests in Sigma-Plot to determine if concentrations were significantly different across these two flow categories (Table S6 in Supporting Information S1).

For constituents with pre-fire data, we used linear and multiple linear regressions using the stats package in R to screen analytes for wildfire impacts on stream water chemistry (Tables S7–S10 in Supporting Information S1). This step allowed us to explore the potential impact of wildfires on stream water chemistry without assuming a definite influence by virtue of having C-Q data before and after the wildfires. Predictors were considered as flow and a pre-fire/post-fire categorical variable. Response variables covered 14 constituents with pre- and post-fire data at three watersheds (Laguna Creek, Majors Creek, and San Lorenzo River). We considered four models to examine the importance of wildfire as a predictor variable on individual stream water constituents. This information was also used to justify comparisons of pre- and post-fire C-Q relationships. The first two models were simple linear regressions that used discharge or fire category as predictor variables and stream water concentrations as the response variable. For the remaining two models, we used multiple linear regression to cumulatively examine the role of both stream discharge and wildfire on stream water concentrations of the 14 constituents individually. Both additive and interaction terms were considered for the multiple linear regression models, and all concentration and discharge data were log-transformed. Equations were first screened so that R² values were over 0.10. After this initial screening, we selected the model with the lowest AIC_C value that had model coefficients with a significance of p < 0.1 or smaller and a standard error below 50%. For constituents with wildfire significance, we categorized the fire response based on three levels: "minimal" (up to 20% improvement in model R^2 relative to baseline model with no fire predictor), "moderate" (over 20% improvement in model R^2 relative to baseline model with no fire predictor), and "major" (over 30% improvement in model R^2 relative to baseline model with no fire predictor). These categories provide more nuanced insight into wildfire impacts. If only fire category (and not stream discharge) had predictive power, we did not require model improvements as we assumed this to be a direct indicator of the importance of pre-versus post-fire change.

2.7. Concentration-Discharge Analysis and Estimates of Concentration Change

For constituents with pre- and post-fire data, C-Q regressions, defined as $C = aQ^b$, and commonly examined in double-logarithmic space, where a is the intercept and b is the slope, were analyzed. Slopes of C-Q regressions can be classified to determine export behavior. Similar to Botter et al. (2020), we used the Student t-test to determine if the slopes of C-Q regressions were statistically significantly non-zero to classify chemodynamic versus chemostatic patterns. Other C-Q metrics (e.g., coefficient of variation, p-values, etc.) are presented in Tables S12–14 of Supporting Information S1.

For constituents with detectable fire responses, we used C-Q relationships (Table S15 in Supporting Information S1), when possible, to estimate the concentration change across different stream flow percentiles (5th, 25th, 50th, 75th, and 90th). We required both pre- and post-fire C-Q relationships to have an $R^2 > 0.25$ to justify use in estimates of concentration change. Stream discharge values used in estimates of concentration change were referenced to one another based on stream flow percentiles (5th, 25th, 50th, 75th, and 90th), which were generated using the EGRET package in R (Table S2 in Supporting Information S1). More specifically, pre-fire and post-fire

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baselines were simply estimates of their respective C-Q regressions at the stream discharge percentile under consideration. The use of stream discharge percentiles allows for more appropriate intercomparisons across sites.

3. Results

3.1. Stream Water Chemistry Comparisons for Constituents With No Pre-Fire Data

To contextualize constituents and sites with little to no pre-fire data to reference, we compared mean base flow and event flow concentrations for all sites and parameters (Table S6 in Supporting Information S1). Differences in means across the two flow categories were often site-dependent, though some broad trends were apparent. SS_{fine} , DOC, POC, and PON concentrations significantly differered between base and event flows, with mean concentrations often an order of magnitude greater during event flows (Table S6 in Supporting Information S1). Mean DOC concentrations were similar across flow categories at each site, with base flow averaging 0.79-1.81 mg L⁻¹ and event flows averaging 0.79-1.81 mg L⁻¹. Mean DIC, cation (0.79-1.81 mg H⁻¹) concentrations as well as SUVA values were generally higher during base flow relative to event flows except for K⁺, though significant differences were not detected for many of these changes. Overall, mean 0.79-1.81 mg PO₄³⁻ concentrations remained low and similar across flows at all sites (0.79-1.81 mg NU₄ mg NU₄

Trace element concentrations show different trends. Some, like total dissolved Li, V, Cr, Co, Ni, As, Rb, and Pb, showed minimal change across base and event flows. Others, like total dissolved Al, Zn, and Ba, had event flow means that were 5.2–15.3, 4 to 10, and 49–142 $\mu g L^{-1}$ higher than base flow means, respectively. Mean total dissolved Sr and U decreased during event flows. Total dissolved Cu had mixed responses, with some sites showing slight increases (0.6–2.8 $\mu g L^{-1}$) and others decreasing (–1.2 $\mu g L^{-1}$) across base flow and event flow means. Trace elements, like total dissolved Ag, Cd, and Cs, were often below detection limits, but the data that were available showed little change across flow categories and low concentrations overall.

3.2. Pre- and Post-Fire Comparisons of Wildfire-Induced Changes in Stream Water Chemistry

C-Q relationships showed measurable shifts for many parameters after the wildfires (Figures 3 and 4), though general C-Q behavior remained relatively similar pre- and post-fire across all sites (Table S11 in Supporting Information S1). For instance, solutes that were chemodynamic pre-fire often remained so after. A few solutes, depending on site, did shift from chemostatic to chemodynamic (e.g., K^+ , Mn, and Fe) and vice versa (e.g., SO_4^{2-} and NO_3^-).

