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NOTE

Smoke deposition to water surfaces drives hydrochemical changes

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Abstract

This study presents a unique data set from a laboratory experiment where we explored changes in the chemical composition of deionized water samples exposed to smoke. Inside a laboratory hood, water samples placed into a chamber were exposed to smoke for up to 60 min. The pattern of variations in hydrochemistry observed over time with increasing smoke exposure was similar in response to two different smoke treatments generated from burning tree litter. To estimate the smoke dosage and assess the consistency of replicate smoke treatments, we conducted additional experiments to evaluate changes in light transmission. Smoke inputs to the deionized water samples drove changes in hydrochemistry, with increases in acidity (with decreasing pH values), the content of organic matter (with increasing concentrations of dissolved organic carbon and dissolved organic nitrogen), and the content of inorganic N species (with increasing concentrations of ammonium, nitrate, and nitrite). The study was conducted on deionized water samples, and the results may not be directly transferrable to natural waters. Stream or lake waters that are low in ionic strength, poorly buffered, or low in acid-neutralizing capacity might respond the most similar to the results of this study. In contrast, well-buffered surface waters having higher acid-neutralizing capacity would be more likely to neutralize acidic inputs from the smoke without significant effects on water quality. The publicly available dataset associated with this study will contribute to further consideration of the relative importance of short-term changes in hydrochemistry driven by in-stream inputs (e.g., changes in water chemistry from direct smoke deposition to the water surface) in contrast to terrestrial inputs (e.g., changes in water chemistry stemming from altered flow paths and source areas of the burned watershed landscape).

KEYWORDS
atmospheric deposition, hydrochemistry, smoke exposure, water quality

1 | INTRODUCTION

With an increasing number and severity of wildfires worldwide, research on the impacts of wildfires on surface water quality is of keen contemporary interest (Martin, 2016). Many studies have focused on understanding how wildfire affects hydrological processes of the aquatic critical zone. Impacts of the burned landscape on water quantity (e.g., changing flow paths that generate runoff) and water quality (e.g., changes in fluxes of sediments delivered to streamflow or reservoirs have been well explored (Martin, 2016, McCullough et al., 2019). After a large fire, precipitation typically flushes increased quantities of sediments, nutrients, and other elements from the

landscape to the streams (Martin, 2016). For example, in a study of wildfire impacts on water quality in the Front Range of Colorado, Murphy et al. (2015) showed that post-fire precipitation events resulted in short-term water quality impairments, with significant increases in sediment and nutrient delivery from the watershed to downstream receiving waters. Less is known about the direct effects of smoke penetrating the water surface in altering water quality, and impacts can even occur from far away fires (Evans et al., 2021). This study presents a unique data set from a laboratory experiment where we explored changes in the chemical composition of poorly buffered, deionized water samples exposed to smoke. The data generate hypotheses about short-term changes in hydrochemistry that could result from smoke exposures to surface waters having low acid-neutralizing capacity. This publicly available data set will be useful to the hydrologic science community, providing further context for considering the impacts of wildfire smoke on surface water quality (Figure 1).

2 | METHODS

2.1 | Smoke generation

2.1.1 | Smoke exposure experiments

The smoke exposure experiment was conducted within a fume hood in a laboratory at the University of California. Details of the smoke chamber design are provided in previous studies (Bell et al., 2013; Calder et al., 2010; Cowan, 2010). Smoke was generated by combusting foliar-litter samples from two native evergreen species common in northern California. Smoke treatment A was generated from Coast Live Oak (*Quercus agrifolia*) litter, while smoke treatment B was California Bay (*Umbellularia californica*) litter. Both ligninaceous litter treatments had been dried and sifted through a 2 mm screen. For each smoke exposure experiment, 0.4 g of the dry litter was combusted, and the resulting smoke was funnelled through plastic tubing into an environmental chamber adapted for this study. The chamber allowed smoke to accumulate in the sealed space, with a glove-box type window to retrieve the water samples as the experiment progressed.

FIGURE 1 Smoke from the Grass Valley wildfire in 2018 near Electric City, Washington. Photo by Chris/Adobe Stock

