Ecosystems (2021) 24: 1853–1874
https://doi.org/10.1007/s10021-021-00620-0

Stream Water Chemistry in Mixed-Conifer Headwater Basins: Role of Water Sources, Seasonality, Watershed Characteristics, and Disturbances

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Abstract

Understanding the transport of dissolved organic carbon (DOC) and nitrogen (N) as water flows through headwater basins is important for predicting downstream water quality. With increased recognition of climatic impact on nutrient transport, more studies are needed in headwater basins experiencing a Mediterranean-type climate, such as those of the Sierra Nevada, California. We analyzed water samples collected over 5 years from eight low-order and mixed-conifer watersheds to elucidate the temporal variation of water chemistry and evaluate their responses to prolonged drought and low-intensity forest thinning. We observed higher stream DOC concentrations in October compared to other months within water years prior to drought and thinning, suggesting the importance of antecedent moisture conditions on seasonal C export. In unthinned watersheds, stream DOC concentrations were lower (62%) and DOC aromaticity was higher (68 and 92%, depending on the index used) during drought compared to non-drought years. In thinned watersheds during drought years, stream water had higher DOC concentrations (66–94% in three consecutive years following thinning) and dissolved inorganic N (24%, in the third year following thinning) compared to unthinned watersheds during drought. Additionally, lower stream DOC concentrations were found in watersheds with higher elevations and lower drainage densities in the year with near-average precipitation; however, these correlations were not significant in years with greater or extremely low precipitation. Taken together, our results suggest that stream concentrations of DOC

Received 28 July 2020; accepted 8 February 2021;
published online 25 March 2021

Supplementary Information: The online version contains supplementary material available at https://doi.org/10.1007/s10021-021-00620-0.

Author Contributions SCH and AAB developed the concept of this manuscript. YY, EPM, EMS, and SCH conducted laboratory analyses. CTH designed and implemented the KREW study, and CTH and DWJ contributed inorganic nitrogen data. MEB performed preliminary data analyses. YY conducted the full data analyses and drafted the manuscript. All authors contributed to revisions.

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and dissolved N in Mediterranean headwater basins are extremely variable over time due to the high temporal climatic variabilities and periodic management practices.

Key words: Aromatic carbon; Dissolved inorganic nitrogen (DIN); Dissolved organic carbon (DOC); Dissolved organic nitrogen (DON); Drought; Forest thinning; Sierra Nevada; Snowmelt; Soil solution.

Highlights

1. Stream water chemistry is influenced by the antecedent soil moisture conditions.
2. Stream DOC increases more rapidly than DIN under drought combined with thinning.
3. Watershed characteristics are poor predictors of stream chemistry during drought.

Introduction

Understanding the exports of dissolved carbon (C) and nitrogen (N) from headwater streams is important for ecosystem management. Ecologically, the amount of dissolved organic carbon (DOC) can influence stream metabolism (Robbins and others 2017; Demars and others 2020), N dynamics (Bernhardt and Likens 2002), and mobility of trace metals (Aiken and others 2011; Felizzola and others 2019). Exported DOC from headwater streams is also a significant flux of terrestrial C into oceans (Cole and others 2007; Koffi and others 2012; Argerich and others 2016). Measurements of dissolved N in streams provide an assessment of terrestrial N demand, where the comparison of stream export and atmospheric input indicates N retention rates in upland ecosystems (Vanderbilt and others 2003; Emmerton and others 2019). Additionally, both dissolved C and N concentrations are key factors determining water quality, as enriched levels cause toxic algal blooms and water anoxia (Smith and Schindler 2009).

Our previous knowledge of stream nutrient export has been recently challenged by the increased recognition of climatic impact (Brevik 2012; Xie and others 2019). For example, stream DOC and dissolved organic nitrogen (DON) are known to be coupled and elevated during spring snowmelt under high flow conditions (Brookshire and others 2005; Raymond and Saiers 2010; Martin and Harrison 2011; Cincotta and others 2019). However, in months that transition between dry to wet conditions, export of stream DOC and DON can still be high during low flow conditions if the antecedent soil condition is dry (Guarch-Ribot and Butturini 2016; Bernal and others 2019). This has been attributed to dissolved organic matter (DOM) being accumulated during the dry period and flushed out in the first precipitation event. Meanwhile, dissolved inorganic nitrogen (DIN) is usually low in streams draining watersheds not experiencing elevated rates of atmospheric N deposition, due to efficient biological uptake of N while water percolates through soil (Vanderbilt and others 2003; Bernal and others 2019). However, stream DIN can be elevated in wet and cold months when rapid snowmelt supplies water directly to streams via overland flow due to frozen soils (Brooks and others 1998; Brooks and Williams 1999). Thus, the dynamics of dissolved C and N can be more complex in headwater streams receiving a larger variation in climatic conditions (that is, temperature and precipitation).

Given the high degree of dry to wet variability inherent in Mediterranean-type climates, the seasonal export of dissolved C and N from streams within this climatic region is expected to be complex. Headwater basins in these regions experience a unique climate as little precipitation falls during the summer growing season, resulting in warm, relatively dry soils. Biological processes in these ecosystems must rely on water stored in the ephemeral snowpack and soil during this period that is replenished during the cool, wet winters (Lionello and others 2006). Stream DOC, DON, and DIN varied substantially across seasons with the highest concentrations in the beginning of a water year that transition between dry to wet conditions in Barcelona, Spain (Bernal and others 2005). However, similar stream DOC concentrations have also been observed across months in Mediterranean basins with a low hydrological variability and attributed to groundwater influences (Roig-Planasdemunt and others 2017). The assessment of water chemistry along hydrological flow paths can provide insights on the potential causes of seasonal variation in stream water chemistry, either due to variations in DOM inputs, hydrological variability, or both.

With the increasing occurrence of severe drought under climate warming (Diffenbaugh and others 2015; Williams and others 2015), Mediterranean basins also experience a large interannual climatic variability, especially the increased occurrence of extremely dry years. Few studies have evaluated regional drought impact on dissolved C and N

dynamics in headwater streams and reported different drought effects. For instance, decreased DOC concentrations have been observed during drought (Szkokan-Emilson and others 2017; Gómez-Gener and others 2020) and attributed to the lower transfer of DOM from soil to stream water under low flow conditions. In contrast, increased DOC concentrations have also been observed (Harjung and others 2019); these increases were attributed to reduced dilution of DOC by stream flow, increases in soil water residence time, and increased release of algal exudates in stream water during drought. With stream DOC dynamics influenced by inter-annual drought length (Mehring and others 2013) and projected longer and more severe drought in the future (Swain and others 2018; Ullrich and others 2018), more research is needed to assess the transport of water chemistry during prolonged drought conditions in headwater catchments within the Mediterranean climate zone.

In addition to the high intra- and inter-annual variability in climate, Mediterranean basins also receive periodic management practices such as forest thinning, which can be an effective approach to mitigate drought impact by reducing the water stress of remaining trees (Elkin and others 2015; Gleason and others 2017). Forest thinning can lead to increases in water yield temporally until the completion of vegetation regrowth (Dung and others 2012; Saksa and others 2017), but forest thinning can also increase concentrations of dissolved C and N in stream water (Bäumler and Zech 1999; Wang and others 2006; Laudon and others 2009; Siemion and others 2011), potentially leading to decreases in downstream water quality (Koralay and Ömer 2018). Past studies have focused on impacts of forest thinning at high intensities (removal of $>$ 40% basal area) rather than low intensity thinning activities (Mupepele and Dormann 2017). Moreover, despite many studies on nutrient export after forest thinning, little is known about the interactive effects of thinning on stream water chemistry during a drought event, as the elevated nutrient concentrations under thinning may be minimized by the limited hydrological connectivity under drought. With increasing interest in employing more widespread, low-intensity thinning operations in the future to increase forest resiliency to prolonged drought as well as reducing wildfire risk (Graham and others 1999; Agee and Skinner 2005), an improved understanding of how drought combined with low-intensity thinning would impact stream water chemistry is essential.

Given the climate and thinning disturbances in these basins, exported stream water chemistry can be highly variable and difficult to model. Watershed topography constrains both hydrological (Soulsby and others 2006; Tetzlaff and others 2009) and soil processes (McCorkle and others 2016; Siles and others 2016; Stacy and others 2019), thus affecting the production and transport of dissolved C and N in stream water. Studies have successfully predicted stream water chemistry using watershed area, slope, and elevation in boreal and humid forests (Clow and Sueker 2000; Sullivan and others 2007; Neff and Schwartz 2011; Chuman and others 2013). However, whether these predictors are still applicable in similar watersheds experiencing a Mediterranean-type climate are largely unknown, particularly in years following a disturbance (that is, drought and thinning).

To unravel the complex interactions of climate and forest thinning on water chemistry, we collected water samples from eight, low-order (that is, headwater) watersheds in the southern Sierra Nevada of California to ask three questions:

1. How does the chemistry of different water sources (that is, snowmelt, soil solution at two depths, stream water) vary monthly and inter-annually prior to drought and thinning?
2. How does drought alone and drought combined with thinning impact water chemistry?
3. Can watershed characteristics predict stream water chemistry over contrasting water years?

We hypothesized that the beginning of the water year (that is, October in the northern hemisphere) would have higher concentrations of dissolved C and N in stream water than other months within a water year, because accumulated nutrients from the antecedent dry summer would be flushed from the upland to the adjacent stream. Drought alone would reduce annual mean concentrations of dissolved C and N in stream water due to the limited DOM production in dry, upland soils (decreased concentrations in soil solution) and limited transport to streams under low flow conditions. And drought combined with thinning would increase annual mean concentrations in soil solution due to the increased DOM input from detritus pools following thinning. However, limited changes would occur to stream water chemistry due to the limited hydrological transport of nutrients from upland soils to streams under drought. We also hypothesized that watershed characteristics such as elevation and drainage density would be correlated with annual mean concentrations of stream nutrients prior to drought and thinning. However, these

relationships would not be applicable under drought and thinning because of the disrupted connections between nutrient source (upland soil), transport, and stream water.

