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Wildfires in the western United States are mobilizing PM_{2.5}associated nutrients and may be contributing to downwind cyanobacteria blooms

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Abstract

Wildfire activity is increasing in the continental U.S. and can be linked to climate change effects, including rising temperatures and more frequent drought conditions. Wildfire emissions and large fire frequency have increased in the western U.S., impacting human health and ecosystems. We linked 15 years (2006-2020) of particulate matter (PM2.5) chemical speciation data with smoke plume analysis to identify PM₂ 5-associated nutrients elevated in air samples on smokeimpacted days. Most macro- and micro-nutrients analyzed (phosphorus, calcium, potassium, sodium, silicon, aluminum, iron, manganese, and magnesium) were significantly elevated on smoke days across all years analyzed. The largest percent increase was observed for phosphorus. With the exception of ammonium, all other nutrients (nitrate, copper, and zinc), although not statistically significant, had higher median values across all years on smoke vs. non-smoke days. Not surprisingly, there was high variation between smoke impacted days, with some nutrients episodically elevated >10,000% during select fire events. Beyond nutrients, we also explored instances where algal blooms occurred in multiple lakes downwind from high-nutrient fires. In these cases, remotely sensed cyanobacteria indices in downwind lakes increased two to seven days following the occurrence of wildfire smoke above the lake. This suggests that elevated nutrients in wildfire smoke may contribute to downwind algal blooms. Since cyanobacteria blooms can be associated with the production of cyanotoxins and wildfire activity is increasing due to climate change, this finding has implications for drinking water reservoirs in the western United States, and for lake ecology, particularly alpine lakes with otherwise limited nutrient inputs.

Abstract graphic:

Conflicts of Interest There are no conflicts to declare.



Introduction

Wildfires are natural disturbances in many ecosystems and can provide positive benefits, such as the creation of early seral habitats.¹ However, climate change effects, including rising global temperatures and increased fuel aridity, are increasing wildfire activity in the United States (number of fires, area burned by fires, and fire season length).^{2–7} This trend is exacerbated in California^{5,6,8} and other regions of the western United States in recent years.^{4,9,10} Fires generate particulate matter (PM) and gas-phase pollutants such as ozone, carbon monoxide, and nitrous oxides.^{11,12} PM mobilizes chemical species with potential impacts on downwind ecosystems.^{13–15} Altogether, fires can lead to negative impacts on air quality and wildlife.¹⁶

Among many other effects, wildfires likely impact downwind ecosystems through the mobilization of nutrients such as nitrogen,^{12,17–20} potassium,^{19,21–27} and phosphorus.^{20,28–32} Elevated phosphorus and nitrogen in PM_{2.5} (PM 2.5 μ m in diameter) have been identified during fires in California,³³ Africa,²⁹ and Australia.¹⁸ Similarly, atmospheric phosphorus concentrations have been elevated during biomass burning seasons in the Amazon^{14,30} and surrounding Lake Tahoe (western United States).³⁴ The atmospheric lifetimes of PM_{2.5} can range from days to weeks, with potential to undergo reactions with strong acids during long-range transport to transform phosphorus- and nitrogen-containing particles into more soluble (bioavailable) forms.^{20,35} There has been an approximately 40% increase in atmospheric phosphorus deposition globally compared to pre-industrial times, attributed in part to biomass burning.³⁶ More recently, atmospheric phosphorus deposition in the western United States has increased 50–100% from 2002–2012 in some subbasins of the Rocky Mountains³⁷ while nitrogen fluxes from fires have increased 326% from 2002–2012 (0.11 to 0.49 Tg/year).³⁸

Atmospheric deposition can be an important source of nutrients to remote, oligotrophic lakes^{39,40} and marine ecosystems^{20,41} where phosphorus and/or nitrogen are often the limiting nutrients for aquatic primary productivity, including the production of algal blooms.^{42–45} Freshwater eutrophication from increased nutrient loadings and other environmental stressors (such as increased temperature⁴⁶) can cause harmful algal blooms (HABs) consisting of cyanobacteria.^{47,48} HABs can produce toxins that are harmful to

human and animal health, and make water non-potable.^{49,50} The frequency and intensity of HABs may be increasing globally along with rising global temperatures.^{46,51–54} As the formation of HABs can be related to multiple stressors, there is potential that wildfire-influenced nutrient emissions serve as an additional stressor to the onset of HABs.

