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Fates and fingerprints of sulfur and carbon following wildfire in economically important croplands of California, U.S.

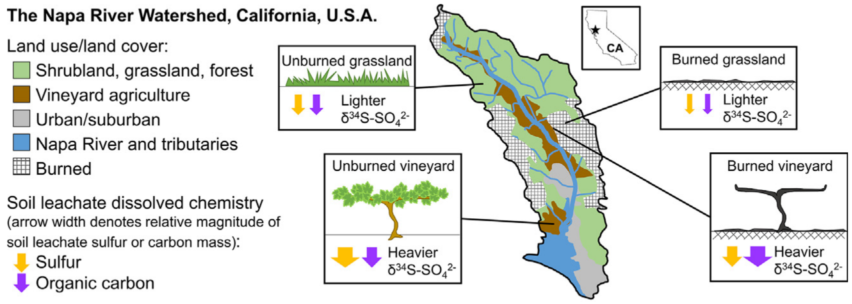
Anna L. Hermes [a,b,*], Brian A. Ebel [c], Sheila F. Murphy [d], Eve-Lyn S. Hinckley [a,b]

[a] *Institute of Arctic and Alpine Research, 4001 Discovery Drive, Boulder, CO 80303, USA*
[b] *Environmental Studies Program, University of Colorado, Boulder, 4001 Discovery Drive, Boulder, CO 80303, USA*
[c] *U.S. Geological Survey, Water Mission Area, W 6th Ave Kipling St., Lakewood, CO 80225, USA*
[d] *U.S. Geological Survey, Water Mission Area, 3215 Marine St., Boulder, CO 80303, USA*

HIGHLIGHTS

- Wildfire and agriculture affect sulfur (S) and carbon (C) chemistry in watersheds.
- Vineyard soils leach ~20 times more S than grassland soils with low rainfall.
- The vineyard S chemical fingerprint is distinct from grasslands.
- Low burn severity wildfire did not significantly alter the vineyard S fingerprint.
- Agricultural and wildfire-mobilized S and C may affect ecosystem and human health.

GRAPHICAL ABSTRACT



Vineyards have a unique sulfur biogeochemical fingerprint—the sulfur quantity and stable isotope value—relative to grasslands. The fingerprint was not significantly altered by low severity wildfire.

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ABSTRACT

Sulfur (S) is widely used in agriculture, yet little is known about its fates within upland watersheds, particularly in combination with disturbances like wildfire. Our study examined the effects of land use and wildfire on the biogeochemical "fingerprints," or the quantity and chemical composition, of S and carbon (C). We conducted our research within the Napa River Watershed, California, U.S., where high S applications to vineyards are common, and ~ 20% of the watershed burned in October 2017, introducing a disturbance now common across the warmer, drier Western U.S. We used a laboratory rainfall experiment to compare unburned and low severity burned vineyard and grassland soils. We then sampled streams draining sub-catchments with differing land use and degrees of burn and burn severity to understand combined effects at broader spatial scales. Before the laboratory experiment, vineyard soils had 2–3.5 times more S than grassland soils, while burned soils—regardless of land use—had 1.5–2 times more C than unburned soils. During the laboratory experiment, vineyard soil leachates had 16–20 times more S than grassland leachates, whereas leachate C was more variable across land use and burn soil types. Unburned and burned vineyard soils leached S with $\delta^{34}S$ values enriched 6–15‰ relative to grassland soils, likely due to microbial S processes within vineyard soils. Streams draining vineyards also had the fingerprint of agricultural S, with ~2–5 fold higher S concentrations and ~ 10‰ enriched $\delta^{34}S\text{-}SO_4^{2-}$ values relative to streams draining non-agricultural areas. However, streams draining a higher fraction of burned non-agricultural areas also had enriched $\delta^{34}S$ values relative to unburned non-agricultural areas, which we attribute to loss of ^{32}S during combustion. Our findings illustrate the interacting effects of wildfire and land use on watershed S and C cycling—a new consideration under a changing climate, with significant implications for ecosystem function and human health.

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* Corresponding author at: Institute of Arctic and Alpine Research, 4001 Discovery Drive, Boulder, CO 80303, USA.
E-mail address: anna.hermes@colorado.edu (A.L. Hermes).

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1. Introduction

Agricultural sulfur (S) use in large-scale crop systems represents a significant manipulation of the S cycle but has received little attention in the scientific literature (Hinckley et al., 2020). The majority of research on anthropogenic S inputs to the environment has focused on elevated atmospheric S deposition from fossil fuel emissions and subsequent environmental effects in remote forested ecosystems, including soil and stream acidification, leaching of soil base cations, and mobilization of heavy metals (Driscoll et al., 2001; Likens et al., 1996). Peak atmospheric S deposition in the eastern U.S. was on average ~ 20 kg S ha^{-1} yr^{-1} in 1973 (Driscoll et al., 2001) and has decreased to 2–3 kg S ha^{-1} yr^{-1} in recent years due to regulation of S emissions (U.S. EPA, 2018). As a result, crops within the U.S., but also internationally, are increasingly experiencing S deficiencies as atmospheric S deposition declines (Camberato and Casteel, 2017; David et al., 2016; Schnug and Evans, 1992). Combined with climate change related pest pressures (Caffarra et al., 2012; Tang et al., 2017) and the need to intensify agriculture to meet the needs of a growing human population (Tilman et al., 2011), agricultural S use in all its forms—as pesticides, fertilizers, and soil conditioners—is likely to increase over time.

Today, agricultural S applications often far exceed peak atmospheric S deposition on local scales, suggesting that many of the same environmental consequences that occurred in response to chronic elevated atmospheric S deposition to forested systems could occur locally and downstream of regional high S crops. For example, in the Florida Everglades Agricultural Area (EAA), elemental S (S^0) applications to sugarcane fields are on average 94 kg S ha^{-1} yr^{-1} (Gabriel et al., 2008) and applications of 280–560 kg S ha^{-1} yr^{-1} are recommended for organic rich soils with $pH > 7.5$ (McCray, 2019); these S applications are over 10 times greater than the highest rates of atmospheric S deposition in the U.S. during the 1970s. In the Florida EAA, excess sulfate (SO_4^{2-}) in agricultural runoff has been linked to enhanced methylmercury production in wetlands (Orem et al., 2011)—a threat to wildlife and people. To date, comprehensive research on the fates of agricultural S has largely been limited to the Florida EAA—a wetland system in a highly managed hydrologic setting—highlighting the need for an improved understanding of S fates and consequences in a broader range of agricultural settings, particularly upland watersheds characterized by complex land use and land cover mosaics.

Understanding the transport and fates of agricultural S applications in the environment requires tools that can differentiate S sources (e.g., agricultural, geologic, and atmospheric) in watersheds. Stable S isotope ratios, $^{34}S/^{32}S$, have long been used to understand S biogeochemistry and differentiate multiple sources of S in terrestrial and aquatic ecosystems (Bates et al., 2002; Krouse and Grinenko, 1991; Peterson and Fry, 1987). Fewer studies have evaluated S cycling in mixed land use watersheds, or developed approaches to trace agricultural S from source areas (croplands) to downstream aquatic ecosystems, including wetlands. To understand the ultimate fates and consequences of high S use in crop systems, it is critical to determine the biogeochemical "fingerprints" of S within watersheds, or the combination of the quantity and stable isotopic composition of S.