2.1.2 | Smoke dosage experiments

To estimate the smoke dosage itself and assess the consistency of replicate smoke treatments, we conducted short experiments to evaluate the change in light transmission, which is typically reduced during fires (e.g., Davies & Unam, 1999). Wavelengths were restricted to photosynthetically active radiation (PAR) in the 400 to 700 nm range for light measurements. PAR was quantified with a quantum sensor (LI-190SA; LI-COR®, Inc.) in units of μmol s^{-1} m^{-2}. The light was generated by a 150-watt incandescent plant growth bulb (Agrosun Dayspot; Hydrofarm®, Inc.), suspended in the chamber ~25 cm above the quantum sensor. PAR measurements during a control experiment were taken in a closed chamber before generating smoke, and measured again halfway through a 15-min smoke treatment segment. We burned 0.4 g of Coast Live Oak litter to generate smoke for each experimental replicate ($n = 8$), and a fan was run to help disperse smoke within the chamber. We evaluated changes in PAR through pair-wise comparisons between control and smoke treatments (see Table S1 in Boyer et al., 2022 supporting data). Based on the reduction in light transmission in the treatment chamber exposures, smoke treatment conditions were always significantly different from measurements for control conditions ($p < 0.001$). Smoke treatments also exhibited minimal variation between replicates (see SE values in Figure S1 of Boyer et al., 2022 supporting data), suggesting that our experimental smoke generation procedure was consistent and repeatable. The reduction in PAR from the smoke treatment was estimated to be 3.1% on average, dropping from 40.2 μmol s^{-1} m^{-2} in the smoke-free chamber to 38.9 μmol s^{-1} m^{-2} during the middle of the 15 min smoke exposure period.

2.2 | Water samples and analyses

Inside a laboratory hood, water samples placed into the chamber were exposed to smoke from each wood treatment for up to 60 min. The samples were collected in glass beakers that had been trace cleaned and combusted in a furnace for 6 h at 450°C. Each beaker was filled with deionized water from a Barnstead® Nanopure water filtration system with an ultraviolet lamp ensuring that the water was free of organic compounds. The primary experiment was run using 120 ml of deionized water in 400 ml beakers, though we re-ran the experiment using 30 ml of water in 400 ml beakers to explore water volume and depth impacts. The deionized water in the beakers was allowed to equilibrate with the air before the smoke exposure experiments. Within the chamber, the water samples were placed atop a standard shaker table and shaken continuously at low speed to ensure well-mixed samples as smoke infused into the water.

In a water quality lab at the University of California, water samples were analysed for pH immediately after their retrieval and

analysed for concentrations of hydrochemical constituents shortly after the experiment. The water quality parameters measured included pH as a measure of acidity, as well as concentrations of dissolved organic carbon (DOC), dissolved inorganic nitrogen (DIN) and total nitrogen (TN), which are nutrients that are relevant to aquatic ecosystems. The pH values were measured using a VWR® benchtop meter. Concentrations of nitrogen species were measured with a total nitrogen unit on a Shimadzu® carbon analyser, with a detection limit of 0.05 mg N/L. TN concentration includes inorganic and organic nitrogen species, and DIN is reported as the sum of inorganic nitrate (NO_3-N) plus nitrite (NO_2-N). The sum concentration of dissolved organic nitrogen (DON) + ammonium (NH_4-N) was estimated by difference, subtracting the (NO_3-N + NO_2-N) from the TN concentration observed in each sample. Concentrations of DOC were measured using a Shimadzu® carbon analyser, following the high-temperature combustion technique in non-purgeable organic carbon mode, according to the procedure described in Bird et al. (2003), with a detection limit of 0.03 mg C/L.

3 | RESULTS

In a controlled laboratory setting, we exposed unbuffered water samples to smoke and observed changes in hydrochemistry over time. The pattern of variations in hydrochemistry (Figures 2 and 3) were similar in response to the two different smoke treatments generated from burning Coast Live Oak litter (treatment A) and California Bay litter (treatment B).

Whereas deionized water theoretically has a circumneutral pH of 7, the water samples were equilibrated with air prior to the experiment, with an initial pH of 5.5 at the onset of each smoke exposure experiment due to the dissolution of atmospheric CO_2 in the water yielding a dilute solution of carbonic acid. In response to smoke, the water's pH decreased from ~5.5 to 4.3 over the hour of exposure (Figure 2). The water became more acidic, increasing in concentration of hydrogen ions by over an order of magnitude.

Concentrations of the nitrogen and carbon species in water increased with the duration of smoke exposure. Direct inputs of smoke to water surfaces caused increases in organic matter content, as evidenced by the increasing concentrations of DOC with exposure.

The majority of the TN dissolved in the water in response to smoke exposure was organic or reduced inorganic in form, with ~95% as (DON + NH_4-N) and ~5% as oxidized inorganic forms (NO_3-N +- NO_2-N). The hydrochemical responses from the smoke exposure experiments were similar when replicated regardless of the source material burned to generate smoke (two smoke treatments, Figure 3a) and the volume of the water sample (two water depth treatments, Figure 3b).