Methods

Site Description

The Kings River Experimental Watersheds (KREW) is a long-term research area located in the southern Sierra Nevada in California. It has two study sites: the rain-snow transition zone (35–60% of precipitation as snow) located within the Providence Creek drainage (Providence; 37°3.120′ N, 119°12.196′ W), and the snow-dominant zone (75–90% of precipitation) located within the Bull Creek drainage (Bull; 36°58.631′ N, 119°4.917′ W). Each site has four adjacent watersheds, with an elevation range from 1485 to 2115 m at Providence and from 2050 to 2490 m at Bull (Figure 1). The climate at both sites is characterized as Mediterranean, with, on average, 90% of the annual precipitation occurring between October and May (Safeeq and Hunsaker 2016). Soils at both sites are derived primarily from granitic parent materials and are classified dominantly as coarse-loamy, mixed mesic Pachic Xerumbrepts at Providence, and mixed, frigid Dystric Xeropsamments at Bull (Johnson and others 2011). Vegetation at the Providence site is dominated by (based on the proportion of the total stand basal area) white fir (*Abies concolor* (Gordon) Lindl. ex Hildebr.; 30–51% of the total basal area, varied by watersheds) and incense cedar (*Calocedrus decurrens* (Torr.) Florin; 29–42%), with lesser amounts of sugar pine (*Pinus lambertiana* Douglas), ponderosa pine (*Pinus ponderosa* Douglas ex C. Lawson), and Jeffrey pine (*Pinus jeffreyi* Balf., Table 1). Vegetation at the Bull site consists predominately of a red fir forest (*Abies magnifica* A. Murray bis, 42–93% of total basal area), with generally smaller proportions of white fir, sugar pine, Jeffrey and ponderosa pines, and lodgepole pine (*P. contorta* Douglas ex Loudon; Lydersen and others 2019).

Thinning treatments were not randomly assigned to watersheds at each site because of the presence of wildlife species of concern and forest conditions

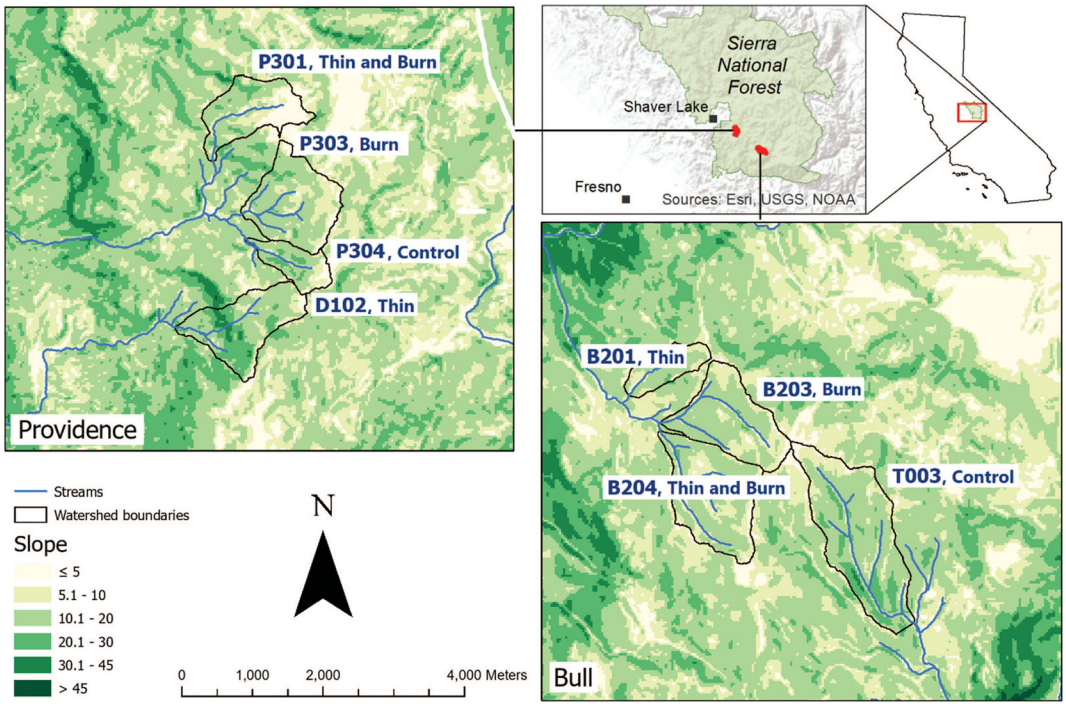

Figure 1. Location of eight watersheds at Providence and Bull Creek sites within the Kings River Experimental Watersheds in the southern Sierra Nevada, California. The map shows degree of slope designated by white to dark green colors that denote low to high slope, respectively. Forest thinning was applied in summer and fall 2012. Prescribed burns were applied to two watersheds at Bull (B203 and B204) in 2013 and two watersheds at Providence (P301 and P303) in 2016. The delayed application of the prescribed burns within the ''thin and burn'' and ''burn only'' treatments at the Providence site allowed us to include the P301 watershed as an additional ''thin only'' treatment and the P303 watershed as an additional control in the study period of WY 2009–2015.

Table 1. Watershed Characteristics in the Kings River Experimental Watersheds.

Site	Watershed	Area (ha)	Mean elevation (m)	Drainage density (km km^{-2})	Channel length (km)	Dominant land cover percent of conifers (%)	Pretreatment live tree basal area (m^2 ha^{-1})	Species composition (% basal area)
Providence	D102	121	1782	10.1	1.4	76	50 (4.5–119.6)	33% CADE, 30% ABCO, 22% PILA, 13% YP, 2% QUKE
	P301	99	1979	7.4	1.5	82	63.4 (3–142.1)	46% ABCO, 29% CADE, 23% PILA, 2% YP
	P303	132	1905	7.4	0.8	94	43.8 (0–97)	51% ABCO, 42% CADE, 7% PILA
	P304	49	1899	6.9	0.9	99	44.8 (15.1–147.2)	49% ABCO, 33% CADE, 18% PILA
Bull	B201	53	2257	6.0	0.8	92	54.1 (0.5–123.5)	57% ABMA, 22% ABCO, 11% PILA, 10% PICO
	B203	138	2373	4.6	2.2	47	46.2 (0–116.3)	78% ABMA, 15% ABCO, 3% PICO, 3% YP, 1% PILA
	B204	167	2365	5.0	2.2	48	54.8 (0–158.2)	93% ABMA, 6% ABCO, 1% PILA
	T003	228	2289	5.5	3.1	78	79.2 (0–211.7)	52% ABCO, 42% ABMA, 3% PILA, 2% CADE

Watershed area, mean elevation, mean slope, and drainage density were calculated using a Digital Elevation Model (Hunsaker and others 2007). Channel length was measured on the ground (Hunsaker and Neary 2012). Dominant land cover was calculated using Landsat (Hunsaker and others 2007). Vegetation composition (adapted from Lydersen and others 2019) prior to forest thinning at eight watersheds at the Kings River Experimental Watersheds. Tree basal area (mean values with ranges in parentheses across 8–19 sampling plots (10 m × 20 m) in upland; Dolanc and Hunsaker 2017) and species composition by basal area represent the pretreatment conditions for trees ≥ 1 cm diameter at breast height (1.4 m). Species codes are ABCO, white fir; ABMA, red fir; CADE, incense cedar; PICO, lodgepole pine; PILA, sugar pine; YP, Jeffrey pine and ponderosa pine; QUKE, black oak.

across the watersheds (Lydersen and others 2019). However, watersheds within each study site were fairly similar in all characteristics assessed (Lydersen and others 2019). Thinning treatments were applied in summer and fall of 2012 at both Providence (P301, D102) and Bull sites (B201, B204). Prescribed burns were applied to two watersheds at Providence (P301 and P303) in 2016 and two watersheds at Bull (B203 and B204) in 2013. The delayed application of the prescribed burns within the ''thin and burn'' and ''burn only'' treatments at the Providence site allowed us to include the P301 watershed as an additional ''thin only'' treatment and the P303 watershed as an additional control during the studying period of WY 2009–2015 (Table 2, see Hunsaker and others 2007, USDA 2011 for more details of the complete experimental design). Thinning treatments included both conventional timber harvest (that is, chainsaw-felling, slash left in the stand, logs skidded to a landing) in mature stands, and precommercial thinning in young (< 30 year old), even-aged stands within the watersheds. Young stands with high shrub cover (> 50%) were masticated to < 10% shrub cover. The thinning prescription in mature stands removed trees across all diameter classes to a target basal area range of 27–55 m^2 ha^{-1}, with target basal areas varying based on tree density and

Table 2. Experimental Design During the Study Period (Water Years 2009–2015) in the Kings River Experimental Watersheds.