In addition, not all C-Q relationships were discernibly different across pre- and post-fire periods. For instance, all stream water constituents registered detectable post-fire changes in solute behavior for at least one of the sites, but not necessarily all (see Table 2 for a summary, Tables S7–S9 in Supporting Information S1). The degree of this change, defined by the relative improvement in pre-versus post-fire regression models, was site and constituent-specific. The wildfires had the most apparent impact on stream water concentrations of Na⁺, Cl⁻, NO₃⁻, and SO₄²⁻, which all had moderate to major responses, in at least at two of three streams with pre-fire data (Table 2). Other constituents, including SS_{fine}, DOC, SUVA, K⁺, and total dissolved Fe showed moderate to major responses to fire in at least one of the three streams (Table 2). The remaining stream water constituents, DIC, Ca²⁺, F⁻, and total dissolved Mn, showed minimal responses to the fire in at least one, but up to three, watersheds. Constituents that were consistently different post-fire at all sites included SS_{fine}, DOC, Ca²⁺, Cl⁻, and NO₃⁻. While no pre-fire data was available for Scott Creek, nearly 1.5 km downstream of our sampling site at a lagoon, differences between pre- and post-fire turbidity measurements indicated a moderate post-fire response (Figure 5, Table S10 in Supporting Information S1).

The magnitude and direction of post-fire concentration changes were site, constituent, and discharge dependent (Figure 6, Table 2, and Table S15 in Supporting Information S1). At all sites, SS_{fine} C-Q patterns exhibited stronger enrichment trends after the fire (Tables S11–S14 in Supporting Information S1), and concentrations

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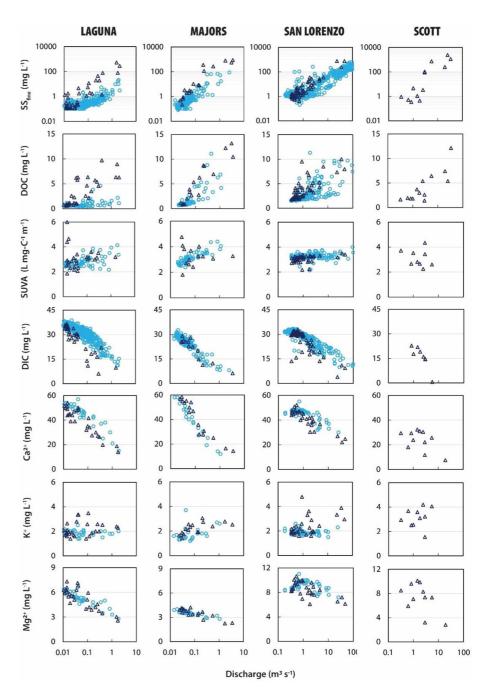


Figure 3. Concentration-discharge relationships for Laguna Creek, Majors Creek, San Lorenzo River, and Scott Creek. Pre-fire data are shown as light blue circles, and post-fire data are shown as dark blue triangles.

increased by 1.1-3.4 and 2.3-40.9 times pre-fire concentrations at normal and above normal flows, respectively (with normal defined as discharge in the 50th percentile and above normal defined as above the 75th percentile, see Tables S2 and S15 in Supporting Information S1). Likewise, post-fire DOC C-Q patterns were enrichment-type both pre- and post-fire with concentrations (Tables S11–S14 in Supporting Information S1) increasing by 1.3-2.6 times pre-fire values at normal flows and by 1.4-6.9 times pre-fire values at above normal flows. For SS_{fine} and DOC, changes were greatest at Laguna Creek, which had the greatest burn extent out of the three sites with pre-fire data. At Laguna Creek and the San Lorenzo River, DIC C-Q trends showed stronger dilution behavior after fire, and, as a result, concentrations were 0.8-0.9 and 0.6-0.8 times lower than pre-fire concentrations at normal and above normal flows, respectively. Stream water K^+ and NO_3^- concentrations as

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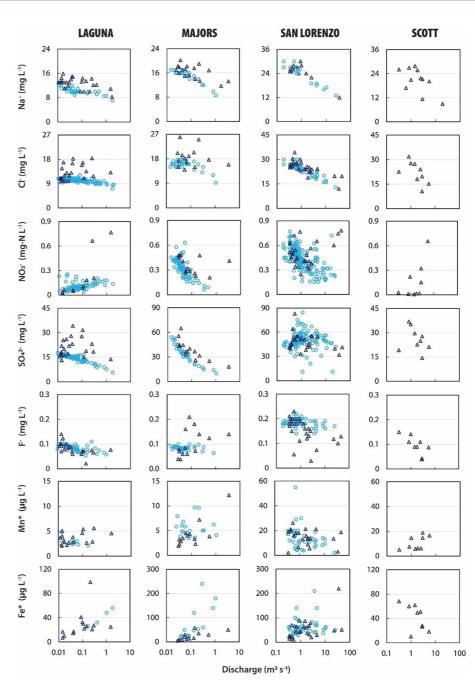


Figure 4. Concentration-discharge relationships (continued) for Laguna Creek, Majors Creek, San Lorenzo River, and Scott Creek. Pre-fire data are shown as light blue circles, and post-fire data are shown as dark blue triangles. Asterisks indicate that values shown are as total dissolved concentrations.

well as SUVA values changed detectably in at least two of three watersheds but did not have significant linear pre- and/or post-fire C-Q relationships to allow for quantitative analysis of post-fire change. Stream water Ca^{2+} concentrations generally decreased in Majors Creek and the San Lorenzo River and increased at Laguna Creek across all flows, though all exhibited dilution trends pre- and post-fire. Stream water Mg^{2+} , SO_4^{2-} , and total dissolved Fe concentrations changed post-fire in two of the three watersheds but could only be estimated for Majors Creek. Specifically, stream water SO_4^{2-} concentrations in Majors Creek increased post-fire by 1.1–1.7 times pre-fire values across all flow percentiles, while stream water Mg^{2+} showed slight increases of 1.1 times pre-fire values that were greatest at low flow percentiles and leveling off to no change at above normal flows. Both SO_4^{2-} and Mg^{2+} showed dilution trends at Majors Creek both before and after the fires. Stream water total

