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To burn or not to burn: An empirical assessment of the impacts of wildfires and prescribed fires on trace element concentrations in Western US streams



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HIGHLIGHTS

GRAPHICAL ABSTRACT

- Compared wildfire and prescribed burn effects on stream trace element concentrations.
- Large, high-severity wildfires increased stream trace element concentrations.
- Small, prescribed burns rarely raised stream trace element concentrations.
- Weather & watershed characteristics affected postfire changes in trace element concentrations.

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ABSTRACT

The use of low-severity prescribed fires has been increasingly promoted to reduce the impacts from high-severity wildfires and maintain ecosystem resilience. However, the effects of prescribed fires on water quality have rarely been evaluated relative to the effects of wildfires. In this study, we assessed the effects of 54 wildfires and 11 prescribed fires on trace element (arsenic, selenium, and cadmium) concentrations of streams draining burned watersheds in the western US. To obtain results independent of the choice of method, we employed three independent analytical approaches to evaluate fire effects on water quality for the first three post-fire years. In general, we observed significant increases in trace element concentrations in streams burned by large, high-severity wildfires, despite substantial variability across sites. Comparatively, we did not observe increases in the spring mean concentration of arsenic, selenium, and cadmium in watersheds burned by prescribed fires. Our analysis indicated that the post-fire trace element response in streams was primarily influenced by burn area, burn severity, post-fire weather, surface lithology, watershed physiography, and land cover. This study's results demonstrate that prescribed burns could lessen the post-fire trace element loads in downstream waters if prescribed fires reduce subsequent high severity fires in the landscape.

1. Introduction

In recent decades, the area burned, burned severity, and length of the wildfire season have risen in many parts of the world (Flannigan et al., 2009; Westerling, 2016; Reilly et al., 2017), increasing concerns about

the immediate and long-term effects on water quality (Emelko et al., 2011; Bladon et al., 2014). Although research on the nature of wildfire impact on forest resources, aquatic systems, and source water supply is still ongoing, there is evidence that wildfires have the potential to degrade downstream water quality (Rhoades et al., 2019; Pennino et al., 2022). In the meantime, the use of low severity prescribed (or controlled) fires in forested environments has increasingly been advocated as an effective tool to mitigate the likelihood and impact of large-scale wildfires (Fernandes, 2018; Neary et al., 1999). Information is scarce, however, on the water quality effects of prescribed fires relative to that of wildfires

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(Harper et al., 2018; Klimas et al., 2020). Given the importance of forested watersheds on downstream water supply and the need to understand the extent to which prescribed fires achieve set targets without severely impairing downstream water quality, comparative studies on the water quality effects of prescribed fires versus wildfires can be valuable (Klimas et al., 2020).

High-severity fires generally result in the loss of overstory canopy and ground cover (vegetation, litter) that intercept precipitation, which raise the potential for post-fire erosion (Moody et al., 2013). Moreover, post-fire changes in soil hydraulic properties can reduce infiltration rates of soils, and lead to elevated runoff (DeBano, 2000; Moody et al., 2013; Agbeshie et al., 2022). These consequences compound the general increase in the availability and mobility of sediments, macronutrients, metals, and other chemical constituents due to the post-fire soil chemical environment, microclimate, and loss of plants (Smith et al., 2011; Abraham et al., 2017b; Terzano et al., 2021; Agbeshie et al., 2022). Consequently, wildfires in upland watersheds can lead to higher stream flows and concentrations of sediment, ash, and heavy metals, which can persist from days to decades (Abraham et al., 2017a; Sequeira et al., 2020; Klimas et al., 2020; Niemeyer et al., 2020).

Prescribed fires are planned fires deliberately set under controlled conditions for specific land management objectives such as to reduce the ground fuel load, curtail the spread of invasive species, manage the landscape, or restore an ecosystem (Neary et al., 1999; Bêche et al., 2005; Fernandes, 2018). While in some cases, moderate-to-high fire intensity are required to achieve specific management objectives (e.g., site preparation for timber seeding), prescribed fires are typically low intensity, low severity surface fires that cause no mortality to mature trees and leave the soil organic matter largely intact (Knapp et al., 2005; Klimas et al., 2020). Consequently, the effect of prescribed fires on runoff, erosion, and availability and delivery of chemical constituents to streams is generally small and short-lived relative to wildfires (Abraham et al., 2018; Hahn et al., 2019; Klimas et al., 2020).

Increases in trace element concentrations in water bodies is of great concern for the health of humans and aquatic organisms because of their prolonged environmental residence time (10-100 years), high toxicity, and potential to bioaccumulate in the food web (Adriano, 2001; Abraham et al., 2017a; Terzano et al., 2021). Consequently, an increasing number of studies have assessed the response of these constituents in streams to fires (Gallaher and Koch, 2004; Stein et al., 2012; Burke et al., 2013; Burton et al., 2016; Rust et al., 2018; Murphy et al., 2020; Rust et al., 2022). In general, the findings indicate that high severity fires in upland watersheds can substantially raise concentrations of trace elements such as arsenic, selenium, and cadmium in streams. For example, Burke et al. (2013) reported two orders of magnitude increase in the median concentration of cadmium in storm runoff from an urban watershed in southern California (USA), following the Station fire in 2009. Murphy et al. (2020) also observed post-fire arsenic concentrations approximately one hundred times greater than pre-fire values in a stream downslope of abandoned mine tailings that were exposed after a fire, during a high-intensity precipitation event. The amplifying effect of fires on downstream trace element concentrations has been attributed to several mechanisms including postfire increases in surface and subsurface flows (Murphy et al., 2020), release and remobilization of metals from vegetative or soil storages during combustion (Abraham et al., 2017b,a; Johnston et al., 2019), higher sediment exposure and mobility (Stein et al., 2012; Burton et al., 2016), and uncovering of legacy mines due to the consumption of groundcover by fire (Gallaher and Koch, 2004; Murphy et al., 2020; Rust et al., 2022).