Site	Watershed	Treatment and year of treatment	Treatment assignment during the studying period	Water Years prior to drought and thinning (2009 and 2010)				Water Years following thinning and during drought (2013–2015)		
				Mean discharge (mm y^{-1})	Snowmelt	Soil solution	Stream water	Mean discharge (mm y^{-1})	Soil solution	Stream water
Providence	D102	Thin 2012	Thin	176	X	X	X	48	X	X
	P301	Thin 2012, Burn 2016	Thin	397	X	X	X	52	X	X
	P303	Burn 2016	Control	236	X	X	X	37	X	X
	P304	Control	Control	332	X	X	X	100	X	X
Bull	B201	Thin 2012	Thin	440	NA	NA	X	90	NA	X
	B203	Burn 2013	Not used	731	NA	NA	X	146	NA	NA
	B204	Thin 2012, Burn 2013	Not used	622	NA	NA	X	115	NA	NA
	T003	Control	Control	587	NA	NA	X	124	NA	X

Prescribed burns were applied to two watersheds at Bull (B203 and B204) in 2013 and two watersheds at Providence (P301 and P303) in 2016. The delayed application of the prescribed burns within the ''thin and burn'' and ''burn only'' treatments at the Providence site allowed us to include the P301 watershed as an additional ''thin only'' treatment and the P303 watershed as an additional control (see Lydersen and others 2019; Hunsaker and others 2007; USDA 2011 for more details of the complete experimental design for the KREW study). ''X'' denotes the water samples were available. ''NA'' denotes ''not available,'' indicating water samples were not taken or not used in this study

species, land ownership, and slope. California black oak, sugar pine, and ponderosa pine were retained preferentially because goals included forest restoration in addition to fuel reduction. Trees removed from Sierra National Forest land had a maximum Diameter at Breast Height (DBH) of 76 cm, but some trees up to 117 cm DBH were cut on privately owned land within thinned Providence watersheds. Approximately 10–25% of the area planned for thinning (or mastication) within thinned watersheds was excluded from operation due to slope steepness (generally > 30% slope) and lack of existing roads (especially in D102). Trees within 15 m of the stream could be chainsaw-felled and skidded, but mechanical equipment was prohibited within 30 m of the streambank (Lydersen and others 2019; USDA 2011).

Daily meteorological variables, including total precipitation (mm) and maximum and minimum air temperature (°C), were monitored at meteorological stations located at the upper and lower elevations of each site (Hunsaker and Safeeq 2018). Daily discharge rate (L s^{-1}) was also monitored in all eight watersheds using flumes and, in one case, a weir at the outlet (T003; Hunsaker and others 2012; Hunsaker and Safeeq 2017). At the Providence and Bull site, mean annual air temperature (MAT) was 9.8 and 7.4°C, and mean annual precipitation (MAP) was 1325 and 1408 mm y^{-1}, respectively (WY 2005–2017, Figure 2A, B). From 2012 to 2016, California experienced a historic multi-year drought (Diaz and Wahl 2015; Robeson 2015; He and others 2017). This prolonged drought event resulted in near-record low precipitation (686 mm at Providence and 813 mm at Bull in WY 2013–2015) combined with above-average temperatures observed at our sites (Figure 2A, B).

Sample Collection

Snowmelt and soil solution were sampled in all four watersheds at Providence. Specifically, snowmelt was sampled during the 2 years prior to thinning and drought (WY 2009 and 2010; Table 2). Soil solution was sampled during the 2 years prior to thinning and drought (WY 2009 and 2010), and in the 3 years following thinning and during drought (WY 2013–2015). We did not sample snowmelt and soil solution at the Bull site because of the difficult accessibility during the winter and limited funding. Stream water was sampled at both Providence and Bull sites in all 5 years (WY 2009, 2010, and 2013–2015; Table 2).

Snowmelt samples were collected using a bottle attached to a funnel to gather snow and allow

meltwater to flow into the bottle placed belowground (Hunsaker and others 2007). Both the bottle and funnel were made from high-density polyethylene (HDPE) that was cleaned with several deionized water rinses before deployment into the field.

Soil solution samples were collected using six Prenart vacuum lysimeters (Hunsaker and others 2007) placed at both 13 and 26 cm mineral soil depths ($n = 6$ per depth). The locations of the Prenart lysimeters in each watershed were selected to be representative of the individual watershed, and as similar as possible among the four watersheds in terms of soil type, vegetation, slope, and aspect (Hunsaker and others 2007). A constant vacuum (-25 to -50 kPa) was applied to the Prenart samplers with constant power supplied by nearby solar panels and batteries. Bottles stored with soil solution were emptied approximately every 2-weeks; these semi-monthly collections were composited by volume for a given sampler to provide a monthly sample during months where soil solution was relatively abundant (winter and spring). Unfortunately, the remoteness of our watersheds did not allow more frequent soil solution collection. Prolonged storage of soil solution in collection bottles may have resulted in unknown changes in water chemistry. However, our collection methodology is commonly used in studies of soil solution chemistry conducted at remote sites (Susfalk and Johnson 2002; Cory and others 2004), and collection bottles were kept relatively cool belowground in an insulated storage shed between collection events (Hunsaker and others 2007). We did not collect samples during the summer and early fall because the infrequent and small precipitation events were insufficient for soil solution collection.

Stream water samples were collected every 2 weeks just upstream of the gauging station of each watershed and were composited by volume to provide a single monthly sample for chemical analysis (Hunsaker and Johnson 2017). All water samples were stored in HDPE bottles at -20°C in the laboratory until analysis.

Laboratory Analyses

Frozen water samples were thawed in a cold room at 4°C, and then homogenized and filtered through 0.45-µm filters (Polythersulfone, EZFlow®, NH, USA). Samples were analyzed for DOC, aromatic C, total dissolved nitrogen (TDN), and pH at the University of California, Merced. Concentrations of DOC and TDN were determined using combustion catalytic oxidation on a Shimadzu TOC-Vcsh Analyzer coupled with a TNM-1 unit (Columbia, MD, USA). Dissolved inorganic N (NO_3-N + NH_4-N) were analyzed at the US Forest Service's Riverside Fire Sciences Laboratory, Riverside, California, USA (Hunsaker and Johnson 2017; Hunsaker and Padgett 2019). Nitrate (NO_3^-) was analyzed using Ion Chromatography (US EPA 1997) and ammonium (NH_4^+) was analyzed by automated colorimetric analysis (US EPA 1993). Check standards were run every 10 samples to ensure sample precision within 10% of known values. Samples that measured below detection limits for NO_3^- (0.011 mg N L^{-1}) and NH_4^+ (0.039 mg N L^{-1}) were converted to half the value between 0 and the detection limit for the purposes of data analysis. Dissolved organic N was calculated by subtracting DIN from TDN. The DOC to DON mass ratio (DOC:DON) was calculated by dividing the DOC concentration by the DON concentration.

The Specific Ultraviolet Absorption (SUVA) of the water solutions were measured (in units of absorbance per m of path length) at wavelengths of 254 and 280 nm using a UV spectrophotometer (Evolution 300, UV–VIS, Thermo Scientific, England). Specific UV absorbances were calculated as the UV absorbance at 254 and at 280 nm ($SUVA_{254}$ and $SUVA_{280}$), respectively, divided by the DOC concentration measured in milligrams per liter (mg l^{-1}). These SUVA values provide an ''average'' absorptivity at these wavelengths for all the molecules that comprise the DOC in a water sample, and both have been used as indices of DOC aromaticity (Chin and others 1994; Weishaar and others 2003).

Sample pH was measured using a regular combination pH electrode (Orion 927007MD, Thermo Fisher Scientific, Waltham, MA, USA) at room temperature after the addition (1:100 mL ratio) of an ionic strength adjuster (Orion 700,003, Thermo Fisher Scientific). The pH meter (Orion DUAL STAR, Thermo Fisher Scientific) was calibrated with low ionic strength buffers (pH 4 and 6.98). The low ionic strength buffer with pH 6.98 was measured every eight water samples as a check standard; if the value was outside of the range 6.97–6.99, the pH meter was re-calibrated and sample unknowns were re-analyzed.

Data Analyses for Temporal Variation of Water Chemistry Prior to Drought and Thinning

We examined the variation of water chemistry among different water sources as well as temporal variation of water chemistry within each water

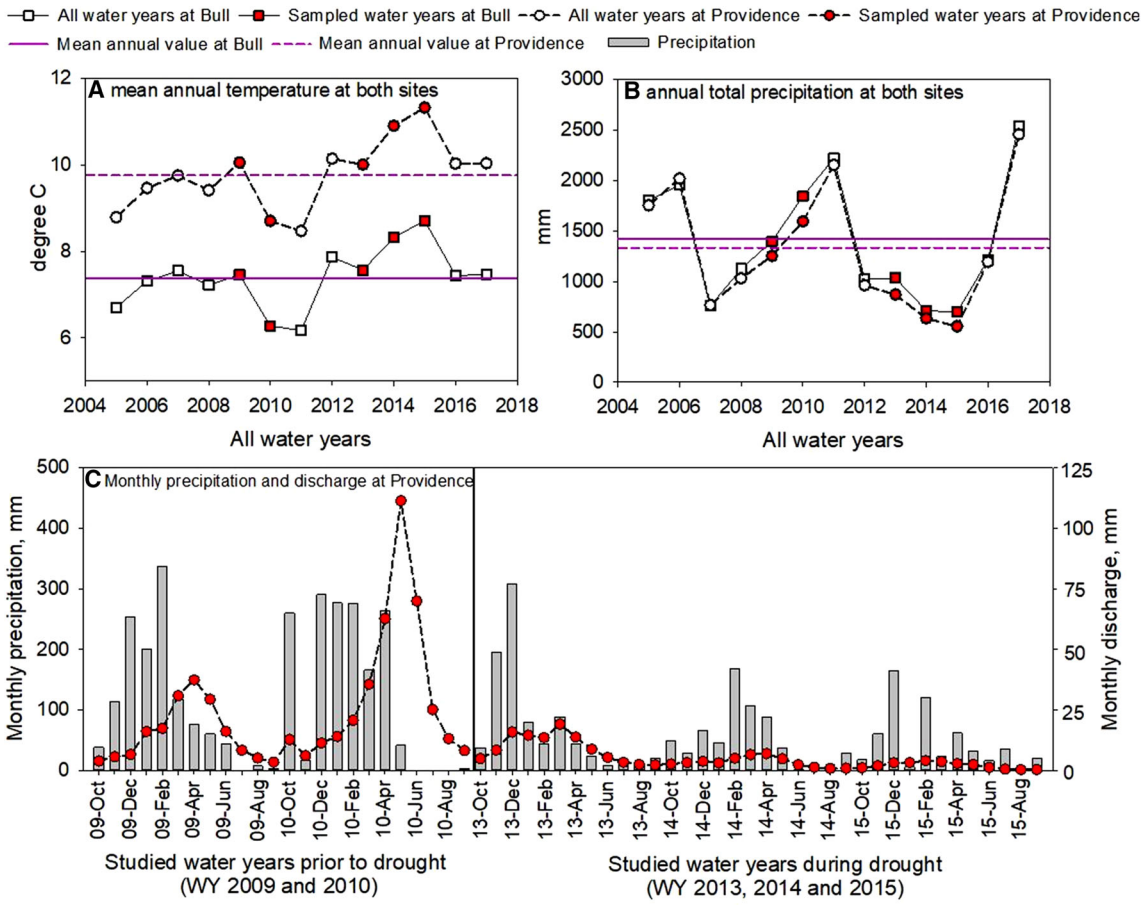

Figure 2. Climatic and stream flow temporal variation within the Kings River Experimental Watersheds in the southern Sierra Nevada, California. Mean annual air temperature (**A**) and total precipitation (**B**) at the Providence and Bull sites for Water Years 2005–2017. Monthly precipitation and stream discharge (**C**) at the Providence site during studied Water Years (data from the Bull site are not shown but followed a similar pattern; Hunsaker and Safeeq 2017, 2018).