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 Table 2

 Summary Table of Stream Water Chemistry Responses to Wildfire

		Laguna	Majors	San Lorenzo
SS_{fine} (mg L ⁻¹)	Wildfire significance	Moderate	Minimal	Minimal
	Stream discharge 50th percentile	Increase, 3.4x	Increase, 4.5x	Increase, 1.1x
	Stream discharge 90th percentile	Increase, 20.1x	Increase, 6.8x	Increase, 2.3x
$DOC \ (mg \ L^{-l})$	Wildfire significance	Major	Minimal	Minimal
	Stream discharge 50th percentile	Increase, 2.6x	Increase, 1.6x	Increase, 1.3x
	Stream discharge 90th percentile	Increase, 5.2x	Increase, 1.5x	Increase, 1.4x
SUVA (L mg- C^{-1} m $^{-1}$)	Wildfire significance	_	Moderate	Minimal
	Stream discharge ^{50th percentile}	_	n.a.	n.a.
	Stream discharge 90th percentile	_	n.a.	n.a.
DIC (mg L ⁻¹)	Wildfire significance	Minimal	Not detectable	Minimal
	Stream discharge ^{50th percentile}	Decrease, 0.8x	n.a.	Decrease, 0.9x
	Stream discharge 90th percentile	Decrease, 0.6x	n.a.	Decrease, 0.8x
Ca ²⁺ (mg L ⁻¹)	Wildfire significance	Minimal	Minimal	Minimal
	Stream discharge 50th percentile	Decrease, 0.9x	Increase, 1.1x	No change, 1.0x
	Stream discharge 90th percentile	Decrease, 0.8x	Increase, 1.2x	Decrease, 0.9x
K+ (mg L-1)	Wildfire significance	_	Minimal	Moderate
	Stream discharge 50th percentile	_	n.a.	n.a.
	Stream discharge 90th percentile	-	n.a.	n.a.
Mg ²⁺ (mg L ⁻¹)	Wildfire significance	Not detectable	Minimal	Minimal
	Stream discharge 50th percentile	n.a.	Increase, 1.1x	n.a.
	Stream discharge 90th percentile	n.a.	No change, 1.0x	n.a.
Na+ (mg L-1)	Wildfire significance	Major	Moderate	Not detectable
	Stream discharge ^{50th percentile}	Increase, 1.2x	Increase, 1.1x	n.a.
	Stream discharge 90th percentile	Increase, 1.3x	Increase, 1.2x	n.a.
Cl- (mg L-1)	Wildfire significance	Major	Major	Minimal
	Stream discharge ^{50th percentile}	n.a.	n.a.	Increase, 1.1x
	Stream discharge 90th percentile	n.a.	n.a.	Increase, 1.3x
$NO_3^- (mg-N L^{-1})$	Wildfire significance	Moderate	Moderate	Minimal
	Stream discharge ^{50th percentile}	n.a.	n.a.	n.a.
	Stream discharge 90th percentile	n.a.	n.a.	n.a.
SO_4^{2-} (mg L ⁻¹)	Wildfire significance	Major	Moderate	_
	Stream discharge ^{50th percentile}	n.a.	Increase, 1.2x	_
	Stream discharge 90th percentile	n.a.	Increase, 1.5x	_
$F^-(mg\;L^{-1})$	Wildfire significance	Not detectable	-	Minimal
	Stream discharge ^{50th percentile}	n.a.	-	n.a.
	Stream discharge 90th percentile	n.a.	-	n.a.
$Mn* (\mu g L^{-1})$	Wildfire significance	-	Minimal	_
	Stream discharge ^{50th percentile}	-	n.a.	_
	Stream discharge 90th percentile	_	n.a.	_

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Tabl	e 2
Cont	inued

		Laguna	Majors	San Lorenzo
Fe* (µg L ⁻¹)	Wildfire significance	Not detectable	Moderate	Minimal
	Stream discharge 50th percentile	n.a.	Decrease, 0.5x	n.a.
	Stream discharge 90th percentile	n.a.	Decrease, 0.4x	n.a.

Note. Minimal, moderate, and major indicate that wildfire, as a predictor variable, improved the baseline model by up to 20%, 30%, and over 30%, respectively. Dashed lines indicate that explanatory variables (discharge, fire category) could not predict response variables with a model R^2 of at least 0.10 (see Tables S7–S9 in Supporting Information S1). For constituents with wildfire significance, we estimated concentration changes where possible (e.g., if C-Q relationships had a $R^2 > 0.25$, see Tables S11–S14 in Supporting Information S1). Asterisks indicate that the values shown are for total dissolved concentrations.

dissolved Fe concentrations in Majors Creek showed post-fire declines of 0.3–0.5 times pre-fire values. Stream water Cl⁻ concentrations, which were impacted by wildfire at all three sites, could only be compared for the San Lorenzo River, where concentrations increased by 1.1–1.4 times pre-fire values.

3.3. Wildfire Responses Across Watersheds With Respect to Burn Extent

Laguna Creek, the most extensively burned watershed (60%) with pre-fire data in our study, had the most detectable responses to wildfire, with major post-fire changes in four constituents (DOC, Na⁺, Cl⁻, and SO₄²⁻) (Table 2). Nearly 37% of the Majors Creek watershed burned, mostly at low severity, and this site registered more moderate to major fire responses in stream water chemistry parameters than its less burned counterpart, the San Lorenzo River. Similarly, Laguna Creek and Majors Creek recorded moderate to major fire responses for 6 of the 14 constituents examined, while the San Lorenzo River, which is much larger and burned only 20% above the point of sampling, only had one post-fire response at moderate strength.