The response of trace element concentrations to fires is typically not uniform across stream sites (e.g., Burke et al., 2013; Burton et al., 2016; Rust et al., 2019; Murphy et al., 2020). This inter-site variability has been attributed to several environmental variables. For example, Burke et al. (2013) did not find a substantial post-fire increase in arsenic and selenium concentrations for streams draining a severely burned urban watershed in southern California—they ascribed this to the geology of the area, which enriched local streams with these constituents even under unburned conditions. Similarly, Rust et al. (2019) reported that the post-fire change in cadmium concentration across their stream sites was inversely correlated with the pre-fire soil organic matter content. Murphy et al. (2020) noted that high intensity summer rainstorms enhanced the post-fire increase in the spring arsenic concentration in their downstream sites. However, current knowledge of the relative effect of different site-specific variables on stream trace element responses to wildland fires is primarily based on studies of individual fires. As such, the role of watershed geology, topography, land use and cover, post-fire weather, and burn extent and severity on post-fire changes in trace element concentrations across stream sites remains poorly understood.

The main objective of our study was to assess and compare the impacts of wildfires and prescribed fires in upland watersheds on trace element (i.e., arsenic, selenium, and cadmium) concentrations in western US streams. To this end, we used data from 65 wildland fires (54 wildfires, 11 prescribed fires) that burned areas of the upland watersheds of 51 stream sites. To evaluate the effects of each fire on downstream trace element concentrations, we analyzed the data using three different analytical approaches. Our specific goals were to (a) determine which wildland fires were associated with substantial increases in trace element concentrations, (b) broadly characterize the post-fire response of trace element concentrations across streams, and (c) identify watershed or environmental variables that influenced the post-fire responses of trace elements across streams.

2. Methods

2.1. Site selection and data sources

We selected stream sites for our study from all available U.S. Geological Survey (USGS) stream water quality gages in the eleven contiguous western U.S. states (Fig. 1a). Streams were evaluated for inclusion based on their watershed burn history, sample data availability, hydraulic regulation, and land use. We first derived watershed burn history for USGS stream sites from the Monitoring Trends in Burn Severity (MTBS; Eidenshink et al., 2007) project database. Next, we imported the historical (1984-2018) water quality data for burned areas from the USGS Geospatial Attributes of Gages for Evaluating Streamflow version 2 (GAGES II; Falcone et al., 2010) dataset. Stream trace element data, besides arsenic, selenium, and cadmium, were rarely available and water samples for arsenic, selenium, and cadmium were typically collected during spring (March–June) months. Hence, we constrained stream site selection to those sites with at least six spring water quality samples of those three constituents over the 3-15 years before a fire and six water quality samples over the first three years after a fire. Finally, we acquired the 2001 National Land Cover Dataset (NLCD 2001; Homer et al., 2007) to derive land use and land cover in the watersheds draining to the USGS stream sites. Analysis of the post-fire change in trace element concentrations is very complex in watersheds where human activities have a strong influence on the stream hydrology and chemistry, and thus we screened out burned streams where the watershed urban and agricultural area exceeded 5 % of the watershed area. We also excluded burned GAGE II sites where more than 5 % of the watershed area was regulated by dams. We retained 37 USGS stream sites with arsenic and selenium data, and 27 USGS stream sites with cadmium data for further analysis (Fig. 1b-d).

To identify possible geophysical variables that influence the inter-site variability in fire effects on trace element concentrations, we utilized several national datasets to derive wildfire characteristics, watershed physiography, hydrologic, and climatic data for the selected stream sites. We used MTBS digital burn severity maps to determine wildland fire type (wildfire or prescribed fire), burned area, and severity, and derived the watershed physiography (elevation, slope, aspect) from the National Hydrography Dataset Plus-Version 2 (NHD Plus V2; McKay et al., 2012). Historical daily streamflow data for the 1984–2018 period were retrieved from the USGS GAGES II stations database. We acquired geochemical characteristics of the surface lithology from two datasets, the Geochemical and Geophysical Characteristics of the Conterminous United States (GGCUS;



Fig. 1. Map of selected USGS stream sites with spring arsenic, selenium, and cadmium data and typology of watershed burns. (a) Location map of the western US region. (b) Stream sites with spring arsenic data and type of watershed burns. (c) Stream sites with spring selenium data and type of watershed burns. (d) Stream sites with spring cadmium data and type of watershed burns.

Olson and Hawkins, 2014) and the Terrestrial Ecosystems—Surficial Lithology of the Conterminous United States (TESLUS; Cress et al., 2010). The State Soil Geographic (STATSGO; Schwarz and Alexander, 1995) database was used to derive the soil characteristics for studied watersheds. We estimated the monthly mean air temperatures and precipitation totals from 1984 to 2018 for each watershed using Parameter-elevation Regressions on Independent Slopes Model (PRISM; PRISM Climate Group, 2020) datasets. Table B.1 shows the watershed attributes and burn characteristics for the stream sites in our study.