Additionally, it is becoming increasingly important to investigate the intersection of high S crops with land cover disturbances like wildfire. This intersection is newly emerging, now that S use in croplands is on the rise (Kurbondski et al., 2019) and wildfire is considered part of the modern landscape, particularly in the Western U.S. (Schoennagel et al., 2017; Westerling et al., 2006). Wildfire has many environmental effects, from altering soil hydraulic properties and runoff generation (Ebel and Moody, 2017; Moody et al., 2016) to mobilizing significant loads of sediment, dissolved organic carbon (DOC), and nutrients (Smith et al., 2011) in forested ecosystems. Fire removes crop debris post-harvest in agriculture, which can alter soil organic matter quantity and quality (Panosso et al., 2011; Virto et al., 2007) and the chemistry of runoff from croplands (Viator et al., 2009). However, immediate and long-term effects of fire on hydrology, soils, and water quality vary based on many factors, including burn severity (Moody et al., 2016), geology (Benda et al., 2003; Florsheim et al., 1991; Moody et al., 2008), post-fire precipitation (Murphy et al., 2015), ecological fire adaptations (Barro and Conard, 1991), and post-fire land management and remediation (Robichaud et al., 2009).

Wildfire has the potential to alter the biogeochemical fingerprint of S in soil and water. In forested ecosystems, wildfire can increase the transport of reactive elements, including S, from hillslopes to streams (Johnson et al., 2007; Murphy et al., 2006). It can also volatilize S from forest foliage and litter (Tiedemann, 1987), and increase S oxidation rates in soils, altering soil S forms (Murphy et al., 2006; Nano, 2012). Wildfire may also change the stable isotopic composition (i.e., $^{34}S/^{32}S$) of agricultural S in soils, similar to how it stimulates preferential losses of lighter carbon (C) and nitrogen (N) stable isotopes from forested ecosystems (e.g. Saito et al., 2007). In watersheds where both high crop S use and wildfire disturbance occur, there is the potential for these two major drivers to affect watershed-scale S biogeochemistry.

In addressing the interactions between agricultural S inputs and wildfire disturbance, C dynamics likely play a role in determining the ultimate fates and ecological effects of S, particularly within wetlands downstream of both agricultural and fire-affected areas. Wildfire can alter and mobilize DOC from forested areas (e.g. Revchuk and Suffet, 2014), an important energy source and mediator of biogeochemical reactions (Graham et al., 2012, 2013; Vergnoux et al., 2011), and a critical component of soil stabilization and microbial processes. Like excess SO_4^{2-}, DOC plays a role in stimulating production of methylmercury. Previous research in both experimental (Graham et al., 2013) and field settings (Hall et al., 2008; Mitchell and Gilmour, 2008) has shown that DOC aromaticity, which increases under a range of forest fire burn temperatures (González-Pérez et al., 2004; Vergnoux et al., 2011), is positively correlated with methylmercury production. Thus, the C biogeochemical "fingerprint," defined here as the quantity and aromaticity of DOC, may elucidate contributions of fire to downgradient aquatic environments. Combined, agricultural S use and wildfire disturbance can increase the potential for significant ecological consequences at watershed scales.

In this study, our objective was to investigate the isolated and interactive effects of intensive agricultural S use and wildfire disturbance in upland watersheds with mixed land cover that include crops receiving high S applications. We focused our research within the Napa River Watershed in Northern California, U.S., where vineyards are intensively sprayed with S^0 as a fungicide to control powdery mildew disease, and in October 2017, wildfires burned ~20% of the watershed. While higher elevation forested areas experienced moderate to high burn severity conditions, vineyards that burned were low severity, because the crop is irrigated and has relatively lower biomass compared to forests. We leveraged this set of conditions to ask: (1) What are the immediate effects of wildfire on agricultural soil S and C dynamics and biogeochemical fingerprints? and (2) How does wildfire affect S and C chemistry at sub-catchment scales? We hypothesized that (1) vineyard soils would have higher S concentrations and leach more S than grassland soils, due to the accumulation of S additions in vineyard soils, and wildfire would increase vineyard S leaching (e.g. Johnson et al., 2007; Murphy et al., 2006); (2) low severity burned soils would have higher C concentrations and leach more C characterized by higher aromaticity than unburned soils, regardless of land use; and (3) stream S and C concentrations would be highest in streams draining sub-catchments with a mix of vineyard land use and wildfire. We expected that the agricultural S fingerprints in both soils and streams could be unique relative to non-agricultural areas, but may be complicated by wildfire, and that C biogeochemical fingerprints could be used as a signature of wildfire.

2. Study area

Vineyard agriculture comprises ~13% of the 1103 km^2 Napa River Watershed (Fig. 1). Other land use/land cover types include forest (36% of watershed area), grassland and shrubland (30%), and urban and residential development (~8%; Yang et al., 2018; Fig. 1). The watershed drains to San Pablo Bay and the greater San Francisco Bay Estuary. The Mediterranean climate results in distinct dry and wet seasons. Average annual precipitation ranges from 518 mm in Napa to 931 mm in St. Helena, California, of which 88–90% falls as rain during the wet season (October through March; Arguez et al., 2012). Thirty-minute average rainfall intensities are 16 mm hr^{-1} in Napa and 22 mm hr^{-1} in St. Helena for storms with a 50% annual exceedance probability (Perica et al., 2014). During the dry season (April through September), winegrowers spray S^0 to vineyards weekly to biweekly, with average cumulative loads of ~80 kg S ha^{-1} yr^{-1} across all vineyards in Napa County (California Department of Pesticide Regulation, 2018). Agricultural S^0 applications are significantly higher than average annual atmospheric S deposition estimates (1.2 ± 0.5 kg S ha^{-1} yr^{-1} for 1989–2017; Hinckley et al., 2020). Wet season rains saturate vineyard soils, mobilizing S in soluble forms (i.e., SO_4^{2-} and ester sulfates) below the vine rooting zone, the total mass nearly equivalent to annual applications (Hinckley et al., 2008; Hinckley and Matson, 2011). Rains also activate streamflow.

The Atlas, Tubbs, and Nuns fires—part of a suite of wildfires known as the North Bay Fires, which burned a total area of 590 km^2—burned ~20% of the Napa River Watershed from 9 to 31 October 2017 (Fig. 1). The majority of the total burned area was classified as unburned, very low, or low soil burn severity (74%), 25% was moderate severity, and ~ 1% was high severity (State of California Watershed Emergency Response Team, 2017a, 2017b, 2017c). The burned area consisted primarily of forest, shrubland, and grassland, but the fires also spread into urban areas and vineyards. The North Bay Fires occurred during a key seasonal transition: at the end of the dry growing season (i.e., high S storage in surface soils) and beginning of the wet dormant season, when the watershed was primed for altered fluxes of water, S, and DOC in vineyard and non-agricultural lands.

3. Materials and methods

3.1. Soil and stream sampling

To assess the immediate effects of wildfire on S and C chemistry in soil and water, we sampled soils from four sites representing a combination of land cover and burned areas: (1) low-severity burned vineyard, (2) low-severity burned grassland hillslope, (3) unburned vineyard, and (4) unburned grassland hillslope (Fig. 1). Both vineyard sites have