3.4. Wildfire-Induced Changes in Stream Water Chemistry at Event Scales

Several stream water constituents had higher frequency, event-based responses hidden amongst the broader C-Q relationship shifts, and here we focus on Laguna Creek to provide a few non-exhaustive examples (Figure 7). Some constituents retained relatively linear relationships with discharge post-fire, with broad offsets in slope and/or intercepts, like SS_{fine} , while others showed evidence of more dynamic changes that were not always captured by the above analyses. For example, stream water K^+ , Na^+ , Cl^- , and SO_4^{2-} were highly variable and often non-linear

with discharge post-fire, with the highest concentrations occurring during the first few rain events in WY 2021, irrespective of the magnitude of stream discharge.

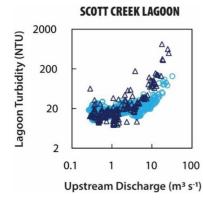


Figure 5. Concentration-discharge relationships for turbidity at Scott Creek Lagoon, roughly 1.5 km downstream of the Scott Creek sampling site. Upstream discharge is the daily discharge at the gauged Scott Creek stream site. Pre-fire data are shown as light blue circles, and post-fire data are shown as dark blue triangles.

4. Discussion

Our study suggests that wildfire impacts on stream water chemistry are highly variable. For instance, the extent and direction of concentration changes were often site, analyte, and discharge dependent (See Table 2, Table S10 in Supporting Information S1). Both similarities and differences in stream water chemistry responses to wildfires across our sites hint at the dynamic chemistry of contributing sources and the importance of wildfire and watershed characteristics in understanding stream water quality changes in post-fire landscapes.

4.1. Similarities in Post-Wildfire Stream Water Chemistry Changes

While fire impacts were often watershed-dependent, some consistencies in fire responses across the watersheds were observed. Changes in stream water SS_{fine}, DOC, Ca²⁺, Cl⁻, and NO₃⁻ were most common, with detectable

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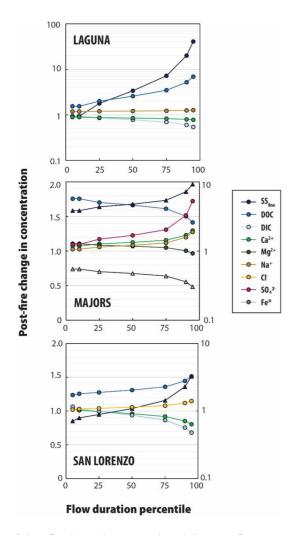


Figure 6. Post-fire changes in concentration relative to pre-fire concentrations across a range of flows. Triangular markers show parameters graphed on the log-scaled secondary axis. Flow duration percentiles are presented in Table S2 of Supporting Information S1. Estimations were only made for constituents if pre- and post-fire concentration-discharge relationships had an $R^2 > 0.25$, see Table S11 in Supporting Information S1 for equations and Table S15 in Supporting Information S1 for values.

shifts in concentrations of these parameters (increasing or decreasing) in all watersheds post-fire (Table 2 and Table S11 in Supporting Information S1). Impacts on SS_{fine} , DOC, and NO_3^- are expected as these changes are amongst some of the most studied in wildfire-impacted watersheds (Moody & Martin, 2009; Raoelison et al., 2022; Smith et al., 2011).

All C-Q relationships for SS_{fine} remained chemodynamic (enrichment-type) after the fire, suggesting that sediment is sourced and mobilized from shallow and surficial paths. Post-fire increases in C-Q slope likewise suggested that wildfire drove increased sediment mobilization, resulting in 0.9 to over 40-fold increases depending on stream discharge (Table S15 in Supporting Information S1), which is unsurprising as enhanced post-fire erosion and mass movement often drive downgradient increases in suspended sediment concentrations (Cole et al., 2020; Coombs & Melack, 2013; Florsheim et al., 1991; Lane et al., 2006; Reneau et al., 2007; Santi et al., 2013; Warrick et al., 2012). Such changes could arise from alterations to both surface sediment properties as well as changes in the hydrological routing of water.

Like SS_{fine}, DOC C-Q patterns exemplified enrichment trends before and after the fire, but with less substantial shifts in slope. Still, concentration changes for DOC were large, ranging from 1.5 to nearly 7-fold increases at higher flows (Table S15 in Supporting Information S1). Though consensus regarding post-fire DOC changes is limited, post-fire increases in stream water DOC concentrations have been found in many ecosystems and climate zones (Raoelison et al., 2022; Smith et al., 2011). Controls on DOC responses in fire-impacted systems are thought to include the oxygen content and the temperature at which pyrogenic C is produced during fire, with more labile forms generated at lower burn temperatures (Alexis et al., 2010). Thus, lower severity burns, like those of our study sites, may lead to more evident impacts on DOC concentrations.

While NO₃⁻ C-Q patterns were not uniform (even pre-fire), fire impacts resulted in a similar positive directional pull on NO₃⁻ C-Q trends, weakening the dilution behavior at Majors Creek and San Lorenzo River and strengthening the enrichment trend at Laguna Creek. This suggests that wildfire NO₃⁻ sources were likely near the surface or at the surface throughout the watersheds. While evaluation of absolute changes in concentration due to fire across flow percentiles was not possible with this study's design, existing work has found changes in stream water NO₃⁻ can range considerably, documenting increases of 1.5–6.5 times pre-fire values (Bladon et al., 2008; Hampton et al., 2022; Mast & Clow, 2008). Drivers of change in NO₃⁻ concentrations are complex and depend on other N cycling processes, where

inorganic and organic N forms can be produced and consumed directly during fire (volatilization) or secondarily from biotic (mineralization, nitrification) processes (Knoepp et al., 2005; Smithwick et al., 2005).