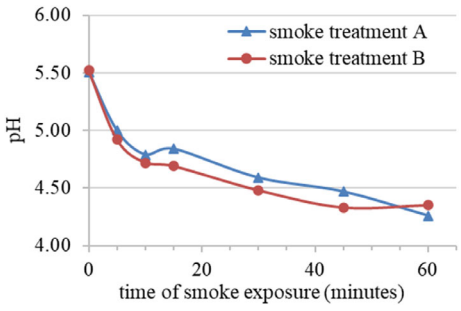

FIGURE 2 An deionized water sample exposed to smoke treatments changes pH, becoming more acidic with duration of smoke exposure

4 | DISCUSSION

This study demonstrates that smoke inputs to poorly buffered water samples has the potential to drive changes in hydrochemistry, including increases in acidity (as evidenced by decreasing pH values), the content of organic matter (as evidenced by the increasing concentrations of DOC and DON), and the content of inorganic N species (as evidenced by increasing concentrations of NH_4-N and NO_3-N +- NO_2-N). In a unique study of the effects of wildfire on water quality in a watershed in southwestern New Mexico, Earl and Blinn (2003) also found that NH_4-N and NO_3-N increased in stream water as a result of smoke deposition. While the chemical composition of wood smoke is complex and can vary depending on what is burned, it typically contains large amounts of reactive organic compounds, including volatile organic compounds, aldehydes, alkylbenzenes, phenols and polycyclic aromatic hydrocarbons (Krstic et al., 2015; Larson & Koenig, 1993).

Our smoke treatments resulted in ~3% reduction in PAR, which is likely to be minor compared to light transmission reduction due to particulate matter production during wildfire events. Our results are consistent with the notion that smoke from regional wildfires could alter stream or lake water quality. For freshwaters with low acid-neutralizing capacity (ANC), exposure to smoke via wildfire emissions could result in short-duration shifts in hydrochemistry and acidification. We emphasize that this study was conducted in the laboratory on deionized water samples, and that results may not be directly transferrable to natural waters. Stream or lake waters that are low in ionic strength, poorly buffered, and/or low in ANC might respond the most similar to the results of this study. In contrast, well-buffered surface waters having higher ANC would be more likely to neutralize acidic inputs from the smoke without affecting water quality. We observed that the deionized water samples increased in acidity, as evidenced by decreasing pH, in response to *smoke* deposition. It is interesting to contrast this result with studies that have evaluated the impact of wildfire *ash* deposition on water quality, where increasing alkalinity (i.e., with increasing pH) in stream water has been observed in some studies (e.g., Earl & Blinn, 2003). The response of surface waters to ash is affected by the quantity of material burned, the burn severity and the associated level of combustion of the ash, and its chemical nature. Bodi et al. (2013) describe that organic carbon (pyrogenic carbon) is the main component of ash at low combustion