2.2. Analyzing fire impact on trace element concentrations

We implemented an analytical framework that included three statistical methods to evaluate the burn effect of each wildland fire on downstream trace element concentrations (Fig. 2). These statistical methods have been shown in previous studies to be useful in assessing wildfire effects on daily streamflow (Beyene et al., 2021), seasonal water temperatures (Beyene et al., 2022), and water quality violations (Pennino et al., 2022). Specifically, our three methods consist of the:

- Bootstrap Method to compute the post-fire changes in stream constituent concentrations and precipitation totals and their statistical significance.
- Concentration-Discharge (C-Q) Regression Analysis to evaluate the change in trace element concentration-water flow relations following a fire.
- Regression based attribution approach to estimate the weather and firerelated changes in stream constituent levels.

We chose to employ multiple statistical methods to evaluate fire effects on trace element concentrations for two reasons. The first reason was to obtain results that were independent of the choice of the analytical approach (e.g., C-Q relation, weather and concentration correspondence). Second, the limited number of water quality data points ($n \le 30$) made it challenging to determine whether the application of any one statistical method was theoretically sound. As such multiple approaches increased the robustness of the conclusion.

We also incorporated two techniques in our analytical framework to broadly characterize the post-fire response of trace element concentrations across burned sites:

- Boxplot comparison to evaluate the post-fire changes in trace element concentrations to prescribed fires and wildfires.
- Random Forest Regression (RFR) to identify the geophysical variables that were strongly related to the inter-site variability in the post-fire response of trace element concentrations.

2.2.1. Bootstrap method

We used bootstrapping (Efron, 1982) to compare post-fire constituent concentration and precipitation total to the baseline (pre-fire) at each site. The advantage of applying this procedure is that it avoids making assumptions or estimating parameters when deriving pre-fire ranges (confidence interval) for constituent concentrations. Instead, we randomly shuffled (with replacement) the pre-fire years to generate 1000 subsamples with three pre-fire years. Then we determined the spring mean concentration or precipitation total for each pre-fire year and the median of the spring



Fig. 2. Procedural framework for assessing the response of trace element concentrations to wildland fires in western US streams.

mean values for each subsample. Lastly, we estimated the post-fire change in constituent concentration or precipitation total as the difference between the median of post-fire spring mean constituent concentrations or precipitation totals (n = 3) and the 500th ranked (or median) sample value. We also assumed the post-fire constituent concentration or precipitation total to be significantly changed at the 0.05th significance level if the median of the post-fire constituent concentrations or precipitation totals was less than the 25th or greater than the 975th ranked subsample values (Fig. 3a).

2.2.2. Concentration—Discharge (C-Q) regression analysis

We used this approach to determine if the daily concentration-discharge (C-Q) relationship for each of the three water quality constituents was affected by wildfire. To this end, we developed and compared constituent C-Q lines for the pre- and post-fire periods separately (restricted) and collectively (unrestricted). These restricted and unrestricted C-Q regression lines had the general form

$$LogC = \beta_0 + \beta_1^{*}(1 - X) + \beta_2^{*}(1 - X) + LogQ + \beta_3^{*}X^{*}LogQ + \varepsilon$$
(1)

where C was the daily constituent concentration, Q was discharge, and the β s represented parameter estimates (coefficients). X was a time parameter that equaled one in the unrestricted regression line. In the restricted regression line, X equaled zero if the observation year preceded the fire year, and X equaled one if the observation year followed the fire year. ε was the residual term of the regression line, modeled by the Auto-Regressive Integrated Moving Average model (ARIMA; Box et al., 2015). The ARIMA model function was described by (p, d, q) with p signifying the number of autoregressive terms, d the number of non-seasonal differences needed for non-stationarity, and q the number of preceding or lagged forecast errors in the prediction equation. We used the optimizing algorithm in the forecast package (Hyndman et al., 2020) in R (R Core Team, 2020) to estimate the coefficients for the regression lines. We also evaluated the compliance of our models for normality of residuals using the Shapiro-Wilk normality test, outliers with the Bonferroni test, and homogeneity of variance using the non-constant variance score test.

We then applied the Likelihood Ratio Test (LRT; Snedecor and Cochran, 1991) to compare the goodness of fit of the two C-Q regression lines. In this



Fig. 3. Depictions of the three analytical approaches used for evaluating the trace element concentrations effect of each fire: (a) Bootstrap Method, (b) C-Q Regression Analysis, and (c) Regression-Based Attribution Method. In the Regression-Based Attribution Method, ΔC_{fire} represents the fire-related change in spring mean concentration.

test, the null hypothesis was that watershed burning did not significantly affect the C-Q relationship of the water quality constituent. Thus, the restricted regression line would not offer an appreciable improvement over the unrestricted regression line in representing the pre- and post-fire C-Q relations. In this study, we rejected the null hypothesis if the LRT score fell below 0.05 (Fig. 3b).