Similarly, fire-driven increases in stream water Ca²⁺ and Cl⁻, which have been documented in a few different aquatic ecosystems, are attributed to solutes leached from ash and other burned materials (Carignan et al., 2000; Earl & Blinn, 2003; Mast et al., 2016; Rust et al., 2018; Smith et al., 2011; Stephens et al., 2004). C-Q patterns for Ca²⁺ were all chemodynamic, with Laguna Creek and San Lorenzo River shifting toward stronger dilution behavior and Majors Creek showing weaker dilution trends after fire. As a result, the impacts of wildfire included both increases and decreases in stream water Ca²⁺ concentrations, depending on the site. Overall dilution trends are expected as Ca²⁺ is a well-known geogenic solute associated with mineral weathering (Musolff et al., 2021; Rose et al., 2018). However, the directional change discrepancy in Ca²⁺ post-fire C-Q responses highlights how fire impacts can be watershed-specific, likely owing to pre-fire variability in the chemistry of contributing source endmembers, like groundwater and shallow subsurface water, that mix with dynamic wildfire-generated solute sources, which can be compositionally and spatially diverse. C-Q trends for Cl⁻, which all showed dilution trends pre-fire, had detectable but unique post-fire impacts at each site, though the net impact appeared to be a shift

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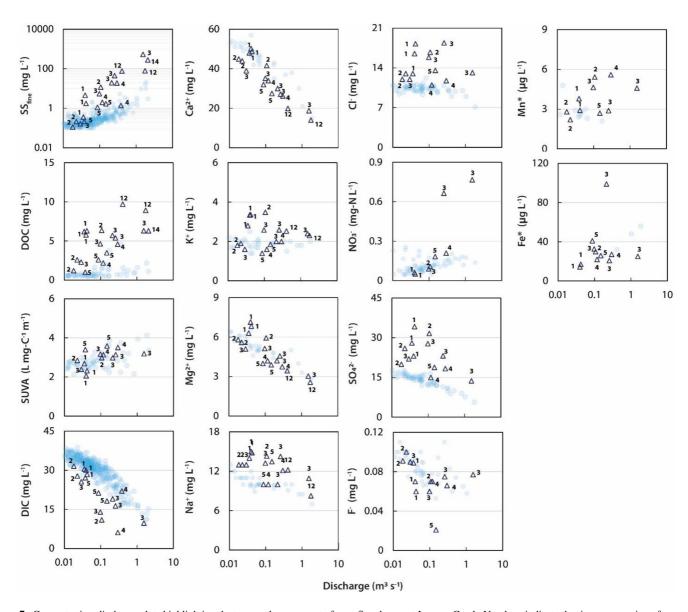


Figure 7. Concentration-discharge plots highlighting the temporal component of post-fire change at Laguna Creek. Numbers indicate the time progression of event flow sampling, with each number indicating month starting with November 2020 ("1") in WY 2021 and ending in December 2021 during WY 2022 ("14"). November 2020 was the start of the rainy season during WY 2021, and samples with a "1" were taken during the first rain events post-fire. No baseflow samples are shown for the post-fire data set (dark blue triangles). Pre-fire data is shown as semi-transparent light blue circles for reference. Asterisks indicate that values shown are as total dissolved concentrations.

toward weaker dilution behavior (and even enrichment at one site). An overall shift toward enrichment trends is unsurprising as Cl⁻ is associated with leachate from burned materials that can be mobilized at higher flows.

4.2. Differences in Post-Wildfire Stream Water Chemistry Changes

Many post-fire changes in stream water solute concentrations were spatially variable across the three sites with pre-fire data (Table 2 and Table S11 in Supporting Information S1). In many cases, post-fire C-Q slope values shifted slightly in magnitude, but still showed responses that retained their pre-fire C-Q chemodynamic patterns. This is not surprising as wildfire generates diverse surface and near-surface solute sources that can impact but perhaps not overwhelm C-Q patterns for many solutes, at least in lower-severity burn watersheds. For example, C-Q patterns for Na⁺ were all dilution-type pre- and post-fire, even though fire was found to have a detectable moderate to major impact on stream water Na⁺ concentrations at two of the sites.

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In addition, fire impacts on post-fire stream water concentrations (or values) of DIC, SUVA, Mg^{2+} , K^+ , SO_4^{2-} and total dissolved Fe were only detected in two of the three watersheds (Table 2). Several stream water parameters (SUVA) and solutes (K^+ , SO_4^{2-} , total dissolved Fe) eluded evaluation of change at one or both sites due to non-linearity in either pre- and/or post-fire C-Q relationships. Some, like K^+ , appeared to increase post-fire, with San Lorenzo River even transitioning from a chemostatic pre-fire C-Q pattern to enrichment after fire. Other stream water constituents (F^- , total dissolved Mn) showed detectable fire impacts on stream water concentrations in only one of the three streams.

These changes in stream water chemistry, while spatially variable, were at least consistent with solutes leached from ash and burned surface soil sources measured in this and other studies (Table S16 and Figure S3 in Supporting Information S1); leaching experiments of water-soluble elements in ash often show high concentrations of major ions, including K+, Na+, Mg²⁺, Ca²⁺, SO₄²⁻, and Cl⁻ (Bodí et al., 2014; Khanna & Raison, 1986; Khanna et al., 1994; Swindle et al., 2021). Some of the most evident changes in stream water chemistry, defined as moderate to major post-fire responses, occurred for Na+, K+, Cl-, NO₃-, total dissolved Fe, and SO₄²⁻ (Table 2). Experimental addition of ash to a stream in southwestern New Mexico showed immediate increases in stream water concentrations of many of these same ions, like Na+, K+, Mg²⁺, Ca²⁺, SO₄²⁻, Cl-, and NO₃- (Earl & Blinn, 2003). Moreover, pre- and post-fire comparisons of select stream water chemistry ratios at our study sites generally showed post-fire deviations consistent with mean ratios measured in the new wildfire generated and impacted sources as well (Figure S4 in Supporting Information S1).