Here, we investigated the nutrients associated within wildfire smoke for the entire western United States over a 15 year period. Specifically, we analyzed data from 309 air quality monitoring stations from 2006 through 2020 in 11 U.S. western states to enable longterm study of airborne nutrient concentrations on wildfire smoke days vs non-smoke impacted days. In doing so, we identified $PM_{2.5}$ -associated nutrients that were statistically elevated on smoke days. In addition, we identified four case study fires with elevated atmospheric phosphorus and other nutrients. Air mass trajectories and satellite cyanobacteria measurements were analyzed for the case study fires to probe the effects of nutrient emissions on downwind lakes. Specifically, this study focused on addressing the following research questions:

- 1. What are the concentrations of atmospheric phosphorus and other nutrients on smoke days compared to non-smoke days in the western United States?
- 2. What are the temporal trends for nutrients released by fire?
- **3.** Are there cases where nutrients in wildfire smoke are associated with cyanobacteria abundance in downwind lakes?

Addressing these research questions will increase our understanding of the potential mobilization of nutrients from fires. Further, quantifying and understanding the nutrients emitted during wildfires in the western United States will provide insight into nutrient emissions from biomass burning in other regions around the globe. Lastly, it may also help water quality managers anticipate and react to potential effects to aquatic systems, such as the possibility that smoke from fires contribute to HABs in downwind lakes and reservoirs.

Methods

Smoke plume identification

To characterize smoke impacted days vs non-smoke impacted days, the Hazard Mapping System (HMS) fire and smoke product (https://www.ospo.noaa.gov/Products/land/hms.html) provided by the National Oceanic and Atmospheric Administration (NOAA) was used to identify daily smoke plumes in the atmospheric column.^{55,56} Satellites with horizontal resolution ranging from 375 m – 2 km (for the S-NPP + NOAA-20 and GOES-16 East + West satellites, respectively) detect smoke plumes by combining multi-spectral imaging and temperature thresholds. These detected smoke plumes are then manually analyzed to determine if smoke is active at that location. The HMS product is made publicly available and updated daily. It has been extensively validated by prior studies,^{57,58} showing only a ~2% false positive rate resulting from highly reflective clouds and water surfaces.⁵⁸ For this study, the HMS product was combined with PM_{2.5} speciation air quality data to compare airborne chemicals present within and outside of smoke plumes.

Particulate matter (PM_{2.5}) measurements

Aerosol chemical speciation data were collected from EPA's Air Quality System (AQS, https://www.epa.gov/aqs)59 stations located in 11 western states (Washington, Oregon, California, Montana, Idaho, Wyoming, Utah, Colorado, New Mexico, Arizona, and Nevada) during the years 2006–2020 (Figure 1). Data from April 1 – December 31 were analyzed to encompass the fire season, per previous work.³³ PM_{2.5} measurements are taken once every 3-6 days, depending on the station. PM_{2.5} samplers and operational requirements are described in EPA's Quality Assurance Guidance document.⁶⁰ X-ray fluorescence was used to quantify elements while liquid chromatography was used for ion analysis. The limit of detection is $<1 \ \mu g/m^3$ and varies per pollutant.⁶⁰ Samplers are cleaned every five days and calibrated, at minimum, every thirty days.⁶⁰ Field and laboratory blanks are also analyzed to eliminate potential contamination from field and laboratory equipment.⁶⁰ Only chemical species identified as macro- or micronutrients for plant life were analyzed in this study.^{61,62} The 13 species selected for analysis were phosphorus, nitrate, ammonium, calcium, potassium, sodium, silicon, copper, aluminum, iron, manganese, magnesium, and zinc. Speciated PM2 5 measurements were labeled as smoke-impacted if the monitor location fell within an HMS smoke plume on the day of measurement (Table S1).³³ Concentration differences for each species (in $\mu g/m^3$ and % above average) were calculated on smoke-impacted and non-smoke days for each station to account for station-specific differences.³³ In addition, a permutation test was used to determine if smoke and non-smoke day concentrations were significantly different for each species and each year, for data grouped by station and year.^{33,63} Data were excluded from the permutation test if fewer than 20 overall or 4 smoke-impacted measurements were observed at a station in a year. Data processing was conducted in Python version 3.8.3 and the permutation test was run in R version 4.1.3.