2.2.3. Regression model-based attribution approach

We employed a regression model-based attribution approach to estimate the portion of the post-fire change in spring mean constituent concentration related to wildland fire effects. This approach involved three steps. First, we built multiple linear regression models for predicting the pre-fire constituent concentration using pre-fire precipitation and air temperature data for each stream site. Out of all candidate models, we then selected the best-fit model for each site. We used the leave-one-out crossvalidation (LOOCV) method to assess the performance of the best-fit models in predicting the spring mean constituent concentration under baseline (unburned) watershed conditions. Next, we input post-fire weather statistics into the best fit models to predict spring mean constituent concentration for each post-fire year. Lastly, we computed the fire-related change in spring constituent concentration as the median difference between observed and predicted spring mean constituent concentrations for the three post-fire years (Fig. 3c). During model building, we considered 14 seasonal weather variables as potential covariates (Table B.2). We developed multiple sets of candidate linear regression models conditioned on these covariates and limited the maximum number of covariates in any model to two, given the small number of water quality data points at many stream sites. We also constrained models, so covariates with Pearson's correlation exceeding 0.7 were not included in the same model to minimize the effects of multicollinearity. During model selection, we used the bias-corrected Akaike Information Criterion (AIC; Akaike, 1974) to compare the relative complexity and goodness of fit of candidate models. We adopted candidate models with the least AICc scores as the best-fit models.

We evaluated the predictive performance of best-fit regression models under baseline conditions using the LOOCV approach. This approach involved (a) withholding weather and constituent concentration data for each pre-fire year, (b) recalibrating the model parameters using the remaining data, (c) making a prediction of the constituent concentration for the year that was left out, then (d) repeating the procedure for all pre-fire years. Using three model forecast performance metrics, we compared the LOOCV predicted constituent concentration value to the observed. First, we used the Nash-Sutcliffe coefficient of model efficiency (NSC; Nash and Sutcliffe, 1970), which measures the total residual error relative to the total variance within the data. Second, we used percent bias, which estimates the tendency of a model to over predict (*%bias<* 0) or underpredict (%*bias*> 0). Third, we used the relative root mean squared error (rRMSE), which measures the standardized absolute error associated with each model.

We input post-fire weather statistics into the best fit models to predict spring mean constituent concentration for each post-fire year. We computed the fire-related change in spring constituent concentration as the median difference between observed and predicted spring mean constituent concentrations for the three post-fire years. The fire-related change in trace element concentrations was assumed to be significant (p < 0.05) if the observed change was not within two standard errors (RMSE) of the model predicted post-fire spring mean constituent concentration.

2.2.4. Boxplot comparisons

We used boxplots and results of the regression-based attribution approach to broadly characterize the post-fire response of a trace element to wildfires and prescribed fires. Moreover, we classified wildfire events into two groups (large and small wildfires) based on whether the percent of the watershed area burned exceeded 1.2 % — the maximum percent of watershed area burned by a prescribed fire event in this study (Table B.1). This was to determine if prescribed fires and wildfires with similar burn extents (i.e., wildfires with burn areas <1.2 %) had comparable effects on trace element concentrations.

2.2.5. Random forest regression models

We used the results of the regression-based attribution approach for stream sites to develop RFR models to characterize the post-fire response across sites. Random forest (Breiman, 2001) is a machine learning algorithm capable of handling large, nonlinear, noisy, fragmented, or correlated multidimensional data for classification or regression. A RFR model is built by constructing ensembles of regression trees trained using recursive subsets of all observations. Predictions are then computed as the expected value of all individual predictions from each tree in the random forest model (Cutler et al., 2007). In this study, we built an RFR model for each trace element by iteratively inputting predictors from a subset of 70 watershed attributes (Table B.3) that were physically interpretable and produced the greatest improvement in the mean squared error of the model. We stopped the selection processes when the addition of any predictor did not reduce the mean squared error by a value of 0.01 or greater. Moreover, we also assessed the importance of a predictor (geophysical) variable in an RFR model by computing the mean decrease in accuracy (mean squared error) observed between model predictions and actual values by randomly permuting the selected variable (Breiman, 2001). We used the randomForest package (Liaw et al., 2002) in the R computing environment to construct random forest regression models for the fire-related changes in spring trace element concentrations.

Our main objective for developing RFR models was to help broadly characterize the post-fire constituent response. However, we also used these models to conduct a thought experiment where we estimated the change in post-fire trace element response for two stream sites if prescribed fires had been implemented to lower the burn severity and size of two historical wildfires. For interested readers, we provide details about this experiment in Appendix C.

3. Results

3.1. Post-fire changes in trace element concentrations

Post-fire spring mean arsenic concentrations were generally higher than in the base (pre-fire) period for 21 (57 %) of the 37 stream sites (Fig. 4a). The median increase in the spring mean arsenic concentrations for the three post-fire years ranged from 4 to 332 % across these 21 sites. However, the post-fire increase in the spring mean arsenic concentrations was statistically significant (p < 0.05) for only 11 (~ 52 %) out of these 21 sites (Fig. 4a). Although post-fire arsenic concentrations at one of the burned sites (USGS-06037500) exceeded the US Environmental Protection Agency's (EPA's) 340 $\mu g/l$ recommended aquatic life water quality criteria set for arsenic (USEPA, 2022, Fig. A.1a,), daily arsenic concentrations at this site were already above 340 $\mu g/l$ prior to the burn. The median postfire spring mean arsenic concentration was lower (6–55 %) than that of the pre-fire period for 13 stream sites.