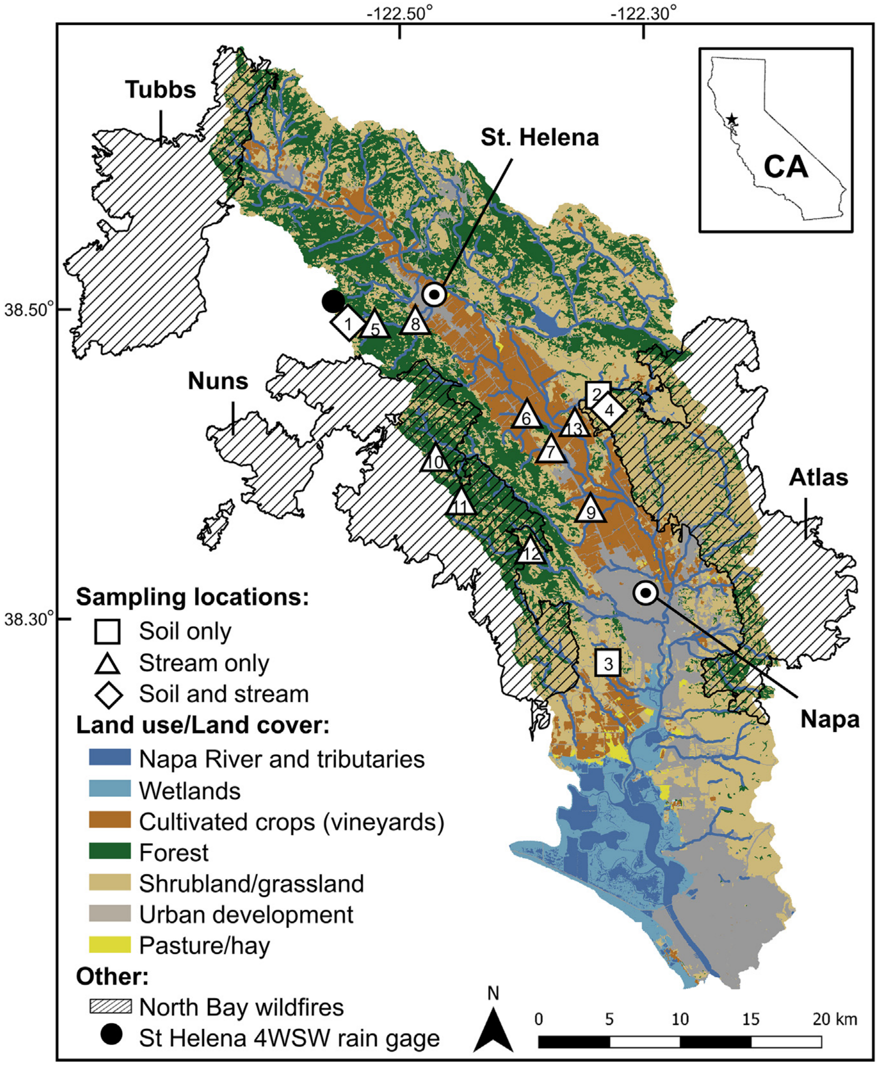

Fig. 1. Map of the Napa River Watershed. Striped polygons depict the geographic areas of the Tubbs, Nuns, and Atlas fires, which account for ~20% of the watershed. Vineyard agriculture, forests, shrubland/grassland, and urbanization dominate the land use/land cover in the watershed (Yang et al., 2018). The St. Helena 4WSW rain gage (black solid circle; GHCND #USC00047646, noaa.gov) informed the soil leaching experiment. Sampling locations (squares, triangles, or diamonds) are numbered according to Table S1.

Bressa-Dibble soils, while the grassland soils are Boomer-Forward-Felta complex (unburned) and rock outcrop-Hambright (burned; O'Geen et al., 2017; Table 1). Both vineyard locations receive S applications (Table S1). Both low-severity burned sites had minimal changes to infiltration, and soil hydrophobicity was not observed in the field or laboratory. Prior work has shown that infiltration is most altered after moderate- to severe-burn severity wildfires (Moody et al., 2016). We observed regrowth of grasses and cover crops at both burned sites, suggesting the burn did not substantially alter evapotranspiration rates over the course of the wet season.

We collected five intact surface cores (0–10 cm, 5 cm diameter) into cellulose acetate butyrate plastic sleeves (AMS, Inc.) from a ~ 1–2 ha area at each site for a laboratory leaching experiment. Within 1 m of each intact surface core, we collected and consolidated three surface soil samples (0–5 cm) into Whirl-Pak bags for chemical analyses, described below. At the burned sites, we sampled soils with low soil burn severity based upon field criteria from Parsons et al. (2010) to best represent the majority of the affected watershed area. We collected vineyard and unburned grassland soils on 11 November 2017 and burned grassland soils on 2 March 2018, due to post-fire access restrictions (Fig. S1). Soil samples were shipped on ice to the University of Colorado Boulder and stored at 4 °C until analysis.

To assess S and C stream chemistry, we sampled the Napa River and nine of its tributaries between March 2–4, 2018 (Figs. 1 and S1). The tributaries drain areas that vary in percent of watershed burned, soil burn severity, and different land cover types (Table S1). At each tributary sampling location, we measured stream flow either using a FlowTracker Acoustic Doppler Velocimeter (SonTek, San Diego, CA, USA) or by recording volume of water delivered over time from culverts. Stream samples were filtered through a 0.45-μm polyethersulfone filter into 250-mL HDPE bottles that were stored on ice in transit and then stored at 4 °C until analyses. Additional sampling at three of the tributaries was carried out between February 3–4, 2018 and May 4–5, 2018.

3.2. Soil leaching experiment

A laboratory soil leaching experiment simulated rainwater infiltration and one-dimensional subsurface leaching from the four soil types representing a combination of land cover and burn conditions. The minimal visual evidence that the wildfire generated overland flow at the burned study sites suggested that these leaching experiments appropriately represented S and C releases from soils in the field.

The laboratory soil leaching experiment simulated the 2017–2018 wet season. This water year had less than half the average annual rainfall (405 mm compared to 931 mm; St. Helena USC00047643, noaa.gov). Rainfall intensities were mimicked after the 30-min tipping bucket record from the St. Helena 4WSW rain gauge (USC00047646, noaa.gov; Fig. 1). This gauge records the highest rainfall in the watershed, so our laboratory experiment represented the high endmember for the 2018 water year. All rainfall events, either recorded or simulated in the experiment, had a recurrence interval of less than one year.

A complete account of the soil leaching experimental design is provided in the Supplementary Materials, Section S2. In brief, for each rainfall "event," defined as rainfall separated by ≥12 h, we pipetted 18.2 MΩ deionized water over the tops of experimental soil cores (four soil types with five replicate cores per type; Fig. S2). After each simulated rain event, we collected soil leachates that passed through the soil core (Table S2) and filtered them through 0.45 μm polyethersulfone filters into 60-mL HDPE bottles for S measurements (SO_4^{2-} and total dissolved sulfur, TDS) and combusted (5 h at 450 °C) amber glass bottles for DOC quantification and characterization. We stored samples at −20 °C until S analyses and 4 °C until DOC analyses.

3.3. Laboratory analyses

The soil sample composites and intact soil cores used in the laboratory leaching experiment were analyzed for total S and C concentrations. The soil sample composites represented conditions prior to the wet season (pre-experiment), while the intact soil cores represented end-of-season conditions (post-experiment). Prior to analyses, soils were dried (60 °C), sieved (< 2 mm), and pulverized for 48 h using a rolling mill. We measured soil total S concentrations using an elemental analyzer (EA) coupled to an isotope ratio mass spectrometer (IRMS), and total soil C concentrations on a carbon-hydrogen-nitrogen (CHN) EA (Table S3). Values are reported relative to kg of dry soil. We calculated the S or C mass difference between pre- and post-experiment soils by multiplying the soil S or C concentration by the soil bulk density and soil core volume. We report mass differences as the average and one standard deviation with propagated uncertainty across the five replicate cores per soil type. We note that these analyses only reflect soil concentrations and mass changes in the top 5–10 cm of the soil profile.

We analyzed aqueous samples (soil leachates and stream samples) for SO_4^{2-}, TDS, and DOC concentrations. Dissolved organic C was analyzed by persulfate oxidation, TDS by either ICP-OES or ICP-MS, and SO_4^{2-} by ion chromatography (complete details of analyte measurements are provided in Table S3). In addition, we measured the decadic absorption coefficient at 254 nm and calculated the specific ultraviolet absorbance at 254, $SUVA_{254}$, an index strongly correlated with DOC aromaticity (Weishaar et al., 2003).