Identification of case study fires

To explore possible linkages between nutrients mobilized by fire and cyanobacteria blooms, we identified the date and location of the ten highest phosphorus measurements on smoke- versus non-smoke impacted days (Figure S1, Figure 2). We then used NASA Worldview Earth Observing System Data and Information Systems (EOSDIS, https://worldview.earthdata.nasa.gov/) satellite images to confirm active fires with visible smoke plumes in the atmospheric column at these locations (Figure S2).^{64,65} This resulted in four case study fires used for additional analysis: the Zaca, La Brea, Williams, and Carr Fire events in California (Figure 3, Figure S3). For comparison and to account for station-specific background concentrations, "No Fire" dates were chosen as the nearest date prior to the fire with no visible smoke plume observed in the atmospheric column. For each case study, the burn boundaries were downloaded from the Monitoring Trends in Burn Severity (MTBS) site and plotted with ArcGIS Pro version 2.8.6.

Air trajectory modeling

After identifying case study fires, NOAA's Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, https://www.ready.noaa.gov/HYSPLIT.php) model was used to simulate the trajectory of air masses before and after passing through each monitoring

station (and does not include deposition flux estimates).^{66,67} HYSPLIT was first utilized to calculate backward trajectories starting at the corresponding AQS station and date of the highest phosphorus measurement for each fire, and then initiating traces every 3 h for 24 h (8 total traces) at 10 m above ground level. Representative backward trajectories were overlaid with the burn boundary of each fire in ArcGIS Pro version 2.8.6. All backward air mass trajectories passed over or near (<70 km) the associated fire boundaries (Figure 4).

HYSPLIT was also utilized to initiate forward trajectories every 3 hours for 72 hours (24 total trajectories) at 10 m above ground level. Heat maps were generated by plotting the percentage of trajectories passing through each grid square (Figure 4). This analysis was used to identify lakes downwind of high phosphorus and nutrient measurements.

Satellite cyanobacteria measurements

In the lakes identified downwind, satellite remote sensing data was obtained from the San Francisco Estuary Institute (https://fhab.sfei.org/) to quantify cyanobacteria concentrations.⁶⁸ Satellites measure the spectral shape at 681 nm that covers spectral peaks in chlorophyll absorption and fluorescence, and a spectral shape at 620 nm which is sensitive to phycocyanin.^{69,70} Phycocyanin is used to distinguish cyanobacteria from phytoplankton.^{70–72}

The MERIS sensor onboard the Envisat satellite operated from 2002 – April 2012, while the OCLI sensor onboard the Sentinel-3 satellite was used for measurements from April 2016 – current. There are no available data for April 2012 – April 2016. Both the MERIS and OCLI satellites use images with nadir pixel resolution of 300 m x 300 m. Each satellite orbits with a revisit frequency of approximately 2–3 days. In 2018 a second Sentinel-3 satellite became operational with the same orbits where Sentinel-3B was 140° out of phase with Sentinel-3A, effectively doubling the number of observations at a given location.