source using water samples collected from all four watersheds at Providence during the 2 years prior to drought and thinning (WY 2009 and 2010). Water chemistry included values of DOC, $SUVA_{254}$, $SUVA_{280}$, TDN, DON, DIN, DOC:DON, and pH. For all analyses below, concentrations were log-transformed to meet the assumption of normality and homoscedasticity of the residuals, except for pH where residuals were normally distributed and homoscedastic in the model.

We used general linear models, with water sources as the main effect, to investigate how water chemistry would vary by water sources (n = 40 for snowmelt, soil solution at 13 and 26 cm depth, and n = 96 for stream water). Tukey's Honestly Significant Difference (HSD) was used as a mean separation test. We examined the monthly and interannual variation of water chemistry individually for each water source. We applied general linear models with Tukey's HSD to explore how water chemistry would vary by month in each year, using sampling month as the main effect (n = 4 for snowmelt, soil solution, and stream water). We also used paired t tests to examine how water chemistry would vary between the two water years, using all values from a given month or watershed as replicates (n = 20 for snowmelt, soil solution at 13 and 26 cm depth, and n = 48 for stream water).

Data Analyses for Drought and Thinning Impacts

We examined the drought and thinning impacts on water chemistry using water samples collected during the 2 years prior to drought and thinning (WY 2009 and 2010), and in the 3 years following thinning and during drought (WY 2013–2015). A different number of watersheds were used for the analysis of each water source due to differences in

sample availability. For soil solution collected at two depths, data were taken from all four watersheds at the Providence site. For stream water, data were from all four watersheds at Providence and two watersheds at Bull (that is, B201, T003). Snowmelt was not included in this analysis due to the lack of collection in years during drought and thinning at both sites (Table 2).

We first calculated the annual mean value for each watershed in each year. The annual mean concentration of an analyte in the soil solution was calculated as the average value of monthly concentrations. Annual mean values in stream water were volume-weighted using the equation described by Williams and Melack (1997):

$$C_w = \frac{\sum_{i=1}^{n} C_i V_i}{\sum_{i=1}^{n} V_i},$$

where C_w is weighted annual mean concentration, C_i is concentration of sample i, and V_i is discharge water volume (L) of sample i. Because discharge was measured every 15 min whereas concentrations were measured monthly, each analyte concentration value was applied to the cumulative discharge volume that occurred midway between the two adjacent sampling dates (Williams and Melack 1997).

We examined the impact of drought alone on water chemistry by comparing water samples collected from control watersheds (that is, P303, P304, T003) in years prior to drought and thinning (WY 2009 and 2010) to those collected from these same watersheds during the drought (WY 2013–2015). We used two-sample t tests to identify the differences in annual values between pre-drought and drought periods, with watersheds across years within each period serving as replicates.

We examined the impact of drought combined with thinning on water chemistry using repeated-measures ANOVA, with thinning treatment, sampling year (repeating factor), and their interaction as the independent variables. When main effects were significant and interactions were not, Tukey's HSD was used as a mean separation test for main effects. To estimate changes in water chemistry under drought combined with thinning in each year (WY 2013–2015), we used the difference in water chemistry values between thinned and the control watersheds in each drought year minus the mean difference between pre-thinned and the control watersheds in the 2 years prior to drought (that is, WY 2009 and 2010), and then divided this difference by the value in the control watersheds in that drought year to provide a relative percent change estimate. For estimating changes in TDN and DON, we only used WY 2009 data for estimating the pre-drought baseline conditions due to the extreme high values observed in WY 2010 (Supplementary Material 1).

Data Analyses for Predicting Stream Water Chemistry

We tested whether watershed characteristics can predict stream water chemistry using samples collected during the 2 years prior to drought and thinning (WY 2009 and 2010), and in the 3 years following thinning and during drought (WY 2013–2015). A different number of watersheds were used for the analysis for each period. Eight watersheds (four at Providence and four at Bull) were used for 2 years prior to drought and thinning (that is, WY 2009 and 2010), whereas six watersheds (four at Providence; two at Bull, B201 and T003) were used for the 3 years following thinning and during drought (WY 2013–2015). For each year, we applied linear regressions to volume-weighted annual values and watershed characteristics. Watershed characteristics included watershed area (km^2), mean elevation (m), mean slope (%), drainage density (km km^{-2}), channel length (km), and dominant land cover percent of conifers (Table 1).

All statistical analyses were conducted in SAS 9.4 (SAS Institute, Inc. 2013). We used an a priori alpha level of 0.10 to evaluate statistical significance because of the greater variation typically found in field studies and the limitation of setting thresholds at 0.05 (Amrhein and others 2019).

Results

Water Chemistry Varied by Water Sources Prior to Drought and Thinning

Monthly concentrations of dissolved C and N varied among different water sources prior to drought and thinning. For DOC ($p < 0.01$; p values are for main effect of water sources in general linear models here and below), soil solution at 13 cm depth (mean ± SE of 25.97 ± 2.75 mg l^{-1}, across months for 2 years) had higher monthly concentrations than soil solution collected at 26 cm depth (16.93 ± 1.55 mg l^{-1}). Snowmelt (9.67 ± 0.89 mg l^{-1}) and stream water (5.33 ± 0.52 mg l^{-1}) had the lowest concentrations (Figure 3A). For TDN and DON ($p < 0.01$ for both), soil solution at 13 cm depth (1.72 ± 0.57 and 1.66 ± 0.57 mg l^{-1}, respectively), soil solution at 26 cm depth (0.94 ± 0.32 and 0.92 ± 0.32 mg l^{-1}), and snowmelt (0.94 ± 0.17 and 0.73 ± 0.18 mg l^{-1})

had higher concentrations than stream water (0.11 ± 0.02 and 0.08 ± 0.01 mg l^{-1}; Figure 3B, C). For DOC:DON ($p < 0.01$), stream water (90.77 ± 6.21) had higher values than soil solution at both depths (51.49 ± 4.23 at 13 cm depth and 61.17 ± 4.88 at 26 cm depth) and snowmelt (43.61 ± 4.6; Figure 3D).

Snowmelt had higher concentrations of DIN and lower pH than soil solution and stream water. For DIN ($p < 0.01$), snowmelt (0.25 ± 0.05 mg l^{-1}) had the highest concentration followed by the soil solution at 13 cm depth (0.06 ± 0.01 mg l^{-1}). Soil solution at 26 cm depth (0.03 ± 0.01 mg l^{-1}) and stream water had the lowest values (0.04 ± 0.01 mg l^{-1}; Figure 3E). For pH ($p < 0.01$), snowmelt (pH 6.09 ± 0.06) was more acidic than soil solutions at both depths (7.52 ± 0.23 at 13 cm depth and 7.79 ± 0.11 at 26 cm depth) and stream water (7.37 ± 0.07; Figure 3F).

Values of aromatic C were similar among different water sources ($p \geq 0.12$). For $SUVA_{254}$, mean values ± SE across months for 2 years were: 1.41 ± 0.11 l mg DOC^{-1} m^{-1} for snowmelt, 1.90 ± 0.10 l mg $DOC^{-1}m^{-1}$ for soil solution at 13 cm depth, 1.91 ± 0.09 l mg DOC^{-1} m^{-1} for soil solution at 26 cm depth, and 1.99 ± 0.12 l mg DOC^{-1} m^{-1} for stream water. For $SUVA_{280}$, mean values ± SE were: 0.94 ± 0.08 l mg DOC^{-1} m^{-1} for snowmelt, 1.47 ± 0.09 l mg DOC^{-1} m^{-1} for soil solution at 13 cm depth, 1.38 ± 0.08 l mg DOC^{-1} m^{-1} for soil solution at 26 cm depth, and 1.34 ± 0.09 l mg DOC^{-1} m^{-1} for stream water.

Temporal Variation of Water Chemistry Prior to Drought And Thinning

Concentrations of dissolved C and N varied significantly across months in the two water years prior to drought and thinning. For snowmelt in WY 2009, concentrations of snowmelt DOC were higher in December and May ($p = 0.05$; Figure 4A), and concentrations of snowmelt TDN and DIN were higher in May than in other months ($p \leq 0.02$; Figure 4B, E). In WY 2010, concentrations of snowmelt DOC were higher in December to February and May ($p < 0.01$; Figure 4A), and concentrations of snowmelt DIN were higher in May than in other months ($p < 0.01$; Figure 4E). All other variables were similar across months within each year ($p \geq 0.18$). For stream water in WY 2009, concentrations of DOC in stream water were higher in October ($p < 0.01$; Figure 4A), and concentrations of TDN in stream water were higher in July than in other months ($p < 0.01$; Figure 4B). In WY 2010, concentrations of DOC, TDN, DON, and DIN in stream water were higher and values of DOC:DON were lower in October than in other months ($p \leq 0.01$; Figure 4). All other variables were similar across months within each year ($p \geq 0.25$). For soil solutions collected at both depths, values of all variables were similar across months within each year ($p \geq 0.34$).