However, interestingly, some stream water solute concentrations showed little evidence of post-fire change, even though they were found in high concentrations in leachate from ash and other burned materials. While anions, like Cl^- and SO_4^{2-} , which are commonly elevated in leachate from ash and burned surface soils (Table S16 in Supporting Information S1) (Bodí et al., 2014), showed moderate to major responses to fire across most sites, cations, like K^+ , Mg^{2+} , and even Ca^{2+} , often showed no or minimal strength fire responses. Compositionally, K^+ (31.3 \pm 18.5%) and SO_4^{2-} (28.4 \pm 4.4%) dominated leached solutes from ash measured in our study. This mismatch suggests that the fate of leached ions from burned materials is solute-specific. Solute specificity in post-fire responses was also observed for stream water concentrations of Cl^- and SO_4^{2-} after the Fern Lake Fire in Colorado and thought to be from differences in landscape solute reactivity and biological demand (Mast et al., 2016).

Solute specificity in stream water quality responses to wildfire was also evident in other ways. In qualitative terms, stream water concentrations of K^+ , Na^+ , Cl^- , and $SO_4^{\ 2^-}$ appeared to deviate the most from pre-fire values as a function of time since fire, with some of these parameters even showing strong linear pre-fire C-Q relationships that disappeared in the aftermath of fire (Figure 7, Table S11 in Supporting Information S1). These changes further suggest that initial rain events in burned areas can selectively mobilize some dissolved constituents disproportionately more than others and mosaic together with more sustained changes that may obscure detection. This is likely partly due to differences in how different wildfire sources (ash vs. soil) are mobilized over time. More broadly, this non-uniform loss of linearity in C-Q relationships post-fire (even while other sites retained linearity with the same solute) strengthens the idea that post-fire water quality responses can be both solute and site-specific.

In addition, not all stream water solutes increased in concentration post-fire. At the sites with detectable fire impacts for DIC, concentrations decreased relative to pre-fire values, likely due to lower DIC concentrations in the new contributing sources/pathways and/or changes in post-fire soil biogeochemistry. Past work found lower CO₂ effluxes in soil from post-fire decreases in respiration and changes in C stores (Adkins et al., 2019; Dove et al., 2020; Sullivan et al., 2011; Wang et al., 2002). At the same time, ash can be compositionally dominated by carbonates that produce DIC upon dissolution, with endmember values that are probably lower in concentration relative to groundwater sources in this region (Balfour & Woods, 2013; Bodí et al., 2014; Gabet & Bookter, 2011; Goforth et al., 2005).

We also found post-fire decreases in stream water total dissolved Fe concentrations, which is different from findings from other studies that have observed increases in stream water total dissolved Fe concentrations post-fire (Burton et al., 2016; Rust et al., 2018; Smith et al., 2011). More pre- and post-fire data are needed to evaluate this finding, as our total dissolved Fe data set had some of the fewest samples of any constituent herein. Like DIC, post-fire declines in stream water total dissolved Fe in our study suggest that the new contributing sources may have lower overall total dissolved Fe concentrations relative to pre-fire sources; such a change could result from fire-induced alterations in surface biogeochemistry that may result in changes in Fe availability and sorption.

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For all other constituents that had no pre-fire data (Table S6 in Supporting Information S1), the absence of significant deviations between base and event flow means suggested that fire either affected surface and subsurface sources of solutes similarly or, more likely, did not cause observable increases in a range of stream water parameters, including PO₄³⁻, NH₄⁺, total dissolved Li, V, Cr, Co, Ni, As, Rb, and Pb. Lack of change in nutrients, like NH₄⁺, is consistent with some studies detailing NH₄⁺ depletion in soils after fire from decreases in NH₄⁺ production and simultaneous increases in NH₄⁺ consumption (Turner et al., 2007). A few parameters (POC, PON, total dissolved Al, Zn, and Ba) did increase with event flows and, for these, it's unclear if fire played a role in the increase or if event flows more generally led to enrichment trends as is common for many non-fire impacted watersheds (Knapp et al., 2020). For POC and PON specifically, it is likely that fire played a part in generating some of the differences across flow categories due to the close connection between processes mobilizing larger material, like suspended sediment and suspended particulate organic matter, that often leads to strong positive correlations in other watersheds (Glossner et al., 2022; Richardson et al., 2023). In addition, many trace elements are found in association with suspended solids, like organic matter and minerals (Brown & Parks, 2001). The absence of deviations between base and event flow concentrations for several dissolved trace elements in our study does not account for export through some colloidal and all suspended phases, which can serve as the primary mode of transport for many trace elements (Gibbs, 1977; Hill & Aplin, 2001; Trostle et al., 2016).

4.3. Factors Driving Variable Stream Water Chemistry Responses to Wildfire

The magnitude and direction of post-fire change ranged considerably across sites, constituents, and with discharge (Table 2, Figure 6). Our results are consistent with existing review studies that have frequently found site-specific changes in stream water quality post-fire (Raoelison et al., 2022; Smith et al., 2011). This variability in stream water chemistry responses to wildfire, both in our study and other studies, likely arises from heterogeneity in the chemical composition, spatial distribution, and amount of wildfire generated and impacted sources in post-fire landscapes and the various physical and biogeochemical processes that drive their transport, transformation, and fate (Figure 8).