For aqueous S stable isotope measurements, leachate and stream samples were treated with excess $BaCl_2$ to precipitate $BaSO_4$ (modified after Carmody et al., 1998; Hinckley et al., 2008). For many soil leachates, we consolidated samples from the same soil core across several simulated rain events to accumulate enough SO_4^{2-} mass for accurate $\delta^{34}S$ measurements. Aqueous-derived $\delta^{34}S\text{-}SO_4^{2-}$ was measured on a custom EA-IRMS (Table S3).

3.4. Statistical analyses

We analyzed bulk soil and soil leachate chemistry data to determine differences across soil types and understand drivers of leachate chemistry. Statistical analyses were performed in *R* (v. 3.4.3; R Core Team, 2017) using the base statistics package (*stats*), and the *lme* function in the *nlme* package (v. 3.1–137; Pinheiro et al., 2019). For all statistical analyses, a *p*-value <0.05 was required for statistical significance. We tested the null hypothesis that median soil chemistry values were the same across soil type groups using the Kruskal-Wallis rank sum test (Kruskal and Wallis, 1952), followed by post-hoc pairwise Wilcoxon

Table 1
Laboratory leaching experiment soil characteristics.

Soil type	Soil series[a]	Soil description[a]	Bulk density (g dry soil cm^{-3})[b]
Unburned grassland	Boomer-Forward-Felta	Moderate to deep, well-drained, metavolcanic, igneous, tuff-derived, gravelly sandy clay loam, 5–30% slope	1.4 ± 0.2[a]
Burned grassland	Rock outcrop- Hambright	Shallow, well-drained, igneous rock-derived, stony loam, 50–75% slope	1.0 ± 0.1[ab]
Unburned vineyard	Bressa-Dibble	Moderately deep, well-drained, sandstone-derived, silt loam to clay loam, 15–30% slope	1.1 ± 0.2[ab]
Burned vineyard	Bressa-Dibble	Moderately deep, well-drained, sandstone-derived, silt loam to clay loam, 30–50% slope	1.0 ± 0.1[b]

[a] O'Geen et al. (2017).

[b] Letters (e.g. [a], [b]) indicate statistically significant differences across soil types ($p < 0.05$).

rank sum tests (Hollander and Wolfe, 1999) with a Holm's *p*-adjustment method (Holm, 1979; Wright, 1992) to determine across-group differences. We selected non-parametric analyses because our S data violated the parametric assumption of normality, which we tested with a Shapiro-Wilk normality test ($p < 0.1$; Royston, 1982). For soil leachate chemistry data, we used a log-likelihood maximized linear mixed effects model to address the question, what controls the quantity of S or DOC leached from soils? We modeled soil leachate TDS and DOC mass (as milligrams) separately, but both models had initial S or C soil concentration, site type (grassland vs. vineyard), burn condition (burned vs. unburned), the interaction between site type and burn (location*burn), leaching event number, leaching event volume, and leaching event intensity as fixed effects and soil sample as a random effect. The models provided estimates of the significance ($p < 0.05$), magnitude, and directional influence of each predictor effect on soil leachate S or DOC mass.

4. Results

4.1. Soil and leachate S and C concentrations

Initial (pre-experiment) total soil S concentrations differed by land use type (vineyard vs. grassland), while initial total soil C concentrations differed by wildfire (burned vs. unburned; Table 2). Both burned and unburned vineyard soils had on average 2–3 times higher total S concentrations than grassland soils. Across the five replicate soil cores, vineyard soil total S concentrations ranged from 0.4 to 2.7 g S kg^{-1} dry soil, showing higher absolute variability than grassland soil total S content, which ranged from 0.1 to 0.7 g S kg^{-1} dry soil. Both burned grassland (57 ± 7 g C kg^{-1} dry soil) and burned vineyard (50 ± 9 g C kg^{-1} dry soil) soils had on average ~ 1.5–2 times higher total C concentrations and higher variability in C concentration across replicate cores than unburned soils (27 ± 4 and 30 ± 4 g C kg^{-1} dry soil in grasslands and vineyards, respectively; Table 2).

Soil leachate S chemistry was more driven by land use (vineyard vs. grassland) than wildfire (burned vs. unburned). For all simulated rain events, unburned vineyard soil leachates had the highest TDS masses, which were 2–60 times higher than the unburned grassland soil leachate TDS masses (Fig. 2c). The TDS linear mixed-effect model supported our finding that land use was the dominant driver of leachate TDS, because the interaction between land use and burn was significant: unburned vineyard soil leachates had on average 2.0 mg S more than the burned grassland soil leachates ($p = 0.0014$; Table 3). Our mixed-effects TDS model highlighted the importance of early, high-intensity rain events, since rain event number had a negative effect (−0.12 mg S event^{-1}; $p < 0.0001$) and event intensity had a positive effect (0.24 mg S hr mL^{-1}; $p = 0.0213$; Table 3) on leachate TDS. Indeed, all soil types leached the largest fraction of cumulative TDS on average (22–26%) during event number 8, the first >50 mm rain event of the simulated wet season (Fig. 2). We found a discrepancy between the change in soil total S concentrations before and after the experiment and the cumulative mass of TDS measured in our soil leachates. Cumulative leachate TDS mass did not equate to the total S mass difference before and after the leaching experiment; leachate TDS mass represented 1.4 to 40% of the S mass change measured in bulk soils (Table 2). Furthermore, while burned vineyard soils had the highest percent change (−80 ± 70%) and total S mass decrease (100 ± 1 mg S) of the soil types, they had ~3 times lower cumulative leachate TDS mass than the unburned vineyard soils.

Wildfire increased C release from vineyard soils, but had minimal influence on C release from grassland soils. Over the course of the experiment, burned vineyard soil C concentrations decreased three times more than unburned vineyard soils (35% and 9%, respectively; Table 2) and burned vineyard soil leachates contained ~1.5 times more DOC than unburned vineyard soil leachates (Fig. 2d). In contrast, the decrease in soil C concentrations was similar between burned (~22%) and unburned

Table 2

Soil chemistry results before (initial) and after (final) the soil leaching experiment. Initial and final soil concentrations are the mean and standard deviation across the five replicate cores per soil type and are relative to kg of dry soil. The percent S and C change and mass differences are the mean differences and standard deviation with propagated error by soil type. The leachate values are the average and one standard deviation of the cumulative dissolved S or C leachate masses across replicate soil cores.

Soil type	S initial[a] (g S kg^{-1})	S final[a] (g S kg^{-1})	% S change	S mass difference (mg)	Total leachate dissolved S[a](mg)	C initial[a] (g C kg^{-1})	C final[a] (g C kg^{-1})	% C change	C mass difference (mg)	Total leachate DOC[a] (mg)
Unburned grassland	0.2 ± 0.05$^{[a]}$	0.2 ± 0.03$^{[b]}$	−30 ± 10	20 ± 0.4	1.7 ± 1.4$^{[ac]}$	27 ± 4$^{[a]}$	19 ± 6$^{[a]}$	−29 ± 10	2000 ± 0.39	4.7 ± 0.55$^{[a]}$
Burned grassland	0.5 ± 0.1$^{[b]}$	0.3 ± 0.07$^{[a]}$	−30 ± 10	30 ± 0.4	0.43 ± 0.50$^{[c]}$	57 ± 7$^{[b]}$	45 ± 9$^{[b]}$	−22 ± 5	2200 ± 0.27	1.6 ± 0.82$^{[b]}$
Unburned vineyard	0.7 ± 0.2$^{[b]}$	0.3 ± 0.3$^{[ab]}$	−50 ± 40	70 ± 0.9	28 ± 13$^{[b]}$	30 ± 4$^{[a]}$	28 ± 4$^{[ac]}$	−9 ± 2	550 ± 0.35	6.8 ± 1.7$^{[c]}$
Burned vineyard	1.0 ± 0.9$^{[b]}$	0.3 ± 0.1$^{[ab]}$	−80 ± 70	100 ± 1	8.7 ± 6.3$^{[a]}$	50 ± 9$^{[b]}$	32 ± 6$^{[bc]}$	−35 ± 9	3070 ± 0.32	16 ± 3.4$^{[d]}$

[a] Letters (e.g. [a], [b]) indicate statistically significant differences across soil types ($p < 0.05$).