The cyanobacteria index (CIcyano) was calculated using a spectral shape algorithm initially described by Wynne et al.,⁷³ then revised and updated by Lunetta et al.⁷⁴ based on new conditions from Matthews et al.⁷⁵ with a detailed description of the algorithm evolution described in Coffer et al.⁷⁶ The CIcyano a unitless index value, which was multiplied by a constant to obtain a scale of 1-1000 by the San Francisco Estuary Institute. Satellite observations were aggregated into 10-day composites that preserved the maximum data value for each pixel. Grey pixels represent non-detections due to quality flagging for issues such as glint, mixed land and water, cloud cover, or cloud shadow and are excluded in this analysis. Black pixels were below the detection limit of the sensor and were assigned a value of 0 but still used in computation of lake-wide CIcyano values. The two pixels nearest shore or overlapping with land are discarded in the final image.⁷⁶ The remaining pixels are colored based on their CIcyano index value, with cool colors such as purple representing low Clcyano and warm colors such as red representing high Clcyano. Pixel values are weighted the same, regardless of their location within the lake. The time series plots show the mean value of the 10-day composites in each water body. Though this method of remote sensing can experience interference with clouds, haze, snow, and ice, studies comparing satellite cvanobacteria measurements with *in situ* measurements show good agreement.^{77–80}

Water quality measurements

Lastly, for the downwind lakes identified, we searched for water quality measurements coinciding with the years of the relevant fires using three databases: the California Water Data Library (https://wdl.water.ca.gov/waterdatalibrary/Map.aspx); the U.S. Geological Survey (USGS) National Water Information System (https://waterdata.usgs.gov/nwis); and the Water Quality Data Portal (https://www.waterqualitydata.us/), a U.S. government database associated with the U.S. Environmental Protection Agency, USGS, states, and other partners. In all, we found monthly water quality data for only two of the lakes. For these two lakes, we downloaded monthly water temperature, dissolved oxygen, specific conductance, and nutrient data (N, P) for the year of the fire, plus the year preceding and the year after. There was either no data for the remaining lakes or data had been collected in years not coinciding with the relevant fires. In many of these lakes, the most recent water quality data had been collected decades prior to the fire.

Results

Particulate matter chemical composition on smoke-impacted vs. non-smoke days

Smoke-impacted days made up 9.2 - 16.2% of all measurements across all years, with the range depending on the chemical species (Table S1). Median values were higher on smoke days for all species except ammonium (Figure 2, Figure S1). Most species analyzed (with the exceptions of ammonium, nitrate, copper, and zinc) were significantly elevated on smoke days with a p-value <0.05 across all stations and all years (Figure 2, Figure S1, Table S2). With the differences in observed concentrations spanning orders of magnitude (Figure 2A, Figure S1A), we also investigated the percent increase in concentration on smoke days vs. non-smoke days for all years (Figure 2B, Figure S1B). All species analyzed were 21 - 226% higher on smoke-impacted days compared to non-smoke days, with maximum percent changes over 1200% for all species (Table S3). The largest percent increase was observed for phosphorus. Mean phosphorus increases were 226% higher on smoke days compared to non-smoke days when comparing station-specific means, with high values measured at certain monitors on select smoke days. For example, the highest value measured (0.08 $\mu g/m^3$) was ~86,000% higher than the non-smoke average at the station located in Los Olivos, California. This measurement was linked to the La Brea fire of 2009.

Median percent increases on smoke days were analyzed as a function of year for phosphorus and nitrogen-containing species to address research question #2. We did not observe a consistent trend but rather episodically elevated concentrations for some years, especially for phosphorus. For example, smoke days in the year 2012 resulted in phosphorus 494% above the median on non-smoke days (Figure 2C). Phosphorus was significantly elevated with p-values <0.05 for the years 2007 and 2008, and all years 2012 and beyond (Table S2). In contrast, ammonium and nitrate were not statistically elevated on smoke days for any year (Table S2). Average percent change in concentration on smoke days compared to non-smoke days for each species and year are listed in Table S4.