Ash and other burned materials can have highly variable inter- and intra-source chemistry due to pre-existing gradients in landscape features and properties (e.g., vegetation structure and composition, soil type and erodibility, topography, etc.) (Figure 8, Table S11 in Supporting Information S1) (Bodí et al., 2014; Harper et al., 2019; Khanna & Raison, 1986; Khanna et al., 1994; Swindle et al., 2021). Wildfire characteristics, like burn temperature and duration, interact with these pre-fire landscape gradients to generate the precise chemistry, amount, and spatial distribution of new fire-generated or impacted sources that may contribute to stream water chemistry (Goforth et al., 2005). This spatial complexity is a known and ecologically important effect of fire disturbance that others have highlighted in the context of nitrogen cycling and ecosystem recovery after fire (Foster et al., 1998; Smithwick et al., 2005; Turner et al., 1994).

The chemical composition of wildfire sources impacting stream water quality can also evolve over time. Ash, for instance, can evade full single-storm washout and chemically shift through time (Balfour et al., 2014). Like ash, burned surface soils may act as both instantaneous and delayed sources of materials that chemically change through time. Time-dependent controls on fire-impacted solutes and their environmental reactivity has been observed in processes controlling particulate versus dissolved pyrogenic organic matter generation in burned watersheds (Abiven et al., 2011; Barton et al., 2024). Time dependency may also be reflected in the temporal persistence of various sources. Loss of vegetation can lead to hillslope instability as roots decay, increasing suspended sediment exports over time (Santi et al., 2013). Similarly, partially combusted surface soils likely contribute to stream water chemistry for longer periods of time relative to other sources, like ash, that may be more readily washed out.

The transport, transformation, and fate of dissolved and particulate material from these varying burned sources to streams depend on other physical and biogeochemical processes that occur after fire as well. Transport of ash and partially combusted surface materials to streams depends on wind and water erosion, with precipitation event characteristics (e.g., intensity, duration, extent), type (i.e., snowfall vs. rainfall), and sequencing (i.e., time since last event) likely important controls on source mobilization (Barton et al., 2024; Murphy et al., 2012, 2015). In places like California, where precipitation type, patterns, and amounts vary considerably across water years and locations, initial impacts may be regionally distinct and/or delayed. Over shorter time scales, atmospheric deposition of wildfire-generated aerosols may also drive stream water quality changes in the immediate aftermath of fire (Boyer et al., 2022; Witt et al., 2009). Moreover, shifts in soil properties can alter landscape hydrology in

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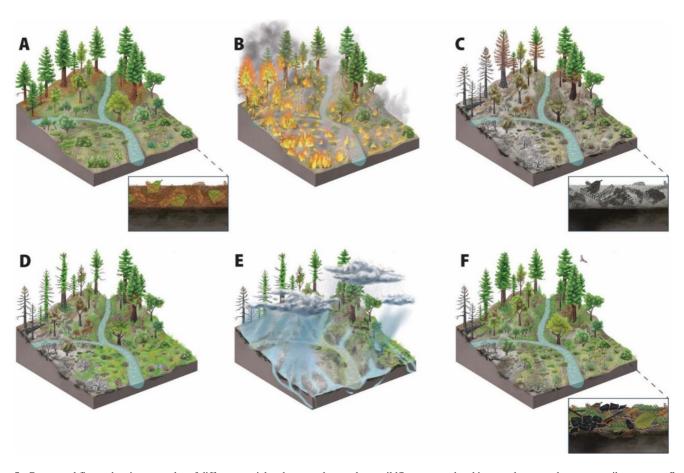


Figure 8. Conceptual figure showing examples of different spatial and temporal controls on wildfire generated and impacted sources that can contribute to post-fire changes in stream water chemistry, (a) natural vegetation gradients pre-wildfire, (b) gradients in wildfire characteristics, (c) immediate post-wildfire heterogeneity in the distribution of new/altered landscape sources (ash, burned soils) due to gradients in vegetation, wildfire, etc., (d) non-uniform recovery of vegetation after a wildfire, (e) natural variability in the spatial distribution, amount, and intensity of precipitation, and (f) 1-year post-wildfire snapshot showing the variability in recovery of vegetation and dispersal/removal/creation of new or altered wildfire material sources (ash, burned soils) through time. Zoom-in sections follow the evolution of a soil parcel (a) before, (c) immediately after fire, and (f) 1-year after fire.

spatially and temporally variable ways (Ebel & Moody, 2017) that may amplify surface routing of water through these new material sources.

Transformations on the landscape can further limit or amplify realized concentrations conveyed to streams post-fire. Solutes, like K^+ and Ca^{2+} , may be selectively immobilized as they are more reactive on landscapes (Riekerk, 1971). Similarly, nutrients, like NO_3^- and DON, which are more biologically relevant, may be taken up by plants or transformed to other forms before transiting to streams. Other transformations in soil and across watersheds likely occur once ecosystems begin to recover or shift in composition (Nelson et al., 2022), generating new indirect fire inputs biotically (e.g., mineralization, nitrification, etc.) and abiotically (e.g., photo-degradation) (Coppola et al., 2022; Dove et al., 2020; Smithwick et al., 2005).

Together, these processes lead to highly dynamic wildfire sources that can vary in space and time, generating intermittent or sustained changes in stream water chemistry that are solute and source-specific, like results found in our study. The site-specificity in the composition of and processes that control wildfire-generated sources that contribute to stream water quality changes also highlights the challenge of synthesizing and generalizing wildfire impacts across watersheds.