Post-fire spring mean selenium and cadmium concentrations were generally lower than in the pre-fire period for more than half of the studied sites (Fig. 4b and c). The median decrease in the mean concentrations during spring for the three post-fire years ranged from 1 to 94 % across these sites. In contrast, we detected a post-fire increase in the spring mean concentrations for six (~ 16 %) out of the 37 stream sites for selenium and five (~19%) out of the 27 stream sites for cadmium (Fig. 4b–c). The median increase in spring mean constituent levels for the three post-fire years ranged from 3 to 100 % for selenium and 1–92 % for cadmium across these sites. Nevertheless, the post-fire increase in the spring mean selenium and cadmium concentrations was statistically significant (p < 0.05) for four stream sites for selenium and two stream sites for cadmium (Fig. 4b and c). Additionally, none of these increases exceeded EPA's 290 μ g/l and 18 μ g/l recommended aquatic life water quality criteria set for selenium and cadmium, respectively (Fig. A.1b-c).

The direction of the post-fire change in the spring mean trace element concentrations across studied stream sites showed some correspondence with the type of wildland fire and percent watershed area burned as well as the post-fire change in the watershed averaged October–June precipitation totals (Fig. 4d–f). For instance, we often detected a significant (p < 0.05) post-fire increase in the spring mean constituent concentrations for arsenic and selenium in stream sites where the upland watershed area burned exceeded 3 % and 4 %, respectively (Fig. 4d–e). Moreover, wildfire burned sites with a significant increase in the spring mean arsenic and cadmium concentrations also had higher post-fire October–June precipitation totals (Fig. 4d and f). In contrast, we did not find a significant (p < 0.05) post-fire increase in the spring mean concentration of the three trace elements in stream sites with prescribed burns (Fig. 4d–f).

3.2. Post-fire changes in the daily C-Q relations of trace elements

The results from our log-likelihood ratio-based comparisons indicated a significant (p < 0.05) post-fire change in the C-Q relation of arsenic for four stream sites, selenium for fourteen stream sites, and cadmium for seven



Fig. 4. Post-fire changes (%) in the spring mean arsenic, selenium, and cadmium concentrations across stream sites, and their linkages to the watershed area burned (%) and post-fire change (%) in October–June precipitation total. Map showing the post-fire changes in the spring mean arsenic (a), selenium (b), and cadmium (c) concentrations for studied stream sites. Scatterplot of the watershed area burned (%) and the post-fire change (%) in the watershed averaged October–June precipitation total associated with the post-fire change in spring arsenic (d), selenium (e), and cadmium (f) concentrations across stream sites. The significance of the post-fire change in constituent concentration was determined using the bootstrap method.

stream sites (Fig. 5a–c). Out of these sites, post-fire constituent yields were significantly higher than pre-fire in only three sites for arsenic and two sites for selenium.

The direction of the post-fire change in the C-Q relations of the three trace elements across stream sites showed some associations with the type of wildland fire and percent of watershed area burned (Fig. 5d–e). For example, we detected a significant post-fire arsenic and selenium yield in wildfire burned sites only. Moreover, sites with a significant increase in constituent yield have a watershed burn area greater than 3 % for arsenic and 8 % for selenium (Fig. 5d–e). Tables B.4a-c show the coefficients and fitness of the unrestricted and restricted C-Q regression lines for studied sites.

3.3. Fire attributed changes in trace element concentrations

We found that the best fit model for spring trace element concentrations at each site explained over half of the total variability in spring constituent concentrations under undisturbed conditions. Tables B.5a-c show the covariates, coefficients, and fitness of the best-fit model (for constituent concentration) for each stream site. During LOOCV evaluations, we also found that model prediction skills for spring mean arsenic, selenium, and cadmium concentrations under undisturbed (pre-fire) conditions were characterized by low rRMSE (< 30 %) and %bias (< 10 %), and high NSC (> 75 %) for most stream sites (Fig. A.3a–i). It therefore made sense to use these models to estimate the fire-related changes in the spring mean constituent concentrations for each studied stream.

We found that the burning of a watershed corresponded to a significant (p < 0.05) increase in constituent concentrations for the following three years in 14 (\sim 38 %) out of the 37 stream sites for arsenic, five (\sim 14 %)

out of the 37 stream sites for selenium, and four (~ 15 %) out of the 27 stream sites for cadmium (Fig. 6a–c). The median fire-related increase in constituent concentration for the first three post-fire years ranged from 2 to 138 % for arsenic, 1.5–197 % for selenium, and 5–233 % for cadmium across these sites. Conversely, this analysis did not show a significant (p < 0.05) fire-related increase in spring constituent concentrations for 62 % of sites for arsenic, 86 % of sites for selenium, and 85 % of sites for cadmium (Fig. 6a–c).

The direction of the fire-related changes in trace element concentrations across study sites displayed some correspondence to the type of wildfire burn and percent of watershed area burned (Fig. 6d–f). For example, we often observed a significant (p < 0.05) fire-related increase in the spring mean constituent concentration in stream sites where the wildfire burn area exceeded 3 % for arsenic, 4 % for selenium, and 4 % for cadmium. The greatest fire-related increases in spring mean arsenic concentrations were also associated with sites where the October–June precipitation totals increased by more than 50 % post-fire. In contrast, we did not find a significant fire-related increase in the spring concentration of the three trace elements in sites with prescribed burns.