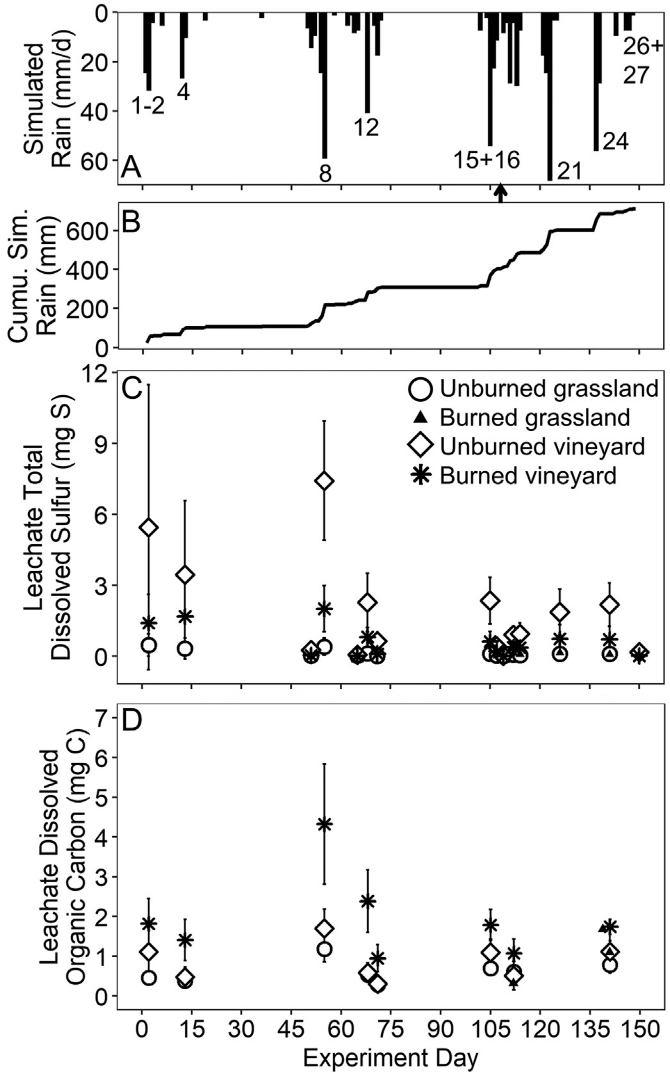

Fig. 2. Soil leaching experiment simulated ("sim.") rainfall and soil leachate chemistry. (A) Simulated rainfall with significant rain event numbers notated, (B) cumulative simulated rainfall, (C) leachate total dissolved sulfur mass (concentration times leachate volume), and (D) leachate dissolved organic carbon mass. In (C) and (D), points show the mean and standard deviation for the five replicate cores per soil type. If error bars are not visible, then they are smaller than the symbol size. Note: Since the burned grassland soils (black triangles) were collected later than the other soils, they were only included in the latter portion of the leaching experiment. The arrow between panels (A) and (B) indicates the relative timing of our stream sampling campaign.

grassland (~29%) soils (Table 2). Our mixed-effects model for DOC supported these results (Table 3), showing that (i) vineyard soils released on average 1.08 mg DOC more than grassland soils ($p = 0.0005$) and (ii) the interaction between land use and burn was significant, meaning that soil burn increased vineyard leachate DOC by 0.93 mg DOC ($p = 0.0071$; Table 3). Similar to leachate TDS mass, 24–28% of the total leachate DOC mass measured was from event 8. These results were supported by the DOC mixed-effects model, which had a slightly negative effect for rain event number (-0.033 mg C event^{-1}; $p = 0.0318$; Table 3) and larger positive effect for rain event intensity (0.14 mg C hr mL^{-1}; $p = 0.0142$; Table 3).

At the end of the soil leaching experiment, soil S concentrations were 30–80% lower than the initial values on average, and concentrations were similar across all soils. Meanwhile, soil C concentrations were 9–35% lower than the initial values. Burned grassland soils retained 2.4 times higher C concentrations than unburned grassland soils after the experiment, while both burned and unburned vineyard soils ended with similar C concentrations (28–32 g C kg^{-1} dry soil; Table 2).

Table 3
Linear mixed effects model results.

Model	Fixed effect	Estimate[a]	SE[b]	DF[c]	p-value[d]
Leachate TDS (mg S)	(Intercept)	0.098	0.48	195	0.8403
	Initial soil S (mg S g^{-1})	0.45	0.27	15	0.1214
	Land cover (vineyard)	−0.19	0.43	15	0.6562
	Burn condition (unburned)	−0.38	0.41	15	0.3635
	Land cover (vineyard) * burn condition (unburned)	2.0	0.51	15	**0.0014**
	Rain event number	−0.12	0.026	195	**<0.0001**
	Rain event volume (mL)	0.0059	0.0029	195	**0.0404**
	Rain event intensity (mL hr^{-1})	0.24	0.11	195	**0.0213**
Leachate DOC (mg C)	(Intercept)	−1.29	0.66	104	0.0545
	Initial soil C (mg C g^{-1})	0.020	0.010	15	0.0658
	Land cover (vineyard)	1.08	0.25	15	**0.0005**
	Burn condition (unburned)	0.24	0.39	15	0.5481
	Land cover (vineyard) * burn condition (unburned)	−0.93	0.30	15	**0.0071**
	Rain event number	−0.033	0.015	104	**0.0318**
	Rain event volume (mL)	0.0084	0.0017	104	**<0.0001**
	Rain event intensity (mL hr^{-1})	0.14	0.056	104	**0.0142**

[a] Estimate of the magnitude and direction of each fixed effect on the response variable, leachate TDS (mg S) or DOC (mg C).

[b] SE = standard error.

[c] DF = degrees of freedom.

[d] Significant effects ($p < 0.05$) indicated in bold text.

4.2. Soil leachate δ^{34}S and SUVA$_{254}$

Vineyard soil leachates had a distinct S stable isotopic composition compared to grassland soil leachates, regardless of burn (Fig. 3a). Unburned and burned vineyard soil leachate δ^{34}S-SO_4^{2-} values were similar, at 18.4 ± 0.9‰ (mean ± 1 standard deviation; $n = 30$) for unburned and 16.5 ± 2.5‰ ($n = 28$) for burned. Vineyard soil leachate δ^{34}S-SO_4^{2-} values were enriched by 9–15‰ on average relative to unburned and burned grassland soil leachate δ^{34}S-SO_4^{2-} values, which were similar at 3.3 ± 3.0‰ ($n = 9$) and 6.7 ± 0.6‰ ($n = 5$), respectively. Variability in soil leachate δ^{34}S-SO_4^{2-} reflected heterogeneity in S stable isotope composition among individual soil cores, rather than changes in δ^{34}S-SO_4^{2-} over the course of the laboratory leaching experiment (Fig. S3).