Particulate matter composition during selected fires

For all case study fires, the amount of phosphorus increased along with nitrate, potassium, manganese, and zinc (Figure 3). These fires were chosen based on phosphorus concentrations above the mean by 10,000% or more; yet in absolute concentrations, rather than percentage increase, phosphorus was not the main component of wildfire smoke during these fires. By concentration, the smoke plumes of these fires were dominated by nitrate and potassium (though these species were also present during no-fire days at the same locations, Table S5). Of the case study fires addressed herein, the La Brea and Williams fires were associated with the highest phosphorus concentrations of 0.08 and 0.05 μ g/m³, respectively. Similar atmospheric phosphorus concentrations of 0.01 – 0.075 μ g/m³ have been reported during wildfires in rural California.⁴⁰ Relative abundances of each species analyzed are shown in Figure S4 and Table S5 for each case study fire and associated non-fire measurement at the same location. It is important to note that phosphorus was not present during non-fire days at these four locations (Table S5).

Cyanobacteria abundance in lakes downwind of fires

In answer to the third question regarding a potential association between nutrients mobilized by fire and cyanobacteria in downwind lakes, satellite imagery showed a spike in cyanobacteria abundance following wildfire-related nutrient concentrations in smoke. In the absence of deposition flux estimates, comparing images captured before and after the La Brea Fire high nutrient measurement indicates an increases in cyanobacteria concentrations at two downwind lakes, Lake Cachuma and Lake Casitas (Figure 5, Figure S5). The CIcyano of Lake Cachuma increased from 1.0 (no cyanobacteria) to 6.7 (some cyanobacteria) within seven days from the start of the La Brea Fire (Table 1). A similar pattern was observed for Lake Casitas with CIcyano values increasing from 1.0 to 1.8 after the start of the La Brea Fire. Cyanobacteria remained elevated for ~10 days in each lake before returning to levels observed before the start of the fire. These were not the only cyanobacteria blooms present at these lakes in the years surrounding the La Brea Fire and, from what we can discern, not all blooms were correlated with overhead smoke. However, the increase in cyanobacteria in August 2009 days after intersection with high nutrient-containing wildfire smoke suggests nutrients from fire may be a contributing factor to the onset of cyanobacteria blooms.

The same analysis was performed for lakes downwind of the Zaca Fire, with observable increases in cyanobacteria present for three lakes near the fire boundary (Figure 6). Pyramid Lake increased in CIcyano from 10.7 to 46.5 after the start of the Zaca Fire (Table 1). The Perris Reservoir and Mystic Lake both experienced marked increases in CIcyano after the Zaca Fire, from 1.0 to 39.4 and 26.6 to 436.4, respectively. Pyramid Lake and Perris Reservoir showed a fairly unique response to fire, with no/minimal cyanobacteria blooms observed during the surrounding years. In contrast, cyanobacteria blooms were frequent in Mystic Lake during the years analyzed. However, in August 2007 Mystic Lake exhibited minimal cyanobacteria until overlap with nutrient-containing wildfire smoke, suggesting cyanobacteria indices were influenced by nutrient additions from smoke in this instance. For ease of viewing, zoomed in satellite images of every lake are provided in Figure S5. Overall, satellite imagery showed increased cyanobacteria abundance in lakes 50–230 km downwind from the Zaca Fire.

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Similarly, satellite imagery shows increased cyanobacteria abundance in lakes up to 185 km downwind from the Carr Fire (Figure 7). Eagle Lake and Tule Lake experienced similar CIcyano increases of 1.4 to 2.4 and 1.4 to 2.7, respectively, after the highest nutrient measurement associated with the Carr Fire. Though Tule Lake is much closer to the AQS station than Eagle Lake (19 km and 133 km, respectively), both are located similar distances from the Carr Fire burn boundary (~140 km; Table 1). Honey Lake and Red Rock Lake experienced slightly more intense cyanobacteria blooms after the Carr Fire, with CIcyanos increasing from 5.1 to 14.6 for Honey Lake and from 9.9 to 13.8 for Red Rock Lake. Of all lakes investigated near the Carr Fire, the West Valley Reservoir experienced the largest increase in CIcyano after the start of the fire (1.1 to 224.8). This was the most severe bloom observed at West Valley Reservoir for the year of 2018 and the years pre- and post-fire. Though other lakes experienced blooms in the years surrounding the Carr Fire, the pre- and post-fire satellite imagery show an increase in cyanobacteria abundance after intersection with nutrient-containing wildfire smoke.