4.4. Wildfire Impacts on Local Communities and Connected Ecosystems

Three of the four studied creeks and rivers are used as local drinking water sources. While several fire impacts on stream water quality were detected, only total dissolved As concentrations were above recommended or required

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US EPA thresholds ($0.018-0.14~\mu g~L^{-1}$) for dissolved solutes (Paul et al., 2022), and concentrations were similar between base and event flows, suggesting that As is likely locally produced in underlying aquifers rather than fire-generated in these watersheds. The effects of fire impacted stream exports on in-stream and downstream connected ecosystems were less clear. Our four study watersheds have direct connections to the ocean, and each watershed terminates in a managed or natural coastal lagoon. These coastal lagoons are critical fish-rearing habitats for endangered steelhead salmon in the area (Hayes et al., 2008). At Scott Creek, lagoon turbidity data suggested that the watershed saw widespread increases in sediment export, demonstrating how upstream changes do propagate to downstream estuarine and marine ecosystems (Figure 5).

4.5. Future Challenges and Opportunities

Concentrations of various stream water parameters are often discharge-dependent, and many of the stream water constituents considered in this study were no different. Adequately characterizing the direction and magnitude of change in stream water solute concentrations owing to landscape disturbances, like wildfire, necessitates consideration for the role of discharge in concentration changes. We found stream discharge-driven changes in concentrations ranged substantially (sometimes several orders of magnitude), highlighting how post-fire comparisons that assign static values of concentration change need to be explicit about points of reference. We also found substantial variability in pre-fire stream water chemistry between our study watersheds, suggesting that using neighboring unburned reference watersheds may be problematic for interpreting fire-driven changes in stream water quality data in some regions. Understanding of pre-fire stream water chemistry is also important for inferring how new contributing sources will impact C-Q relationships, as even adjacent watersheds can have pre-fire contributing sources with distinct endmember chemistry.

These factors add to existing difficulties of understanding post-fire change as they potentially allow for inadvertent misrepresentation and misattribution of the magnitude of wildfire's impact on stream water chemistry. Our study provides new insight into how these limitations could complicate interpretations of fire impacts amongst ongoing efforts to synthesize changes across watersheds.

Finally, in a broader context, extreme climate events, like droughts and heavy precipitation, can drive dynamic changes in C-Q relationships (Murphy et al., 2018), and our sampling periods represent below-normal water years that also had a couple of heavy precipitation periods courtesy of atmospheric river events. In addition, past work demonstrates how C-Q relationships can respond to antecedent conditions (Knapp et al., 2022) and vary at event scales (Knapp et al., 2020). The influence of event-scale changes and/or hydroclimatic extremes on our observed changes are difficult to contextualize due to data limitations but were likely somewhat minimized across the interannual data sets as only one day of the two water years was estimated to exceed even 2-year return period rainfall frequencies for 24 hr. However, higher-frequency data are needed to explore the role of hydroclimatic variability in driving short- and long-term changes in C-Q dynamics after wildfire. In the context of water year variability, WY 2021 and 2022 were below average, and pre-fire C-Q data was also comprised of several below-average water years.

Future work could focus on understanding how physical and biogeochemical processes interact with and control chemical and spatial heterogeneity in potential new solute sources, like ash or burned soils, along the source-to-stream continuum. Using high-frequency sensors to monitor stream water chemistry would be especially beneficial. In addition, methodologically consistent and explicit details are needed for wildfire studies on chemical and hydrologic changes to ensure that results are comparable across sites. This information is critical to improving our ability to predict post-fire stream water chemistry responses and therefore effectively manage potential environmental and drinking water quality issues during and after wildfire.

5. Conclusions

Stream water chemistry responses to low to moderate severity wildfire were examined in four watersheds for a suite of over 40 constituents. Three of the four watersheds also had pre- and post-fire concentration-discharge data for 14 of these constituents (suspended sediment, SS_{fine}; dissolved organic carbon, DOC; dissolved inorganic carbon, DIC; specific ultraviolet absorbance at 254 nm, SUVA; major ions, Ca²⁺, K⁺, Mg²⁺, Na⁺, Cl⁻, SO₄²⁻, NO₃⁻, F⁻; and select trace elements, total dissolved Mn, Fe). This relatively rare data set allowed for new insight into fire impacts on stream water quality and C-Q relationships. Here, we show how wildfire can impact stream

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water chemistry responses in variable ways and relate these impacts to heterogeneity in the sources driving these changes.

Specifically, we found that stream water chemistry responses were often distinct across sites, constituents, or with discharge, though gradients appeared across the designated fire response categories that broadly mirrored watershed wildfire extent. Of the sites with pre-fire data, wildfire generally had the greatest impact, defined as moderate to major post-fire responses, on Na⁺, K⁺, Cl⁻, NO₃⁻, Fe, and SO_4^{2-} , and the most common impact, defined as any fire response, on SS_{fine} , DOC, Ca^{2+} , Na^+ , Cl^- , NO_3^- , and SO_4^{2-} concentrations, which were detectably altered for at least two of the three sites.

For most stream water constituents, discharge-driven changes in concentrations significantly altered the magnitude of post-fire change. SS_{fine} concentration changes, for instance, were 0.9–40.9 times pre-fire values, depending on stream discharge. Other stream water chemistry responses also hinted at event-scale differences, where the highest concentrations in stream water K^+ , Na^+ , Cl^- , and $SO_4^{2^-}$ seemed to occur during the first few storm events after fire, regardless of stream discharge. Measurements of leached solute concentrations in ash, burned surface soils, and burned plant materials in our study watersheds were somewhat consistent with changes in stream water chemistry and also dynamic in composition. Together, our results suggest that heterogeneity in new contributing sources, which can be highly variable in chemistry, location, and amount in space and through time, contribute to stream water chemistry changes within and across watersheds after wildfires.

Data Availability Statement

All data are available as described in the Methods and summarized in Table S3 of Supporting Information S1, with most data directly available through CUASHI HydroShare: http://www.hydroshare.org/resource/ccbaedcab7dc47c8a565511795e444ac.

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