With respect to SUVA$_{254}$ results, DOC leached from burned vineyard soil differed substantially from the unburned vineyard and grassland soil leachates. DOC leached from burned vineyard soil had an average SUVA$_{254}$ value of 3.9 ± 0.5 L mg C^{-1} m^{-1} ($n = 35$), higher than SUVA$_{254}$ values from unburned vineyard (3.0 ± 0.8 L mg C^{-1} m^{-1}, $n = 33$, $p < 0.0001$) and unburned grassland soils (3.2 ± 0.6 L mg C^{-1} m^{-1}, $n = 35$; $p < 0.0001$; Fig. 3b). Burned grassland soil leachate SUVA$_{254}$ values were between those of the unburned grassland soil leachates and burned vineyard soil leachates (2.0 to 3.6 L mg C^{-1} m^{-1}), but were only measured once during the experiment ($n = 5$). During the simulated rainfall experiment, all soil leachate SUVA$_{254}$ values increased by ~1 L mg C^{-1} m^{-1} from the 1st to 8th rain event, and then remained relatively unchanged for the remainder of the experiment (Fig. S4).

4.3. Stream S and DOC chemistry

Land use type drove distinct differences in stream S concentrations and stable isotopic composition, similar to the soil leaching experiment results. Streams draining vineyard areas had ~2–4 times higher SO_4^{2-} concentrations and were enriched by ~10‰ compared with streams draining catchments with little to no vineyard land cover (Fig. 3c). Streams draining burned areas—predominantly mixed grassland and forested areas—tended to have lower SO_4^{2-} concentrations than streams draining unburned areas: 2.7–13.3 mg S L^{-1} for burned areas versus 1.9–35.2 mg S L^{-1} for unburned areas (Fig. 3c). Streams draining subcatchments with mixed land use and 60–75% burned area had a similar range in δ^{34}S-SO_4^{2-} (−7.4 to −0.9‰), compared to streams draining

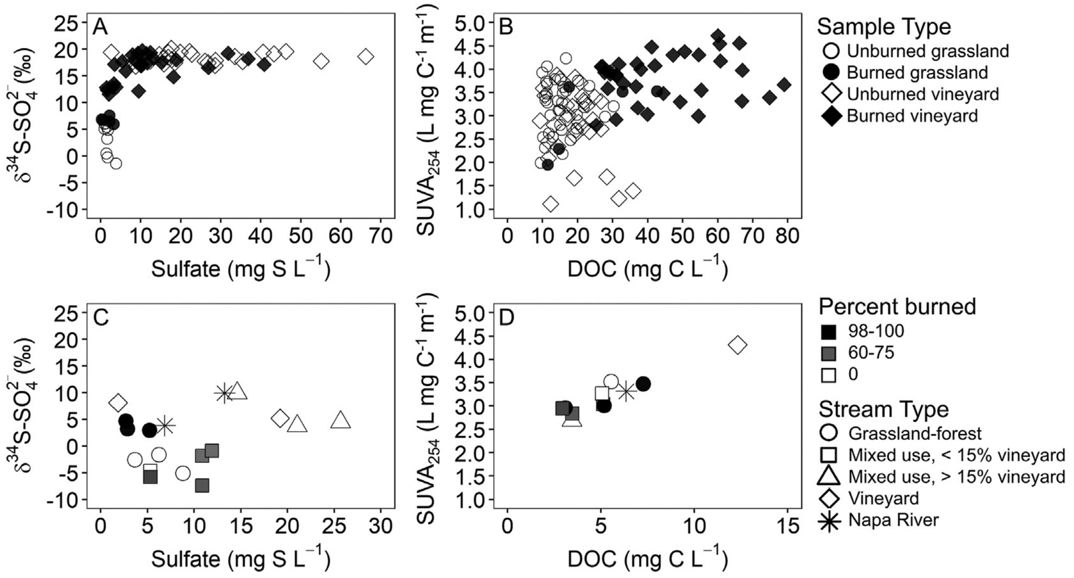

Fig. 3. Sulfur and carbon biogeochemical fingerprints in soil leachates (A and B) and stream samples (C and D). In (A) and (B), points represent leachates from individual soil core replicates over the course of the laboratory experiment. Note the different x-axis scales.

unburned forested-grassland sub-catchments (−5.1 to −1.6‰). However, samples from streams draining 100% burned forested catchments all had enriched δ^{34}S-SO$_4^{2-}$ values relative to unburned forested areas (Fig. 3c).

In contrast to S, stream DOC did not have a clear relationship to land use. Stream DOC concentrations ranged from 2.2–12.3 mg C L^{-1} and did not differ by land use or wildfire as a percent of catchment burned (Fig. 3d). Stream SUVA$_{254}$ measurements ranged from 2.7–4.3 L mg C^{-1} m^{-1} ($n = 9$; Fig. 3d). Despite higher SUVA$_{254}$ on average in burned vineyard soil leachate (Fig. 3b), stream SUVA$_{254}$ did not show a relationship with percent catchment burned or percent vineyard land cover ($p > 0.05$), but was positively correlated with DOC concentration (Fig. 3d). The highest SUVA$_{254}$ value was from a culvert draining a vineyard (4.3 L mg C^{-1} m^{-1}; Fig. 3d).

5. Discussion

5.1. Leaching of soil S and C immediately after wildfire

Our study focused on understanding changes to S and C cycling due to the effects of wildfire disturbance and land use (vineyard agriculture). This is a new interaction that is important to investigate, particularly in California, a region of critical agricultural resources that is also increasingly susceptible to wildfire. Interestingly, our laboratory soil leaching experiment demonstrated that wildfire and land use have different effects on S and C dynamics: high S applications to vineyards primed soils for significant S leaching, whereas wildfire primed soils for significant C leaching. Vineyards receive S applications that are on average ~ 100-fold greater than background atmospheric S deposition (Hinckley et al., 2020). Given the high S inputs, and that vineyard soils store S during the dry growing season (Hinckley et al., 2011), the higher S concentrations in vineyard soils compared to grassland soils at the onset of the wet season led, as we hypothesized, to significantly higher mobilization of soluble S from vineyard than grassland soils, regardless of burn condition (Fig. 2; Table 3).

We observed higher C concentrations in burned compared with unburned soils, independent of land use, and likely the result of accumulated charred litter (Knicker, 2007; Krishnaraj et al., 2016) and/or microbial cell lysis (Santos et al., 2016) in surface soils from the low burn severity conditions. The higher concentrations of soil C in burned vineyard soils resulted in greater mobilization of DOC over the course of the laboratory experiment compared to unburned soils (Fig. 2d; Table 2). These findings are in contrast to studies of forested ecosystems, which reported decreased soil C concentrations post-wildfire (Murphy et al., 2006). However, they are consistent with laboratory experiments by Santos et al. (2016) in which low (150 °C) to moderate (250 °C) burn temperatures resulted in ~5–10-fold higher water-extractable DOC concentrations. Thus, our study, which used vineyard soils that burned in the field, provides evidence that low-severity fires increase mobility of soil C to the aqueous phase.

The effects of low burn severity wildfire on soil S concentrations and mobilization were more nuanced than for soil C. Low burn severity increased average S concentrations in grassland and vineyard soils, but this increase was only significant in grassland soils (Table 2). Elevated soil S concentrations in burned soils, regardless of land use, may have increased total S losses from soils, but this pattern was obscured by (1) underestimation of burned grassland S losses due to sampling these soils at a later date than the others, and (2) wide variability in vineyard S concentrations across replicate cores. There is some evidence that low burn severity fire decreased the aqueous mobilization of S: the fraction of leachate TDS relative to the total soil S mass difference pre−/post-experiment was lower for burned soils than unburned soils (Table 2). This finding suggests that low burn severity wildfire may have enhanced export of non-dissolved forms of S. Particulate S mobilization (similar to Murphy et al., 2006) or gaseous S losses to the atmosphere, which we did not measure, may explain these results.