3.4. Environmental correlates of post-fire trace element response across streams

The developed RFR models explained about 26–56 % of the total intersite variability in fire-related changes in spring arsenic (54.8 %), selenium (26 %), and cadmium (56.2 %) concentrations. They also indicated that watershed burn characteristics, surface lithology, physiography, land cover, and post-fire weather were important predictors of the fire-related changes in concentrations of the three trace elements (Fig. 7a–c). The partial dependence plots for the eight most important predictors of post-



Fig. 5. Post-fire change in the C-Q slope for spring arsenic, selenium, and cadmium across stream sites, and its connection to the watershed area burned (%) and post-fire change (%) in October–March precipitation total. Map showing the post-fire change in the C-Q slope for spring arsenic (a), selenium (b), and cadmium (c) at studied stream sites. Scatterplot of the watershed area burned (%) and the median post-fire change (%) in the watershed averaged October–March precipitation total associated with the post-fire change in the C-Q slope for arsenic (d), selenium (e), and cadmium (f) across sites. The significance of the post-fire change in the C-Q slope of constituents was determined using the Likelihood Ratio Test.

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Fig. 6. Fire-related change (%) in the spring mean arsenic, selenium, and cadmium concentration across stream sites, and its correspondence to the watershed area burned (%) and post-fire change (%) in October–March precipitation. Map showing the fire-related change in the spring mean arsenic (a), selenium (b), and cadmium (c) concentration across stream sites. Scatterplot of the watershed area burned and post-fire change in watershed averaged October–March precipitation totals related to the fire-related change in spring arsenic (d), selenium (e), and cadmium (f) concentration across stream sites.

fire arsenic indicated that the likelihood of detecting a fire-related increase in arsenic levels in stream sites was positively correlated to the watershed and riparian burn severity and area, post-fire winter air temperature change, average watershed elevation, and developed open space area, and negatively associated with watershed area, sample point distance from the burned area, and lithological magnesium and phosphorus oxide content at ground surface (Fig. A.5a–i). Similarly, the partial dependence plots for the eight most important predictors of post-fire cadmium showed that the likelihood of a wildfire increasing the spring cadmium concentration in selected streams was positively related to watershed burn severity and area, surface lithological sodium oxide and potassium oxide content, and silicic residual material and negatively related to the watershed's wetland area, surface lithological sulfur oxide, calcium oxide, and magnesium oxide content, and non-carbonate residual material (Fig. A.6a–i).

4. Discussion

4.1. Response of trace elements to wildland fires

The results of our three empirical analyses across 51 stream sites with upland watershed burns indicated that the impact of wildfires on trace element concentrations was highly variable (Fig. 8a-i). We did not detect a fire-related increase in spring mean arsenic, selenium, and cadmium concentrations for most wildfire burned studied sites, and this might be related to the wildfire burn size and severity, watershed characteristics, and postfire weather (which we discuss in the coming sections). Also, none of the post-fire daily trace element concentrations exceeded the corresponding EPA recommended water quality criteria for aquatic life. However, we did find a few wildfire events that were associated with a significant firerelated increase in spring mean trace element concentrations for the first three years. This is consistent with the finding of previous studies that wildfire can raise the trace element concentrations of streams and downstream waters (e.g., Murphy et al., 2015; Rust et al., 2022; Pennino et al., 2022).

There are several likely mechanisms by which wildfire burns may raise the concentration of arsenic, selenium, and cadmium in downstream waters. The heating of soil, even at moderate temperatures, greatly increases the enrichment and mobility/solubility of these elements via thermal breakdown (pyrolysis) of soil minerals and organic matter (Johnston et al., 2019; Terzano et al., 2021), deterioration of soil structure and cohesion (Moody et al., 2005; Verma and Jayakumar, 2012; Terzano et al., 2021), changes in the soil chemical environment (Burke et al., 2013; Campos et al., 2016; Abraham et al., 2017b), or decreases in soil hydraulic properties (Stein et al., 2012; Agbeshie et al., 2022). Trace elements such as arsenic, selenium, and cadmium, even at low concentrations in soils, can easily get absorbed and accumulate in plant stems and foliage (Jovanovic et al., 2011: Moreno-Jiménez et al., 2012: Gupta and Gupta, 2017): the combustion of vegetation causes the release and deposition of these elements on the surfaces of soils. The burning of trees and soil cover (e.g., duff, litter) also exposes soil and mine tailings to erosion, alters flow paths, increases overland and subsurface flow velocity and volume (Burton et al., 2016; Murphy et al., 2020; Rust et al., 2022), which often enhances the delivery of sediments enriched with trace elements from the hillslopes to waterways.

Our results from the three analyses indicated that prescribed burns did not correspond to a significant increase in trace element concentrations for the following three years. This is likely due to their low burn severity, a.



Fig. 7. Variable importance plot for the random forest regression model for post-fire arsenic (a), selenium (b), and cadmium (c) concentrations. These models explained about 26-57 % of the total inter-site variability in the post-fire concentration of arsenic (54.8 %), selenium (26 %), and cadmium (56.2 %) concentrations.

which indicates that the protective soil cover was largely intact, and tree mortality was minimal (Keeley, 2009). Extent of riparian areas burned by these fires was also small (< 0.01 %), and so the natural filtering effect of the unburned riparian vegetation and soil on the post-fire runoff would not be expected to be compromised. Moreover, the percent of the watershed area burned by these fires was low (< 1.2 %) and the dilution effect of water from the much larger, unburned part of the watershed could be an influence. Finally, rapid post-fire vegetation regeneration is more likely in low severity burn areas than in high severity burn areas (Lydersen and North, 2012; Kemp et al., 2016), and this could have masked any immediate increase in trace element concentrations after prescribed burns. Our finding that prescribed fires were not related to significant stream water quality degradation is consistent with the findings of previous studies (Bêche et al., 2005; Hahn et al., 2019; Klimas et al., 2020).