Concentrations of dissolved C and N varied between the two water years prior to drought and thinning (that is, WY 2009 vs. 2010). For snowmelt and soil solution at both depths, WY 2010 had higher concentrations of TDN and DON than WY 2009 ($p \leq 0.05$; Figure 4B, C). For stream water, WY 2010 had higher concentrations of DOC, TDN, DIN and DON, and lower DOC:DON than WY 2010 ($p \leq 0.01$; Figure 4). All other variables were similar between these 2 years ($p \geq 0.24$).

Water Chemistry Under Drought and Thinning

Drought alone altered DOC and SUVA in stream water, and DOC:DON in soil solution in unthinned (control) watersheds. Volume-weighted concentration of DOC was 62% lower ($p < 0.01$; Figure 5A) and DOC:DON was 82% lower ($p = 0.004$; Figure 5B) in stream water in years during drought (WY 2013–2015) than in years prior to drought (WY 2009 and 2010). Volume-weighted values of $SUVA_{254}$ and $SUVA_{280}$ in stream water were 68% ($p = 0.03$; Figure 5D) and 92% higher ($p = 0.03$; Figure 5E), respectively, during drought than prior to drought. In contrast, values of TDN, DIN, DON, and pH in stream water were similar ($p \geq 0.23$, Supplementary Material 1). All chemical variables were similar ($p \geq 0.14$) in soil solutions collected in years during drought to those collected prior to drought, except for DOC:DON in the soil solution at 26 cm depth, which was 47% lower ($p < 0.01$; Figure 5C).

Drought combined with thinning altered DOC and DIN in stream water, and DON and TDN in soil solution. For stream water, volume-weighted concentrations of DOC were 66–94% higher in thinned watersheds than in control watersheds for all three consecutive drought years following thinning ($p = 0.06$ for WY 2013; $p = 0.01$ for WY 2014; $p = 0.05$ for WY 2015; p values from repeated measures ANOVAs here and below; Figure 6A). No differences in DOC concentrations were found between thinned and control watersheds before thinning ($p = 0.50$ for WY 2009; $p = 0.74$ for WY 2010). Volume-weighted concentrations of DIN were 24% higher in thinned than in control watersheds only in the third drought year (WY

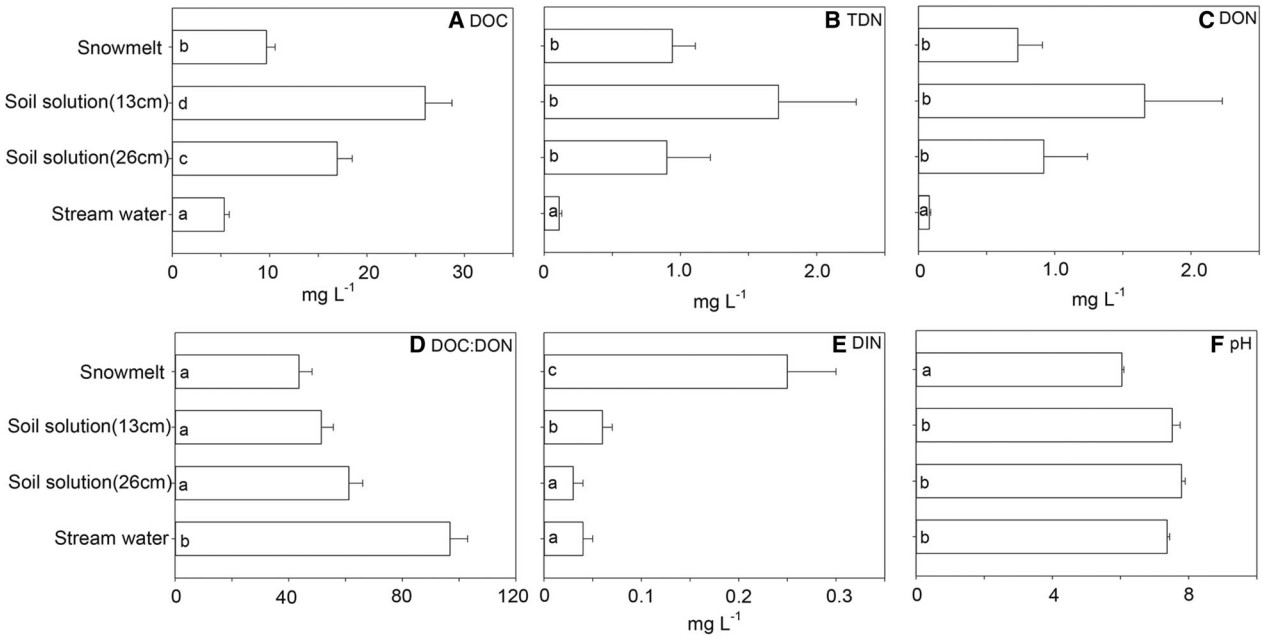

Figure 3. Water chemistry in various ecosystem pools at the Providence site across months in two Water Years prior to thinning and drought (WY 2009 and 2010). Mean concentrations of (**A**) dissolved organic C (DOC), (**B**) total dissolved N (TDN), (**C**) dissolved organic N (DON), (**D**) dissolved organic C to organic N mass ratio (DOC:DON), (**E**) dissolved inorganic N (DIN), and (**F**) pH. Dissolved inorganic N data are from Hunsaker and Johnson (2017). Error bars denote standard errors across months in four watersheds over 2 years. Different letters in each panel indicated significant differences based on Tukey HSD tests ($\alpha = 0.10$).

2015) following thinning ($p = 0.04$; Figure 6B); no differences of DIN concentrations were found between thinned and control watersheds prior to thinning ($p \geq 0.44$ for WY 2009 and 2010) or in the first two drought years following thinning ($p \geq 0.11$ for WY 2013 and 2014). Values of $SUVA_{254}$, $SUVA_{280}$, pH, DOC:DON, TDN, and DON in stream water were similar between thinned and control watersheds for all years ($p \geq 0.12$). For soil solution measured at both depths, values for all variables were similar between thinned and control watersheds for all years ($p \geq 0.14$), except for concentrations of TDN and DON in soil solution at 26 cm depth in WY 2010 and 2015. In WY 2010 (prior to drought and thinning), the significant differences of TDN and DON concentrations in soil solution at 26 cm depth between thinned and control watersheds were due to the extremely high values in watershed D102. In WY 2015 (following thinning and during drought), concentrations of TDN and DON in soil solution at 26 cm depth were 103 and 112% higher, respectively, in thinned than in control watersheds ($p = 0.08$ for both; Figure 6C, D).

Prediction of Stream Water Chemistry Using Watershed Characteristics

Watershed characteristics explained inconsistently the variation in volume-weighted mean annual values of stream water chemistry among different watersheds. In WY 2009, watersheds at higher elevations ($R^2 = 0.85$, $p < 0.01$; Figure 7A), with lower drainage density ($R^2 = 0.77$, $p < 0.01$; Figure 7B), and with longer channel length ($R^2 = 0.62$, $p = 0.02$; Figure 7C) had lower concentrations of DOC. Watersheds at higher elevations ($R^2 = 0.87$, $p < 0.01$; Figure 7D), with lower drainage densities ($R^2 = 0.69$, $p = 0.01$; Figure 7E), and shallower slopes ($R^2 = 0.59$, $p = 0.03$; Figure 7F) had lower stream water pH. Watersheds at higher elevations had higher $SUVA_{254}$ ($R^2 = 0.66$, $p = 0.01$; Figure 7G) and $SUVA_{280}$ values ($R^2 = 0.64$, $p = 0.02$; Figure 7H). However, none of the above relationships were significant in undisturbed watersheds during WY 2010 and in WY 2013–2015 in watersheds following drought and thinning ($p \geq 0.27$, Supplementary Material 1).