Given results from previous studies (Barro and Conard, 1991; Nano, 2012; Williams and Melack, 1997), we expected to observe greater dissolved S in leachate and stream water from burned areas. For example, in a laboratory study by Nano (2012), increased extractable SO$_4^{2-}$ after soil heating was attributed to oxidation of reduced organic S compounds and was highly temperature dependent. Prescribed burns in forested and chaparral ecosystems also increase stream SO$_4^{2-}$ concentrations (Barro and Conard, 1991; Williams and Melack, 1997). Our study was likely different, however, due to the minimal effects of low burn severity on soil S concentrations. The response of an agricultural versus a forested system to fire is an important distinction; again, relatively lower biomass and use of irrigation likely led to low burn severity in Napa Valley vineyards, and, thus, different impacts on biogeochemical cycling than moderate-to-high burn severity wildfire in forested areas.

Our leaching experiment results pointed to the disproportionate influence of early-season precipitation events for both S and C in soil leachates (Fig. 2). Both soil leachate TDS and DOC followed a "first flush" behavior—when a higher concentration or load of a chemical constituent is transported during a large rain event early in the wet season (Obermann et al., 2007). First flush behavior is characteristic of Mediterranean climates (Louchart et al., 2001; Obermann et al., 2009) like the Napa Valley, and suggests that the timing and magnitude of TDS and DOC transport from fields to streams depends on inter-annual variation in early-season rain events. Given this pattern, it is important to consider that we collected our burned grassland soils in the middle of the wet season; it is possible that we underestimated initial soil S and C concentrations and leachate masses, since the soils had already experienced the first flush in the field. This factor may explain why we did not find as strong an effect of wildfire on DOC in grassland soil leachates compared to the vineyard soils.

At the end of the simulated wet season, vineyard soil S concentrations were only slightly elevated relative to the grassland soils (Table 2). Our findings suggest that despite below-average rainfall during the 2017–2018 wet season, post-wet season vineyard soils approximated background S values from non-vineyard areas. In contrast, residual C concentrations in burned soils were ~ 1–2 times higher than in unburned soils (Table 2), and, thus, may continue to leach in subsequent year's wet seasons depending on the form of C and inter-annual variability in precipitation and hydrology. Indeed, Prieto-Fernández et al. (1998) showed that water-extractable DOC can remain elevated for four years after wildfire in pine/shrubland ecosystems, and streams draining moderately burned forested catchments can have elevated DOC concentrations for as long as 14 years post-wildfire (Chow et al., 2019).

5.2. The S biogeochemical fingerprint of soil leachates and streams

A notable result of our investigation was that the S biogeochemical fingerprint of soil leachates from burned and unburned vineyards was virtually the same and unique relative to that of grasslands. The similarity between burned and unburned S biogeochemical fingerprints (Fig. 3a) suggests that low burn severity wildfire did not alter S fingerprints at local scales. The average burned and unburned vineyard soil leachate δ^{34}S-SO_4^{2-} measured in our laboratory experiment was 2–4‰ higher than previous field-based soil porewater measurements in Napa Valley vineyards (~14.5‰; Hinckley et al., 2008), not a substantial difference considering the variability in δ^{34}S-SO_4^{2-} values across our soil core measurements within a field. Enriched δ^{34}S-SO_4^{2-} has been attributed to microbial sulfate reduction (MSR) in other systems (Alewell and Gehre, 1999; Kaplan and Rittenberg, 1964), suggesting that it may contribute to enriched vineyard δ^{34}S-SO_4^{2-} values. These enriched stable isotope values suggest that at times, vineyard soils experience episodic anoxia or have low oxygen microsites within the soil matrix, conditions necessary for MSR. We have observed standing water in vineyards periodically during the wet season, which provides evidence that these conditions occur. However, the mechanism leading to enriched δ^{34}S-SO_4^{2-} in vineyard soil porewaters has not yet been investigated. The more depleted δ^{34}S-SO_4^{2-} values from grassland leachates (−1.5 to 7.5‰; Fig. 3a) were similar to the typical observed range for Californian soils (−6 to 8‰), likely reflecting local geologic weathering and atmospheric S sources (Mitchell et al., 1998).

Like the soil leachates, streams draining vineyard-dominated areas had higher S concentrations and more enriched δ^{34}S-SO_4^{2-} values than streams draining forests and shrubland/grasslands, constituting a unique S biogeochemical fingerprint (Fig. 3c). The similarity between the biogeochemical fingerprint of vineyard soil leachate and vineyard-dominated streams suggests transport from soils to streams during the wet season. However, we do not know whether the S fingerprint in streams reflects rapid transport of S or the signal of accumulated applied S stored in soils. We hypothesize there is rapid transport between vineyards and streams, because (1) tributary hydrographs in the region are extremely flashy in response to rainfall events, (2) we observe that shallow subsurface flow is often routed through tile drains that connect to the stream network, and (3) vineyard soils nearly returned to grassland-like S concentrations after the simulated wet season. Inter-annual variability in precipitation during the wet season likely determines this balance between net soil S storage versus export.

Despite showing the influence of the vineyard S fingerprint, stream δ^{34}S-SO_4^{2-} values were lower relative to soil leachates (for both vineyards and non-agricultural areas), suggesting additional processes at play between soils and streams (Fig. 3). Since the leachate δ^{34}S-SO_4^{2-} values did not change significantly over the course of the laboratory experiment (Fig. S3), we assume that the vineyard and grassland endmembers essentially remain constant during the wet season. If true, then differences between our soil leachates and stream samples may be due to microbial processing of S along hydrological flow paths or mixing of S sources within streams. Few processes other than MSR strongly fractionate ^{34}S/^{32}S; processes that would singularly decrease the δ^{34}S-SO_4^{2-} values (e.g. microbial oxidation, adsorption/desorption) would only result in a decrease of 0.3–2‰ (Kaplan and Rittenberg, 1964; Van Stempvoort et al., 1990). However, combined, the balance between microbial oxidation, mineralization of organic S, and reduction within soils and along flow paths could affect the net change in δ^{34}S-SO_4^{2-} between soils and streams and is likely to be related to cycles of wetting and drying between rain events (e.g. Mitchell et al., 2008) and with soil depth (Marty et al., 2019). Our stream sampling campaign occurred during a storm event after a relatively long dry period (Fig. 2a), which may mobilize S that has been secondarily produced through mineralization or oxidation processes (Marty et al., 2019). Alternatively, the stream samples may reflect mixing of the enriched agricultural S soil source with depleted S sources (e.g., atmospheric, geologic), yet to be fully characterized in the watershed.

Our limited stream samples from near-completely burned areas suggest that the most significantly burned locations may have altered S biogeochemical fingerprints. Streams draining a high proportion of moderate- to-high burn severity wildfire areas (grassland and forested) had enriched δ^{34}S-SO_4^{2-} and lower S concentrations relative to unburned or low burn severity areas (Fig. 3c). One possible explanation for this observation is that wildfire may preferentially volatize ^{32}S. Previous studies of C and N dynamics have shown preferential losses of the lighter ^{12}C and ^{14}N isotopes after soil burning or wildfire. For example, laboratory studies simulating burning of Sierra Nevada Mountain soils showed an increase in δ^{13}C of 1.5‰ and δ^{15}N of 2–3‰ relative to non-heated soils (Saito et al., 2007). The lower SO_4^{2-} concentrations in streams with enriched δ^{34}S-SO_4^{2-} may reflect partial volatilization of S depending on local burn temperatures (e.g. Knicker, 2007; Tiedemann, 1987). Thus, our dataset of stream water S suggests that across the Napa River Watershed, enriched stream δ^{34}S-SO_4^{2-} values may be derived from either strongly affected wildfire areas or areas of vineyard S export. When using S stable isotope data to explore changes to watershed S biogeochemistry, it will be important to evaluate both land use and wildfire history within sub-catchments.