We did not find a substantial difference in the effects of prescribed fires and wildfires that burned less than 1.2 % of the watershed area on downstream spring trace element concentrations. In this study, both types of fires generally did not correspond to significant increases in spring trace element concentrations. This is perhaps because most of these small wildfires were low severity fires. Moreover, given that over 98 % of the watershed area was unburned, the excess trace elements produced in burned areas is likely to be trapped within the unburned part of the watershed or get diluted by the waters from the unburned part of the watershed. Nonetheless, there were two stream sites with small wildfire burns where our analysis detected significant fire-related increases in spring trace element concentrations. Given that this makes little physical sense, we attribute these results to deficiencies in our approach which are described in detail in the coming sections

There were many sites with wildfire burns where we found a substantial post-fire decrease in the concentrations of trace elements particularly for selenium and cadmium. This finding was a bit surprising, but it could be attributed to many mechanisms. High severity fires cause the release of trace elements into the atmosphere by volatilization and particulate transport in turbulent updrafts (e.g., Johnston et al., 2019), which then can reduce the amount of a trace element at or near the forest floor. Unusual post-fire weather conditions have been shown to dampen the post-fire water quality responses (e.g, Moody et al., 2013) as high precipitation amounts and subsequent flow conditions dramatically diminish constituent concentrations in streams following a fire, while low precipitation amounts disrupt the post-fire delivery of constituents from hillslopes to streams. After a low severity wildfire, the additional sunlight and open space in a forest can help young trees and other plants to grow (e.g., Klimas et al., 2020); thereby reducing the availability and mobility of trace elements. Finally, deficiencies in our analytical approaches might explain this finding as well.

4.2. Environmental correlates of the post-fire trace element response across streams

Our results from the RFR models for all three trace elements indicated that the extent and severity of watershed and riparian area burned were positively correlated to the increase in the spring trace element



Fig. 8. The changes in trace element concentrations associated with studied wildfires and prescribed fires as determined by three empirical approaches. The abbreviation BA stands for watershed burned area.

concentrations for the three post-fire years. These findings can be related to the fact that moderate and high-severity wildfires consume most of the vegetation and soil organic matter that sequester constituents and moisture (Abraham et al., 2017a; Agbeshie et al., 2022) and expose sediment to erosion (Moody et al., 2013; Murphy et al., 2020; Rust et al., 2022). The severity and extent of wildfire burn also determines the scale at which wildfire affects erosion processes in a watershed (Rhoades et al., 2019). Post-fire vegetation recovery rates, particularly for trees, can be slow in high severity burn areas (Turner et al., 1999; Rhoades et al., 2011; Tepley et al., 2014) this in turn enhances the persistence of the increase in post-fire trace element concentration.

Post-fire weather patterns influence the water quality response of streams to wildland fires (Ranalli, 2004; Smith et al., 2011; Murphy et al., 2015; Abraham et al., 2017a). High intensity storms during post-fire periods generate runoff carrying large ash and sediment loads enriched with various chemical constituents to downstream surface waters (Moody et al., 2013; Murphy et al., 2015, 2020). In contrast, post-fire drought conditions can impede vegetation re-establishment in high severity burned

areas (Abatzoglou and Williams, 2016), potentially prolonging post-fire water quality changes. We found that higher summer precipitation totals during the post-fire years enhanced the likelihood of an increase in the selenium concentrations during the following spring (Fig. A.5a and i). This is likely because summer precipitation at our study sites is characterized by intense thunderstorms (Changnon, 2001), which can induce sediment mobilization from hillslopes. Interestingly, post-fire winter (January–March) mean air temperature condition was also found to be an important factor in the response of spring arsenic concentration to wildland fires across sites (Fig. A.3a). This is perhaps due to the correspondence between winter air temperatures and winter snowpack—a determinant of spring runoff amounts—across western US regions (Cayan, 1996).

The magnitude and persistency of wildland fire impacts on downstream water quality is dependent on the physiography of burned watersheds (Ranalli, 2004). Smaller watershed areas, steeper slopes, and well drained soils enable rapid hydro-geochemical linkages between burned areas and streams (Emmerton et al., 2020). Delayed post-fire tree regeneration is more common in burned landscapes with steeper topographic settings

and more westerly or southerly aspects (Lydersen and North, 2012; Kemp et al., 2016; Ziegler et al., 2017). In this study, we found that physiographic variables such as watershed area and elevation were important predictors of post-fire spring trace element concentrations (Fig. 7a-c). Watershed area was negatively correlated with the post-fire change in spring arsenic concentrations (Fig. A.3d), while watershed averaged elevation was positively associated with post-fire change in spring arsenic and cadmium concentrations (Fig. A.3g and A.4g).