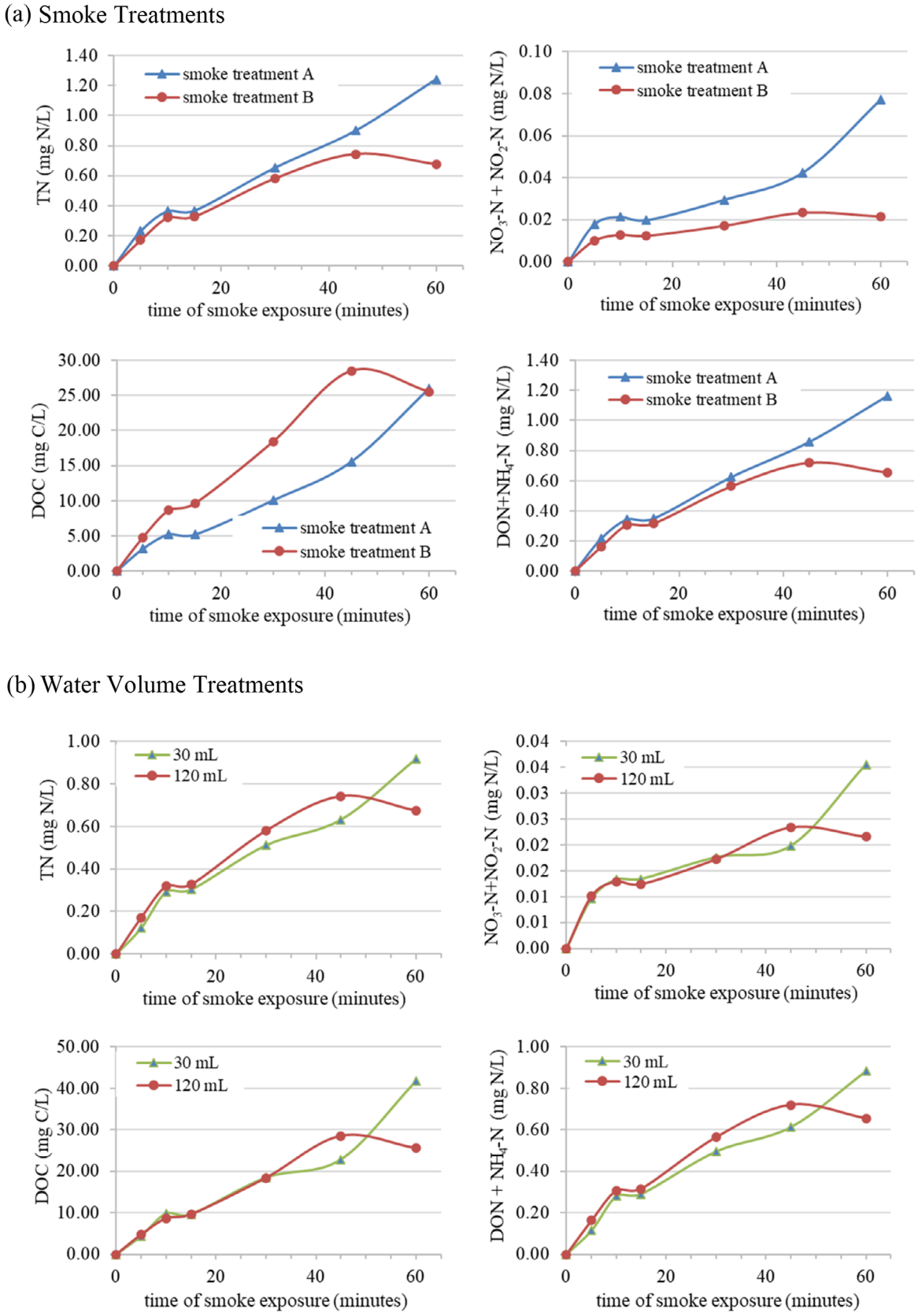

FIGURE 3 Changes in hydrochemistry of deionized water samples over time in response to direct exposure to smoke in a controlled laboratory setting. The hydrochemical responses were similar regardless of: (a) type of litter burned to generate smoke (with two smoke treatments, using 120 ml water samples); or (b) depth of the water sample (with two water volume treatments, using a single smoke source)

completeness (temperature < 450°C), which might contribute to organic acidity. However, at high combustion completeness (temperature > 450°C), the organic matter is volatilized, and the resulting mineral ash is made up primarily of inorganic carbonates of calcium, magnesium, sodium, potassium, silicon and phosphorous (Bodi et al., 2013), which can elevate pH when in water. At very high combustion completeness (temperature > 580°C), the most common chemical forms are oxides (Bodi et al., 2013). Prescribed fires are often designed to reduce understory vegetation without killing overstory vegetation or generating substantial ash, whereas mixed severity burns from wildfires are more likely to burn overstory and understory vegetation and soils, forming significant ash. Ranalli (2004) note that few natural fires burn hot and long enough for complete combustion of organics, and that ash produced in vegetation fires typically has a significant content of organic matter.

The data set associated with this study will contribute to further consideration of the relative importance of short-term changes in hydrochemistry driven by in-stream inputs (e.g., changes in water chemistry from direct smoke deposition to the water surface) in contrast with terrestrial inputs (e.g., changes in water chemistry stemming from altered flow paths and source areas of the burned watershed landscape). Future lab experiments to learn more about the impacts of smoke on water quality could use waters of known chemical composition (e.g., soft to hard water composition, and varying levels of ANC). Future experiments could also measure other water quality parameters and explore the impacts of the strength and duration of smoke exposure events. Further research is also needed in natural field settings to understand the integrated responses of smoke on aquatic ecosystems in different environmental locations. One such study is pioneering work by Scordo et al. (2021), who explored changes in water quality and ecology of Castle Lake in northern California, resulting from direct exposure to smoke for 55 days in response to the devastating Carr Fire. Wildfire smoke penetrated the freshwater lake, causing significant changes in water transparency, primary production and temperature, yet did not have a substantial effect on ecological biomass or community composition. There is still much to learn about the different impacts of smoke exposure on waters in natural and human-altered ecosystems.

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DATA AVAILABILITY STATEMENT

Data supporting this manuscript are provided in the HydroShare digital data repository of the Consortium of Universities for the Advancement of Hydrologic Sciences, Inc. (Boyer et al., 2022). Investigators can access the data at this link: https://www.hydroshare.org/resource/33c36d2fc1c94d96ba9e40f0460f665e/. This data set is published under an open-access licence that requires attribution for any use, shared under the Creative Commons Attribution Non-Commercial Share-Alike licence CC BY-NC-SA (https://creativecommons.org/licenses/by-nc/4.0/).

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