5.3. The C biogeochemical fingerprint in soil leachates and streams

Our soil leachate C biogeochemical fingerprints showed that burned vineyard leachates had higher DOC concentrations and $SUVA_{254}$ on average compared with all other soils (Fig. 3b). $SUVA_{254}$ values reflect DOC aromaticity, with higher values indicating more aromatic humic DOC ($SUVA_{254} \geq 4$ L mg C^{-1} m^{-1}) and lower values less aromatic and more aliphatic DOC ($SUVA_{254} < 2$; Revchuk and Suffet, 2014; Weishaar et al., 2003). Higher $SUVA_{254}$ values in the burned vineyard soil leachates were consistent with our hypothesis that even low burn severity wildfire in vineyards could enhance mobilization of C with higher aromaticity. Mechanisms for this pattern are highly temperature dependent, however. For example, some studies have shown that low-to-moderate soil burn temperatures (≤ 350 °C) can lead to higher organic matter solubility and higher proportions of aromatic structures in water-soluble organic matter—often attributed to a combination of physical and chemical thermal alteration to soils (Santos et al., 2016; Hohner et al., 2019). Yet, other studies have found that $SUVA_{254}$ values after wildfire vary depending on burn temperature and duration (Retuta, 2018; Revchuk and Suffet, 2014; Santos et al., 2016), possibly explaining the wide variability in our $SUVA_{254}$ values (Fig. 3b). One novel finding of our study is that the C biogeochemical fingerprints of unburned grassland and unburned vineyard soil leachates were similar, suggesting that viticulture does not affect the quantity or aromaticity of soil C (Fig. 3b). This finding may be explained by the fact that most vineyards are cover-cropped during the wet season, mimicking the native grassland environment; hence, vineyards do not have a unique C biogeochemical fingerprint.

For all soil leachates, the shift in $SUVA_{254}$ over the course of the leaching experiment reflects a change in DOC composition during the simulated wet season (Fig. S4). The general increase in $SUVA_{254}$ suggests that there was a preferential flush of aliphatic, labile DOC early in the experiment, progressing to release of more recalcitrant, aromatic DOC during the latter half of the simulated wet season, especially from the burned vineyard soils. These results are consistent with field studies by Van Gaelen et al. (2014), which found that soluble DOC accumulates in soils during periods of dryness, and then is rapidly mobilized during soil rewetting.

It is important to note that we found the DOC biogeochemical fingerprints in soil leachates and streams were not consistent. Whereas burned vineyard soil leachates diverged from other soil leachates with higher $SUVA_{254}$ and DOC values (Fig. 3b), stream $SUVA_{254}$ and DOC values were not related to either burn or land use (Fig. 3d). The most likely explanation of our results is that the stream sampling campaign, which occurred on day 120 in the leaching experiment, may have missed the largest fluxes of DOC post wildfire. We invoke this explanation because our leaching experiment results point to early-season DOC leaching from burned vineyard soils (Fig. 2). Other possibilities include hydrologic factors, like the absence of high-intensity rainstorms, which have driven overland flow and large DOC fluxes in other systems (see Murphy et al., 2015; Murphy et al., 2018) or physiochemical or biological factors, which affect DOC quantity and composition along flow paths (see Kaiser and Kalbitz, 2012; Roth et al., 2019). Finally, the signal of wildfire on stream C may have been diluted relative to contributing unburned areas (Table S1). While the explanation for these results requires more intensive future study, our data reinforce the difference between the mobilization of S from vineyard soils to streams and more complex dynamics for C biogeochemistry, especially post-wildfire.

5.4. Basin-scale implications and future research directions

Ultimately, the enhanced transport of S from vineyard fields to streams and of DOC from burned areas of the watershed have important implications for soil management, water quality, and ecosystem and human health, pointing to important future research needs. Elevated S leaching from vineyard soils may enhance base cation leaching (e.g., calcium and magnesium), similar to the effects of acid rain (e.g. Driscoll et al., 2001; Likens et al., 1996) if not counteracted with lime and fertilizer applications (Hinckley et al., 2020). Field trials would provide valuable information regarding these local-scale implications, taking into consideration S forms and soil conditions (e.g., pH). Losses of C within burned vineyard soils could compromise soil structure (DeBano et al., 1979) and essential soil microbial and fungal functions like N uptake and organic matter decomposition (Holden et al., 2013; Koyama et al., 2010; Prieto-Fernández et al., 1998).

There are many unknowns related to S, C, and mercury interactions within the Napa River Watershed and other upland watersheds dominated by regional crop systems. Most prior work on these interacting biogeochemical cycles has been done in the Florida Everglades Agricultural Area—a very different management and ecological context than the Napa River Watershed. Our study points to the hydrologic and S biogeochemical connection between agricultural fields and adjacent tributaries in an upland watershed. Mercury is likely to be present throughout the region, since it can be transported in fog (Weiss-Penzias et al., 2012) and the area has a history of mining (Alpers and Hunerlach, 2000; Slowey et al., 2007). Furthermore, our enriched vineyard $\delta^{34}S\text{-}SO_4^{2-}$ soil leachate measurements suggest low redox conditions within soils, since these conditions are necessary for MSR. Together, the high S concentrations from agriculture, potentially low redox conditions within soils, and presence of mercury in the region, may lead to methylmercury production within vineyard soils, along subsurface flow paths, or in tributary hyporheic zones. Although a small proportion of the Napa River Watershed area overall (~ 0.2%; Fig. 1), wetlands may also be hot spots for methylmercury production. Wildfire may enhance this potential, since transport of C-rich material could increase anoxia in areas where it settles or pools.

On a regional scale, high rates of methylmercury production have been measured in the vast wetlands of San Pablo Bay (Marvin-DiPasquale et al., 2003; Robinson et al., 2018), just downstream of the intensive vineyard agriculture within the Napa River Watershed. The potential link between methylmercury production in the San Pablo Bay and agricultural S runoff has not yet been studied. The effects of agricultural S on methylmercury production could be exacerbated by aromatic DOC transported from wildfire areas within the watershed, which can also enhance methylmercury production (Graham et al., 2013). Future research is required to address the implications of agricultural S and wildfire-derived C runoff for stimulation of methylmercury production in wetland areas. This information is critical for informing sustainable S management plans that balance continued agricultural prosperity with supporting ecological and human health.

6. Conclusions

This study addressed a knowledge gap in biogeochemistry by determining how S and DOC mobilize under conditions of both intensive agricultural S use and wildfire disturbance in a complex upland watershed. Using a laboratory leaching experiment, we found that the biogeochemical fingerprint of agricultural S was distinct from non-agricultural areas, and minimally affected by low severity burn wildfire at field scales. The fingerprint of agricultural S was detectable in streams draining vineyards, suggesting significant transport of agricultural S from soils to streams. However, interpreting S stable isotope data at watershed scales warrants caution, since streams draining moderate-to-high burn severity forested areas had a similar S stable isotopic signature to streams draining vineyards. In contrast, wildfire increased the concentration of C in surface soils and clearly increased the quantity and aromatic character of DOC in vineyard soil leachates. These patterns were not apparent in streams, however, suggesting that the effects of low burn severity wildfire on stream DOC may have occurred earlier in the season and were not captured by our sampling, or that additional biogeochemical processes affected DOC quantities and composition between soils and streams. Our findings indicate that wet season rainfall mobilizes agricultural S from soils to streams, and that wildfire can enhance transport from vineyard and grassland/forested areas, particularly for DOC. These results have significant implications for soil quality locally and the function and health of downstream aquatic ecosystems.

CRediT authorship contribution statement

Anna L. Hermes: Conceptualization, Methodology, Formal analysis, Investigation, Writing - original draft, Visualization. **Brian A. Ebel:** Conceptualization, Methodology, Investigation, Writing - review & editing. **Sheila F. Murphy:** Conceptualization, Methodology, Investigation, Resources, Writing - review & editing. **Eve-Lyn S. Hinckley:** Conceptualization, Methodology, Investigation, Funding acquisition, Project administration, Supervision, Writing - original draft.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.142179.

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