Wetlands and waterbodies typically act as nutrient and contaminant sinks within landscapes (Lane et al., 2018; Fritz et al., 2018). In this study, percent watershed and riparian areas that are wetland were negatively correlated with the fire-related changes in cadmium concentrations, and the %open water area within the watershed was negatively correlated with the fire-related change in spring arsenic concentrations across sites. Unlike the study by Sequeira et al. (2020), however, we did not find the agricultural area within the watershed to be a strong determinant of post-fire arsenic concentrations across studied sites. This could be because of our intentional exclusion of burned watersheds with larger (> 5 %) agricultural land areas when selecting sites for this study.

Underlying lithology is a source of trace elements in watersheds (Gupta and Gupta, 2017; Kubier et al., 2019). It also influences the mobility of trace elements in soil and water by determining soil structure (e.g., particle size), and chemistry (e.g., pH, inorganic minerals) (Kubier et al., 2019; King et al., 2019). In this study, we found that contents of constituents such as aluminum oxide, phosphorus pentoxide, calcium oxide, silica, and others in the lithology were strong predictors of the fire-related change in trace element concentrations (Fig. 7a-c). This finding was surprising as we employed a single, watershed averaged index to represent each chemical constituent for the whole watershed. Conversely, this finding makes some sense in that chemical constituents such as aluminum oxides, phosphates, and silica have strong affinities to trace elements (Moreno-Jiménez et al., 2012; Kubier et al., 2019), and thus can control storage and accumulation of trace elements in the pre-fire environment. Moreover, it is likely that the presence and content of these constituents influences the post-fire soil chemical environment, which is critical to the mobility and solubility of trace elements. Unlike previous studies (Abraham et al., 2018; Rust et al., 2018), however, we did not find that soil organic matter or clay content were good predictors of the fire-related changes in trace element concentrations across studied sites. This may be due to the large range in watershed and riparian burn severity and size across studied stream sites-as such, the importance of soil organic matter and clay content in influencing fire impact on trace elements concentration may be muted.

4.3. Study limitations

Our study has several key limitations. Our inferences on wildland fire impacts on the three constituent concentrations in the western US primarily rely on the results from 51 studied stream sites. These are a relatively small number of fires relative to the number of fires across the western US during this time. Therefore, clearly, not all wildland fires are represented, nor all the possible site characteristics captured given the extreme heterogeneity in climate, physiography, geology, and land cover. Moreover, our findings on prescribed fire impacts are based on low-severity controlled burns with sizes much smaller (%watershed area burned <1.2 %) than the total watershed area (Tables B.1). Nevertheless, this study is consistent with previous findings on wildfire and prescribed burning as detailed above, and likely captures at least in part the central tendencies.

Although this study employed three independent analytical approaches to broadly infer wildland fire impacts, individual results can still be influenced by the choice of these analytical methods and number of data points. The C-Q regression analyses assumed that the response of stream constituent concentration to changes in daily discharge is linear within the log-log space. The regression-based attribution approach employed not more than two seasonal weather variables to predict the mean spring concentration of trace elements under unburned conditions. Unfortunately, this study could not verify if any method in theory fits the data given (a) the absence of sufficient concentration data points (>30) at most sites, and (b) available tests cannot evaluate if data truly fit method assumptions. Moreover, our analyses at some sites were based on only three years of pre-fire data. Hence, our overall findings should be emphasized and not the individual results.

This study evaluated multiple wildland fire events, including prescribed burns, to broadly assess wildland fire impacts on trace element concentrations of western US streams. Besides Rust et al. (2018), we are not aware of any other empirical study that has attempted to broadly characterize the response of trace element concentrations to western US wildfires. Moreover, more than one analytical approach for detecting fire effects was used here to reduce uncertainty in our findings stemming from scarcity of temporal constituent concentration data. Only a handful of wildfire studies (e.g., Emmerton et al., 2020; Beyene et al., 2022) have utilized multiple analytical methods to infer fire effects on water quality. Hence, we believe that this study can serve as a good basis for future research on assessing and quantifying western US wildland fire effects on trace element concentrations, despite its limitations.

5. Conclusions

Analysis of the water quality effects of wildfires and prescribed fires, including their tradeoffs, can help inform forest fuel management decisions. In this study, we conducted an empirical assessment of the impacts of 54 wildfires and 11 prescribed fire burns on the spring concentrations of three trace elements (arsenic, selenium, and cadmium) in downstream waters for the initial three post-fire years. Our results indicated that the impact of high-severity wildfire burns on spring mean trace element concentration were highly variable across sites. However, significant increases in trace element concentrations were often associated with stream sites with relatively large, high-severity wildfire burns in their watersheds. Prescribed fires generally did not correspond to an increase in the spring mean concentration of arsenic, selenium, and cadmium. We also found that the impact of wildland fire burns on spring trace element concentrations across streams was influenced by the watershed and riparian burn area and severity, post-fire weather, surface lithology, watershed physiography, and land cover. Finally, we suggest that reducing the size and severity of historical wildfires through landscape management such as prescribed burns could potentially lead to substantial water quality improvements.

Data availability

Data will be made available on request.

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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CRediT authorship contribution statement

Mussie T. Beyene: Conceptualization, Data curation, Methodology, Writing - Original draft preparation. Scott G. Leibowitz: Conceptualization, Validation, Supervision, Funding acquisition, Writing - original draft. Christopher J. Dunn: Conceptualization of this study, Writing - review & editing. Kevin D. Bladon: Conceptualization of this study, Writing - review & editing.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2022.160731.

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