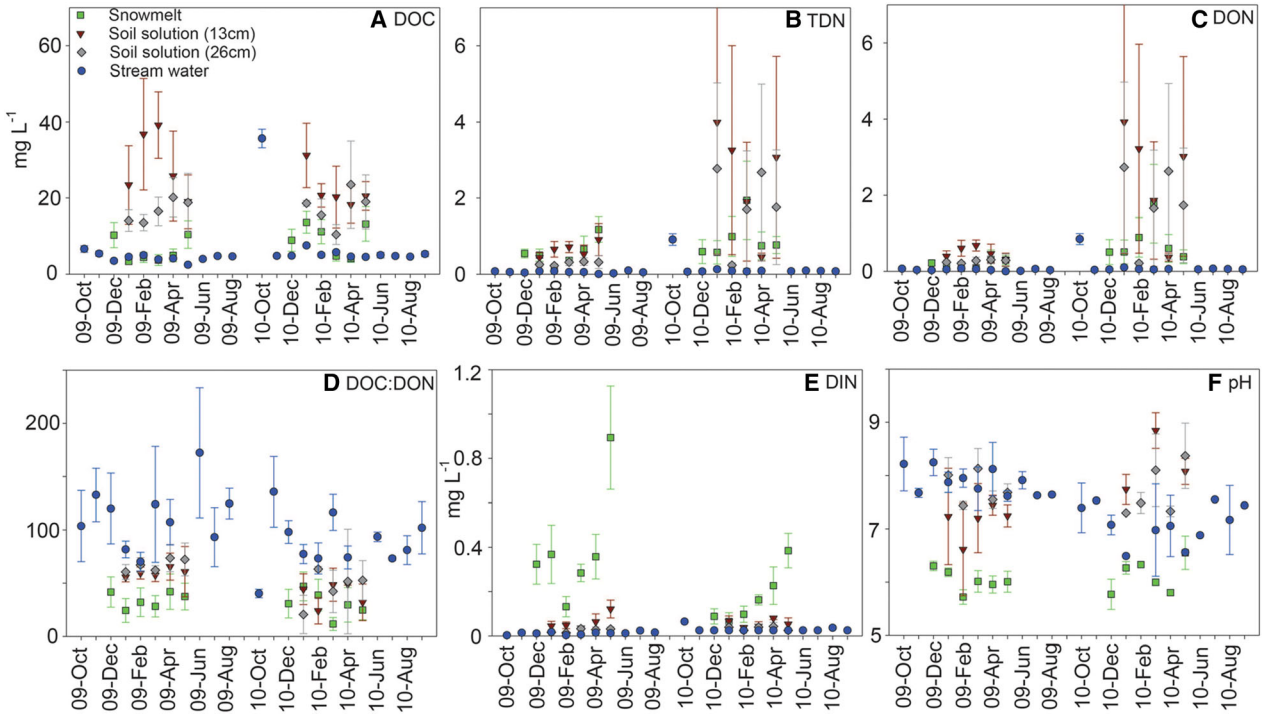

Figure 4. Water chemistry in various ecosystem pools at the Providence site from October to September in Water Year (WY) 2009 and 2010. Mean concentrations of (**A**) dissolved organic C (DOC), (**B**) total dissolved N (TDN), (**C**) dissolved organic N (DON), (**D**) dissolved organic C to organic N mass ratio (DOC:DON), (**E**) dissolved inorganic N (DIN), and (**F**) pH. Dataset of DIN was acquired from Hunsaker and Johnson (2017). Error bars denote standard errors across the four watersheds prior to thinning and drought.

Discussion

Water Chemistry Among Different Water Sources

We found that variation of water chemistry among different water sources at our sites were mostly consistent with observations in other climatic regions. As water moved from snowmelt to stream, we observed higher concentrations of DOC and DON in soil solution and lower DIN concentration in stream water (Figure 3). Similar variations have also been observed in humid (Michalzik and others 2001; Fuss and others 2015), boreal (Ågren and others 2010), and alpine regions (Boyer and others 1997; Brooks and others 1999; Kaushal and Lewis 2005; Williams and others 2009). This suggests that terrestrial biological (for example, microbial processing, plant uptake) and chemical processes (for example, sorption, geological weathering) along the hydrological flow path (Kaiser and Kalbitz 2012; Keller 2019) have similar impacts on dissolved C and N across different climatic regions.

In contrast, SUVA values of the DOC did not change significantly along the hydrological flow path, suggesting little change in DOC aromaticity in headwater basins from the Mediterranean climatic zone. This result is somewhat surprising given the recognized importance of soil regolith in influencing DOM chemical composition along the hydrological flowpath (Ågren and others 2008; Ledesma and others 2018). For instance, theoretically, soil solution from shallower soil should have higher DOC aromaticity than soil solution from deeper soil as shallower soil has more DOM derived from plant lignin compared to deeper soil, where the DOM is more of microbial origin (Kaiser and others 2004). Moreover, increased pH with depth should have led to an increase in the solubility of higher molecular weight DOM and presumably its aromaticity (Miller and others 2016). In alpine regions, decreases in DOC aromaticity in the soil solution with increased soil depth has been observed using a similar sampling approach (Cory and others 2004). Clearly, more research is needed to better understand mechanistically the alterations in the chemical composition of DOC while water moves through the soil profile in Mediterranean-type climatic regions.

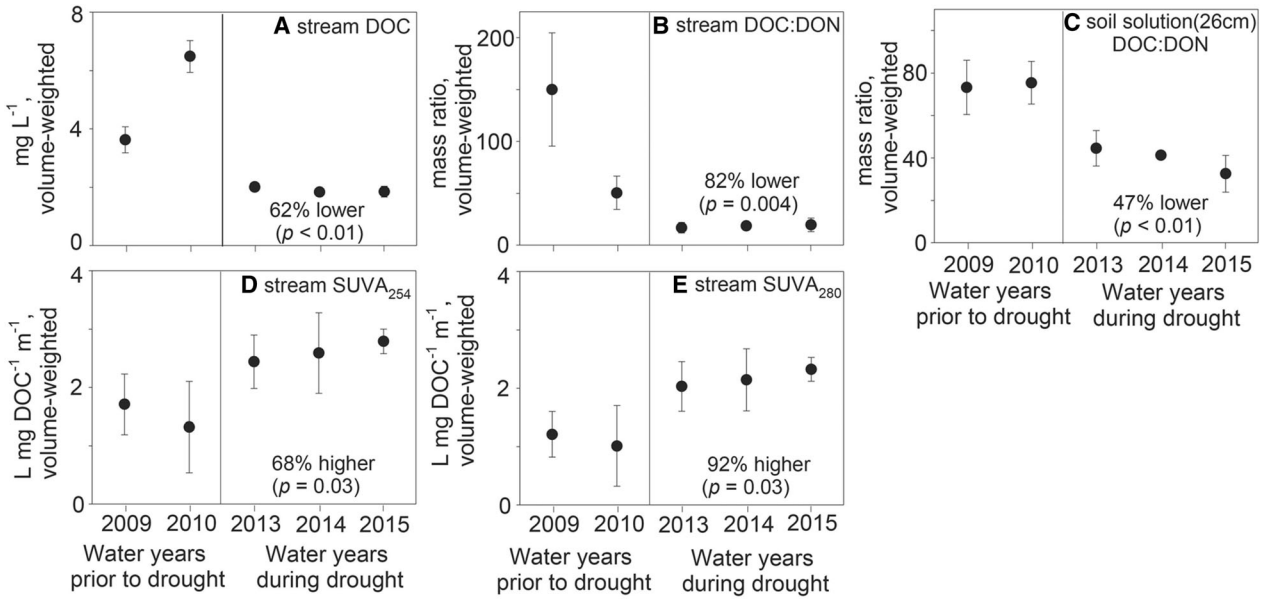

Figure 5. Water chemistry in stream and soil pools in untreated (that is, control) watersheds during Water Years 2009, 2010, and 2013–2015 in the Kings River Experimental Watersheds. Mean (and standard error) volume-weighted annual concentrations of (**A**) dissolved organic C (DOC) in stream water, (**B**) dissolved organic carbon to organic nitrogen mass ratio (DOC:DON) in stream water, (**C**) DOC:DON in soil solution (26 cm depth), (**D**) $SUVA_{254}$ in stream water, and (**E**) $SUVA_{280}$ in stream water. $SUVA_{254}$ and $SUVA_{280}$ = Specific ultra-violet absorption at wavelengths of 254 and 280 nm, respectively. Two sample *t* tests were used to compare water chemistry in years during drought (n = 3, WY 2013–2015) to those years prior to drought (n = 2, WY 2009 and 2010). Vertical black line in figure panels separates these two periods. Each data point is the mean value of three replicates (two Providence watersheds and one Bull watershed) for stream water and two replicates (two Providence watersheds) for soil solution.

Temporal Variation of Water Chemistry

The monthly variation of stream DOC concentrations observed prior to drought and thinning supported our hypothesis that the beginning of a water year would have higher concentrations than the following months due to the flush of accumulated soil DOC in antecedent dry summer with the first significant precipitation. We observed a 49% higher concentration in October than the mean value of the rest months in WY 2009 (5.37 and 3.60 mg l^{-1}, respectively, Figure 4A), and this difference was largely amplified in WY 2010 during a higher stream discharge rate in October (Figure 2C). Higher concentrations of stream DOC have also been observed in the months transit from dry to wet conditions (September–December) than the rest months within a year in other Mediterranean basins (Bernal and others 2005; Guarch-Ribot and Butturini 2016). This suggests that seasonal variation of stream DOC is more likely driven by the antecedent moisture condition rather than the hydrological flow conditions in Mediterranean-type climatic regions, as stream discharge is usually not the highest in the beginning of a water year (for example, Figure 2C). Note that the climatic impact on seasonal variation in stream DOC might not be obvious in Mediterranean basins with low hydrological variability where groundwater is the main source of stream flows (Roig-Planasdemunt and others 2017).

We also observed higher concentrations of stream dissolved N in October compared to other months in WY 2010, similar to the study in the Sierra Nevada foothills where pulses of stream DIN were observed during fall rains rather than from spring snowmelt (Jackson and others 2002). However, the higher concentrations of dissolved N in October compared to other months were not observed in WY 2009, suggesting that the influence of antecedent moisture condition are less consistent over years for dissolved N than for DOC. A higher concentration of DIN in stream water has also been observed during snowmelt season than during other months in the Emerald Lake Watershed in the southern Sierra Nevada (Williams and others 1995), similar to the seasonal patterns observed in other climatic regions such as boreal and alpine (Boyer and others 1997; Ågren and others 2010).