Some commonalties are evidenced when examining these blooms. A two-to-seven-day delay was observed between high nutrient wildfire smoke concentrations and the associated increase in cyanobacteria abundance across all fires. Similar bloom formation timelines have been reported for marine algal blooms after receiving nutrient inputs.^{81,82} Moreover, all the blooms occurred alongside August fires when water temperatures were undoubtedly warm and favorable for cyanobacteria growth. Cyanobacteria analysis was not performed for the Williams Fire due to lack of satellite data for September 2012.

Water quality in lakes downwind of fires

As noted previously, we located monthly water quality data for two lakes (Perris Reservoir and Pyramid Lake) coinciding with the timing of the relevant fire (the Zaca Fire, August 2007). These lakes both experienced the highest monthly water temperatures of the year in July and August, leading up to- and during the month of the Zaca fire (Figure S7, Figure S8). Samples also recorded a sharp decline in dissolved oxygen in September of 2007 (Figure S7, Figure S8), suggestive of an algal bloom the prior month.^{83,84} By contrast, we did not observe significant changes in concentrations of nitrate-N, total N, total P, or specific conductance in the lakes at the monthly timestep coinciding with the fire or subsequent algal bloom.

Discussion

Overall, we observed elevated nutrients associated with $PM_{2.5}$ during wildfires in the western United States. Most nutrients analyzed were statistically elevated on smoke days (Table S2), with phosphorus the most elevated of all nutrients when considered on a percentage basis. Of the many nutrients shown to be elevated here, phosphorus and the nitrogen-containing species are likely the most relevant for eutrophication in downwind freshwater ecosystems, and therefore we focus mostly on those results in this section. For each of the case study fires investigated, phosphorus concentrations ranged from 0.01 – 0.08 µg/m³ and were not present on non-fire days at the same locations while nitrogen concentrations ranges from 1.6 – 4.4 µg/m³ (84 – 3278% higher than concentrations on non-

fire days at the same locations, Figure 3, Table S5). Each case study fire was associated with two to five downwind lakes displaying observable increases in cyanobacteria abundance. This is suggestive that mobilization and subsequent atmospheric deposition of airborne nutrients from wildfires may be contributing to downwind algal blooms in some cases.

Mobilization of atmospheric nutrients from wildfires

Whereas our study focused on the potential for atmospheric deposition, most related studies to date have focused on movement of nutrients via waterways. In a recent review, Paul et al. found that nutrients typically increase in nearby waterways and may stay elevated for several years following fire.⁸⁵ In most cases, nutrient concentrations returned to starting levels within two to four years, however nutrient levels in some fire-impacted streams remained elevated up to ten years post fire.^{86,87} Several studies have reported increased primary productivity for up to three years following wildfire-influenced nutrient fluxes from runoff.^{88–91} These studies all focused on runoff as the mechanism by which nutrients enter local waterways. However, we show that nutrients can be mobilized and transported long distances in the air and across watershed boundaries.