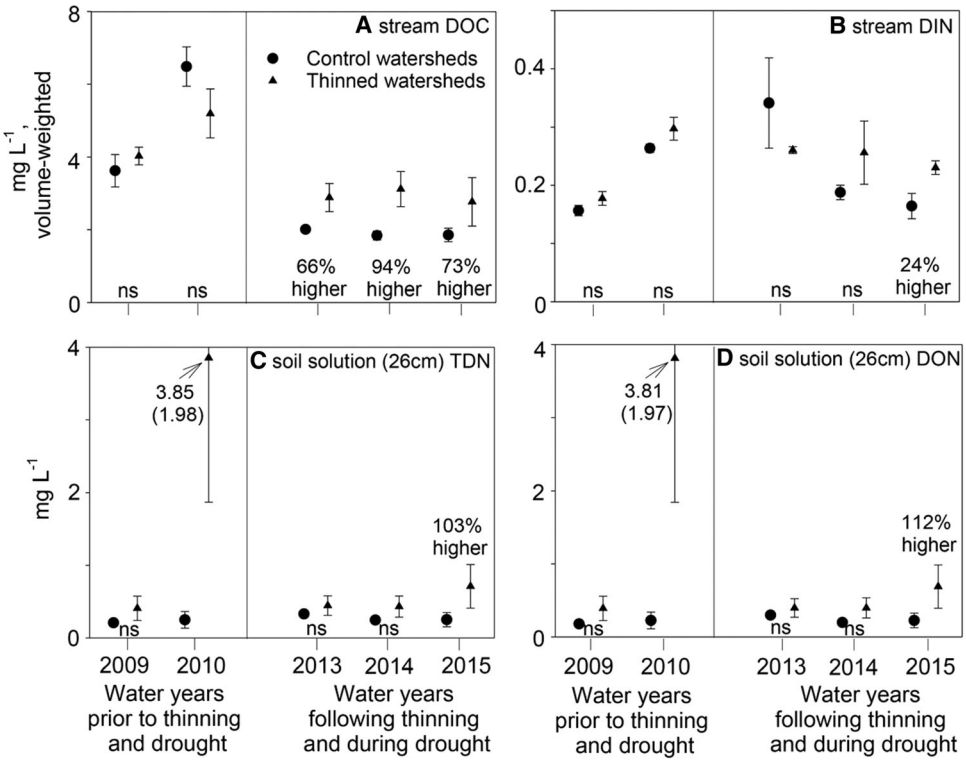

Figure 6. Impact of drought combined with low-intensity thinning on stream water and soil solution chemistry during Water Years (WY) 2009, 2010, and 2013–2015 in the Kings River Experimental Watersheds. Mean (and standard error) annual concentrations of (**A**) dissolved organic C (DOC) in stream water, (**B**) dissolved inorganic N (DIN) in stream water, (**C**) total dissolved N (TDN) in soil solution (26 cm depth), and (**D**) dissolved organic N (DON) in soil solution (26 cm depth). WY 2009 and 2010 were prior to the disturbances (drought and thinning), and WY 2013–2015 were following a forest thinning during drought. Vertical black line in figure panels separates these two periods. Repeated measures ANOVA was used to compare values between control and thinned watersheds for different years. Each data point is the mean value of three replicates (two Providence watersheds and one Bull watershed) for stream water and two replicates (two Providence watersheds) for soil solution.

Thus, both antecedent moisture condition and hydrological flow condition play important roles in regulating seasonal variation of stream dissolved N in headwater basins experiencing Mediterranean-type climates.

The significant difference of stream water chemistry observed between the two water years prior to drought and thinning suggests a large interannual variability in hydrological nutrient transport. The higher concentrations of stream dissolved N in WY 2010 than WY 2009 could be attributed to the higher production of dissolved N in soils as we observed higher concentrations of dissolved N in both soil solution and precipitation (Figure 4B, C). The greater precipitation in WY 2010 than WY 2009 would also result in a higher water table and allow more lateral water transport of dissolved N into streams (Montgomery and Dietrich 1995; Sanderman and others 2009). We observed higher DOC concentrations in WY 2010 than WY 2009 in stream water but not in snowmelt nor in soil solution. Thus, the higher concentrations of stream DOC might be simply due to more transport of DOC from upland soils to streams under higher flow rates. Note that our measurements of snowmelt and soil solution were limited to the wet season (December–May). Higher DOC concentrations in soil solution in WY 2010 than WY 2009 might occur in the beginning of the water year that transits from dry to wet period, as seasonal variation of stream DOC was driven more by the antecedent moisture condition than hydrological flow.

Drought Effects on Water Chemistry

Different concentrations of stream water chemistry observed between drought years and years prior to drought supported our hypothesis that drought alone would decrease mean annual concentrations of dissolved C and N in stream water. Interestingly,

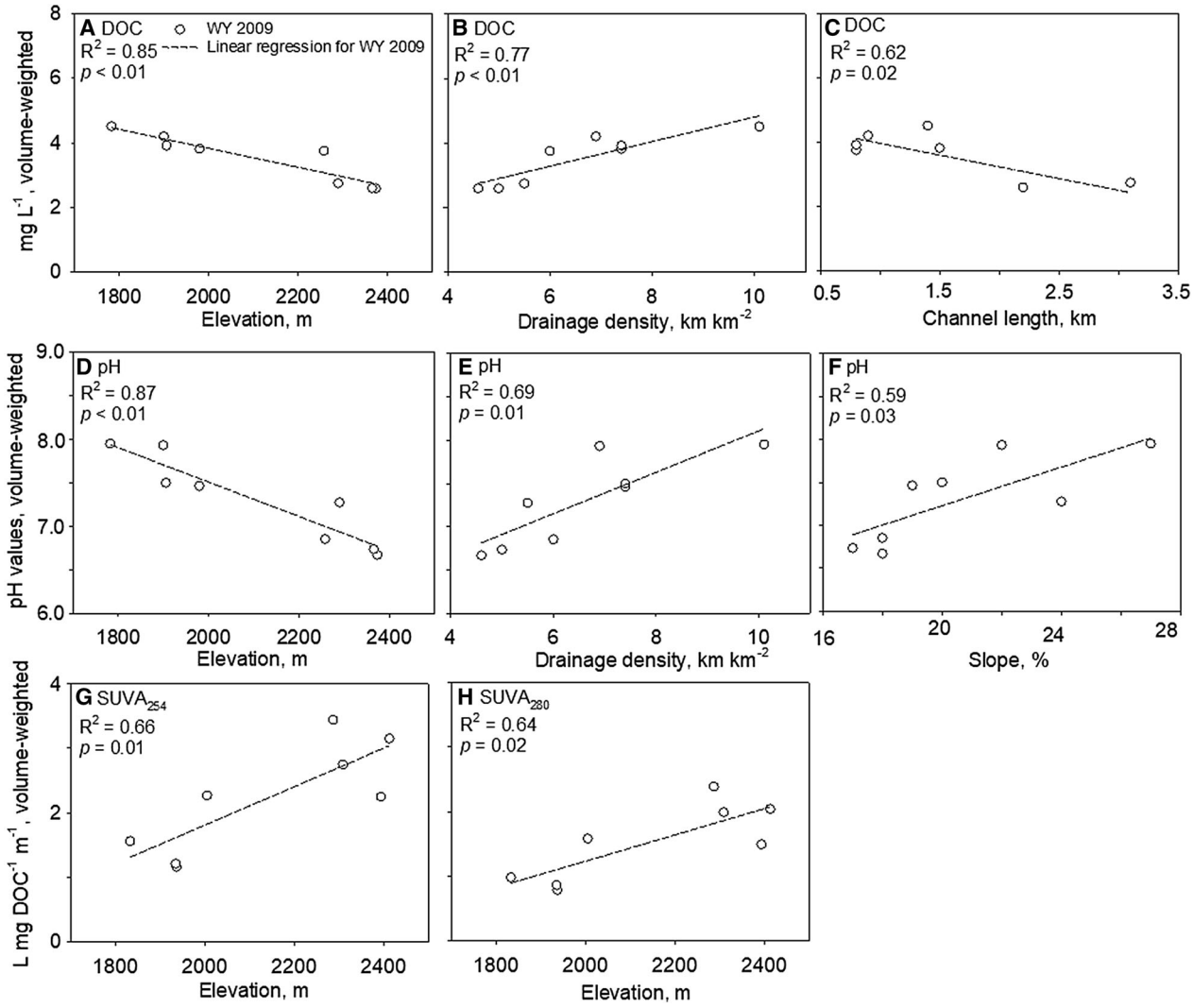

Figure 7. Relationships between selected watershed characteristics and volume-weighted annual values of (**A–C**) dissolved organic C (DOC), (**D–F**) pH, (**G**) $SUVA_{254}$, and (**H**) $SUVA_{280}$ in stream water across the eight Kings River Experimental Watersheds in WY 2009 ($n = 8$). Each data point indicates a single watershed. $SUVA_{254}$ and $SUVA_{280}$ = specific ultra-violet absorption at wavelengths of 254 and 280 nm, respectively.

the reduction of stream DOC and DOC:DON occurred immediately when the drought event began (Figure 5A). This suggests that the disrupted connections between upland soils and stream water under drought were not delayed by the water supply from preserved snowpack at high elevations. This might be due to the high water demand from deep-rooted trees with and year-round photosynthesis in this semi-arid region (Kelly and Goulden 2016). We also observed an immediate increase in stream SUVA under drought, suggesting increases in water aromaticity and humic contents. Note that our values of stream SUVA during drought (~ 2.3 l mg DOC^{-1} m^{-1}) were still relatively low compared to headwater streams in Colorado, Pennsylvania, and Maryland in non-drought water years (~ 4.0 l mg DOC^{-1} m^{-1}; Miller and others 2016).

Very few studies have examined the potential impacts of drought on the water chemistry in headwater basins (Kovach and others 2019). Decreased concentrations of stream water DOM during drought have been attributed to reductions in DOC production in upland soils, as well as decreased hydrological coupling with the stream (Lake 2003; Szkokan-Emilson and others 2017). During the drought period, increases in ionic strength of the soil solution should reduce the solubility of DOC, and the accompanying higher surface soil temperature may increase oxidative

decomposition of the DOC to CO_2, at least when soil moisture is non-limiting to microbial activity (Worrall and Burt 2008; Clark and others 2005, 2012). Our changes in stream water DOM during drought were only reflected in the soil solution (26-cm depth) in the case of DOC:DON, but not for DOC concentrations or DOM aromaticity. Thus, decreases in DOC concentrations and increases in DOC aromaticity in stream water during drought may be due to the altered in-stream processing of organic matter under drought (Bilby and Likens 1980). However, our measurements of soil solution were conducted only during the wet season (December–May); concentrations of DOM in soil solution might be lower at the beginning of a water year during drought, and this mechanism might also be responsible for the reduction in stream DOC during these climatic periods.