Previous studies have identified wildfire-related mobilization of nitrogen-containing species. A recent nitrogen inventory states nitrogen emissions in the United States are largely driven by the agriculture sector and are trending downward, though N emissions from forest fires are becoming significant in some basins in the western United States.³⁸ In 2020, fires contributed up to 83% of total nitrogen emissions in the western United States.⁹² Lightning is a natural ignition source for fires and also contributes to the amount of nitrogen in the atmosphere.^{93,94} In this work, we generally found higher PM_{2.5}-associated nitrate but lower PM2 5-associated ammonium. Boaggio et al. 2022 analyzed a subset of the data included in this study and also reported lower ammonium concentrations on smoke days in California.³³ Other studies have reported seasonal contributions of ammonium nitrate to PM, with summertime concentrations in California appreciably lower than wintertime concentrations $(3.2 \,\mu\text{g/m}^3 \text{ vs } 8.4 \,\mu\text{g/m}^3, \text{ respectively})$.^{95,96} This is likely due to enhanced partitioning of ammonium into the particle phase during lower temperatures.⁹⁵ Our analysis was limited to the fire season (April 1 – December 31),³³ hereby missing the majority of wintertime ammonium measurements. Additionally, the high temperature of fires⁹⁷ drives the ammonium-ammonia equilibrium to favor gas-phase ammonia^{98,99} which was not measured in the PM2 5 dataset analyzed herein. Finally, a laboratory-based study found ammonia is retained in soil by fire-derived organics.¹⁰⁰ Altogether, these likely account for the decreased amounts of ammonium observed across smoke-days in this study.

Studies of wildfires in remote regions have identified elevated atmospheric phosphorus in the Amazon Rainforest,^{14,30} Africa,²⁹ Australia,¹⁸ and Lake Tahoe,³⁴ similar to observations reported herein. Like nitrogen, approximately 90% of national phosphorus inputs are attributed to agriculture.³⁷ Estimated phosphorus emissions from wildfires range from 0.6×10^{10} g/year¹⁰¹ to 2.5×10^{12} g/year.^{34–36,102–104} Approximately 10% of global phosphorus emissions are attributed to fires.²⁰ Phosphorus and other nutrients contained in plant biomass and the forest floor are mobilized by fire and through increased soil particle aeolian transport during and after the fire.^{20,105,106} Phosphote/phosphorus actively adsorbs to solid surfaces in

soil.¹⁰⁷ Silicon, an element commonly found in soil and fertilizers,^{108,109} was statistically elevated for many of the same years as phosphorus, thus supporting this hypothesis.

The National Atmospheric Deposition Program routinely monitors the atmospheric concentration and deposition of nitrogen-containing species.¹¹⁰ Both ammonia and nitrate deposition have been decreasing in the western United States for the past decade (< 3 kg/ha in 2021 compared to ~4 kg/ha in 2011).¹¹⁰ However, several studies examining total NOx or organic nitrogen have identified increased nitrogen deposition after wildfires.⁹² In 2020, fires were attributed to a 78% increase (from 7.1 to 12.6 kg/ha) in nitrogen deposition in California.⁹² Our study, particularly the case study fire analysis, identified wildfire smoke concentrations of PM_{2.5}-associated nitrate with potential for deposition in downwind environments.

In contrast, atmospheric phosphorus concentrations and deposition are less frequently monitored.¹¹¹ Atmospheric phosphorus deposition was generally small but increased 50–100% (0.05 - 0.25 kg/ha) from 2002–2012 in some areas near the Rocky Mountains.³⁷ Few additional studies have investigated atmospheric phosphorus deposition following wildfires in the western United States. Phosphorus in streams increased 40x after fire during a period of no precipitation, suggesting dry deposition as the leading pathway of nutrient transport.¹¹² Other studies have identified atmospheric deposition of phosphorus as an important contributor to phosphorus accumulation in alpine lakes.^{40,113} Phosphorus concentrations in lakes and streams are increasing in the western United States, likely influenced by increases in atmospheric deposition.^{40,114} As lakes have longer water residence times than streams and rivers, fire effects on lake ecosystems are more prolonged than for other freshwater systems.¹¹⁵ Phosphorus is often the limiting nutrient in aquatic systems to produce algal blooms,^{42–45} therefore understanding phosphorus and nutrient mobilization is crucial when considering regional water quality.