Interactive Effects of Drought and Thinning on Water Chemistry

We observed increased mean annual concentrations of stream DOC, but unchanged DOC concentrations in soil solution during the wet season following thinning conducted during a drought. This was inconsistent with our hypothesis that increased DOC would be observed only in soil solution but not stream water due to the extra input of detritus pools to soils following thinning and limited hydrological transport from soils to stream during drought. Increased stream DOC following thinning has been attributed to increased transport of DOM derived from the extra detritus pools (Swank and others 2001; Palviainen and others 2004). We speculate that soil DOM at our sites was likely to increase in the beginning of the water year as we did not find changes in soil DOM during the wet season. Increased stream DOC under thinning has also been attributed to a raised groundwater level that connects organic matter-rich soil horizons with stream water (Laudon and others 2009). However, this mechanism is likely not responsible for the patterns we observed because the annual discharge rate at our sites was similar between thinned and control watersheds during drought ($p \geq 0.35$ using repeated-measures ANOVA, 63 mm y^{-1} vs. 87 mm y^{-1} averaged over three watersheds and three water years). Indeed, thinning impacts on groundwater levels were observed to be minimal under drought in our region (Saksa and others 2017).

We found a more complex impact of drought combined with thinning on dissolved N than DOC, as changes in dissolved N were only observed in the 3rd year following thinning (Figure 6). Commonly, increases in stream DIN are observed immediately after forest thinning (for example, Likens and others 1970; Binkley and Brown 1993; Tiedemann and others 1998; Jewett and others 1995; Hughes and Quinn 2019), which have been attributed to reduced plant and microbial uptake of soil inorganic N following vegetation removal (Hart and Stark 1997; Hughes and Quinn 2019). A similar delayed increase in DIN following a clear-cutting has been observed in boreal headwater streams (Palviainen and others 2015). The authors explained this delay by the immobilization of N in logging residues during the first years of decomposition (Palviainen and others 2004) and a delayed nitrification response (Vitousek and others 1979). Our delayed response of dissolved N could be due to the interactive effects of vegetation removal and drought, as drought likely reduced both rates of organic matter decomposition and nitrification in soil (Clark and others 2005; Worrall and Burt 2008), as well as transport rates of soil water to streams (Lake 2003).

Increased stream concentrations of dissolved C and N have been reported in years with near-average precipitation and under higher-intensity forest thinning (for example, removal of ~ 33% basal area in the Catskill Mountains in New York USA, Wang and others 2006; removal of ~ 40% basal area in the Bavarian Alps in Germany, Bäumler and Zech 1999; clear-cutting in boreal forests in northern Sweden, Schelker and others 2012, 2014). Our findings suggest that drought combined with a relatively low-intensity forest thinning (removal of ~ 10% basal area) could significantly alter stream water chemistry in conifer-dominated forests of headwater watersheds of the Sierra Nevada. Despite increases in stream DOC concentrations, drought combined with low-intensity thinning did not alter DOC aromaticity, as we found no differences in stream water SUVAs ($SUVA_{254}$ and $SUVA_{280}$) in water years following thinning and during drought. This result was consistent with the observations made during the summer following clear-cutting of headwater watersheds dominated by black spruce trees (*Picea mariana* (Mill.) Britton, Sterns & Poggenburg) in Canada (Glaz and others 2015). Although we observed losses of dissolved C and N from the ecosystems following thinning, these losses are considerably lower than losses that generally occur after prescribed fire and stand-replacing wildfires (Johnson and others 2008, 2014; Dove and others 2020).

Watershed Characteristics Related to Stream Water Chemistry

We observed strong correlations between watershed characteristics and stream water chemistry only in WY 2009 but not WY 2010, which was partially consistent with our hypothesis that the accuracy in prediction of stream water chemistry using watershed characteristics would be applicable only in years prior to disturbance (that is, drought and thinning). In WY 2009, we observed lower DOC concentrations in watersheds at higher elevations, which was probably due to lower DOC production rates under slower organic matter decomposition (Sjögersten and Wookey 2009) in these colder climates (Hunsaker and others 2012). Similarly, positive correlations between stream DOC aromaticity ($SUVA_{254}$ and $SUVA_{280}$; Figure 6G, H) and watershed elevation were likely the result of slower decomposition rates in colder environments (Donnelly and others 1990; Duboc and others 2014). Positive correlations between DOC concentrations in stream water and drainage density (Figure 6B) were presumably due to increased transport of DOC from the uplands to streams under increased drainage density (Hope and others 1994), as upland is the main source of DOC in these low order streams (Moeller and others 1979; Hongve 1999). And the negative correlation (in WY 2009 only) between DOC concentrations in stream water and stream channel length may reflect the greater consumption of DOC during its transport within the stream (Bilby and Likens 1980; Kalén 2007).

The correlation between watershed characteristics on the pH of stream water in WY 2009 suggests a strong impact of upland leaching. Stream water pH is the result of several biogeochemical and hydrological processes occurring within the upland and within the stream itself (Piñol and Avila 1992; Soulsby 1992; Ohte and others 1995). If the colder temperatures at higher elevations result in lower DOC inputs to streams as speculated above, then we would also predict higher stream water pH at higher elevation given that DOC can significantly contribute to stream water acidity (Likens and Buso 2006; Erlandsson and others 2010); however, the opposite trend was found (Figure 6D). Thus, stream water pH appears more impacted by upland leaching than in-stream processes, as lower pH was also found in soils at our higher elevation sites (Johnson and others 2011). Additionally, presumed shorter hydrologic flowpaths between soils and stream water due to greater drainage density or steeper watershed slopes should reduce buffering of precipitation acidity by soil processes, resulting in a hypothesized negative relationship between drainage density and slope and stream water pH (BalajiAvhad and others 2013); however, again the opposite relationship was observed (Figure 6E, F). This further suggests the importance of upland leaching, as our higher elevation watersheds had lower drainage density and less steep slopes than those found at lower elevations.

Importantly, none of the above predictions of stream water chemistry using relatively easily measured watershed characteristics were applicable in WY 2010 prior to drought and in WY 2013–2015 during drought and thinning. In WY 2010, we observed both a higher amount of precipitation and a higher stream discharge rate compared to WY 2009 (Figure 2C), which likely resulted in similar groundwater levels across the studied watersheds and limited the extent of in-stream processes by decreasing water residence time (Cory and others 2015). In WY 2013–2015, considerable decreases in DOM production and hydrological connectivity that occur during drought may limit the prediction of stream water chemistry using watershed characteristics alone. These results suggest that the regular constraints of watershed characteristics on both biological (for example, microbial activities) and hydrological processes (for example, water flow paths and residence times) are likely altered in years with both relatively high and extremely low precipitation conditions.

Summary and Limitations

In the 2 years prior to drought and thinning, we observed higher concentrations of stream DOC in the first month of a water year (that is, October) compared to the rest of the months of that water year. This suggests that the antecedent soil moisture condition plays an important role in stream water chemistry in Mediterranean-type climatic regions. Similar seasonal variation was also observed for stream dissolved N but only in 1 year, suggesting that the influence of antecedent soil moisture condition was less consistent for dissolved N than DOC. During drought years following thinning (removal of ~ 10% basal area), we observed immediate changes in stream C (that is, decreased DOC and increased SUVA in unthinned watersheds, and increased DOC in thinned watersheds), but a delayed increase in stream DIN in thinned watersheds during drought. This suggests that influences of drought and thinning are less pronounced for dissolved N than DOC in streams.

Our evaluation of intra-annual variation in water chemistry was limited by sample availability. Because of the difficult accessibility of these remote watersheds particularly during the winter months, snowmelt and soil solution were only sampled at the lower elevation site (Providence). At the higher elevation site (Bull), there might be a tighter coupling of water chemistry with snowmelt, soil solution, and stream water compared with the lower elevation site in part due to lower microbial activity in the colder environment. Our evaluation of the inter-annual variation in water chemistry was also limited, as we were unable to identify the thinning impact alone given the potential for interactions between drought and thinning in altering water chemistry.

Our ability to accurately predict stream water chemistry using watershed characteristics was only applicable in a single year with near-average precipitation (WY 2009). Poor predictability in stream water chemistry was found in years with above-average and extremely low precipitations (WY 2010, 2013–2015). Thus, forecasting headwater stream chemistry using relatively easily measured watershed characteristics will be more difficult in the mountainous western United States, given increased climatic variability and frequencies in disturbances (both drought and thinning) projected in the future.

ACKNOWLEDGEMENTS

This study was conducted in the Kings River Experimental Watersheds (KREW) project, which was established and is managed by the Pacific Southwest Research Station of the USDA Forest Service. The KREW study was implemented using funds from the National Fire Plan of the USDA Forest Service. Additional funding for this work was provided by the Pacific Southwest Research Station of the USDA Forest Service and the National Science Foundation through its support of the Southern Sierra Critical Zone Observatory (SSCZO; EAR-0725097, 1239521, and 1331939). We would like to thank many others from UC Merced for their dedicated work in collecting field samples and laboratory processing for the SSCZO project. We thank staff from the Pacific Southwest Research Station for their ongoing support of all aspects of KREW and for providing data and water samples for this research. We also thank Professors Amy Burgin and Sarah Ledford, and three anonymous reviewers for their helpful feedback on the manuscript.

DATA AVAILABILITY

Data can be found at: https://doi.org/10.2737/RDS-2017-0037; https://doi.org/10.2737/RDS-2018-0028; https://doi.org/10.2737/RDS-2017-0040.

Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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