Nutrients and other factors that affect cyanobacteria blooms

Higher temperatures, sunlight, and excess nutrients create favorable conditions for the formation of cyanobacteria blooms.¹¹⁶ Rising global temperatures are increasing the growing period of cyanobacteria,⁴⁶ and cyanobacteria blooms themselves may also contribute to warming water temperatures through the absorption of sunlight.^{117,118} Warming of water bodies contributes to thermal mixing, usually leading to nutrient depletion and algal blooms during early summer.¹¹⁹ This effect was observed most readily in the springtime blooms on Lake Cachuma for all years analyzed (Figure 5c). Here, we observed wildfire-associated cyanobacteria blooms later in the summer (August). Water temperatures above 25°C favor cyanobacteria growth over other species of green algae.^{46,120} The water quality data included herein (Figure S7, Figure S8) show water temperatures slightly above 25°C in two of the lakes identified. Although we did not have water temperature data for the remaining lakes, water temperatures were likely highest during August relative to other times of the year in those lakes as well. Thus, warmer water temperatures likely were an antecedent condition before any potential nutrient deposition from the fires, suggesting water temperature is a critical covariable that contributes to cyanobacteria blooms during fire season.

Changes in sunlight due to smoke could also impact bloom activity. One recent article found wildfire-induced smoke coverage reduced incident radiation and heat transfer to mountain lakes, hereby altering lake ecology.¹²¹ The authors noted an increase to primary production in shallow waters due to a release from photoinhibition.¹²¹ To evaluate this mechanism of smoke-influenced cyanobacteria bloom production, we investigated the smoke coverage for all case study fires. Smoke remained present in the atmospheric column from August 8 – 20, 2009 following the La Brea Fire, July 29 – August 25, 2007 for the Zaca Fire, and from July 20 – September 3, 2018 for the Carr Fire. While smoke coverage overlaps with the cyanobacteria blooms observed on lakes near the La Brea Fire, smoke was present in the atmospheric column for two to three weeks prior to the cyanobacteria blooms near the Zaca and Carr Fires. For these examples, cyanobacteria blooms were only observed following high airborne nutrient pulses over lakes, suggesting atmospheric deposition as a contributing factor in bloom formation. Scordo et al. 2021 also noted primary production at the surface of the lake increased linearly with PM_{2.5} mass concentrations present in smoke and stated one possible explanation as deposition of nutrients from ash.¹²¹ The higher trophic status and light attenuation of the case study lakes compared to the clear mountain lake used in Scordo et al.¹²¹ suggests that photoinhibition was not a major factor in the cyanobacteria blooms investigated herein.

Deposition from a summertime wildfire could lead to an infusion of nutrients to the top of the water column at a time of year when the water temperature is already warm. Deposition of iron from wildfires has been shown to trigger algal blooms in marine ecosystems.¹²² In this study, iron was not always higher during the case study fires when compared to non-fire days at the same locations, and moreover it is unlikely these freshwater systems are iron limited (Figure 3, Table S5). Instead, it is more likely that nitrogen or phosphorus limits primary productivity in these lakes. While some lakes are nitrogen limited,¹²³ most lakes in California are phosphorus limited.^{42,44,124,125} The concentration of nitrogen-containing species was higher during the case study fires, yet these species were also present in the air during non-fire days. By contrast, phosphorus was only present at the case study locations in smoke plumes and absent on non-smoke days (Figure 3, Table S5). This suggests the primary limiting nutrient may have been phosphorus, causing the observed increase in CIcyano in downwind lakes, but we cannot definitively separate out its effects from nitrogen and other nutrients.

Like other studies downwind of wildfire,^{14,15,39,41,45,103,122} nutrient concentrations in the downwind waterbody were generally lacking in this study, with the exception of two lakes. Water sampling downwind of fires can be difficult given the stochastic nature of when and where fires occur and whether smoke will intercept a waterbody. Additionally, the temporal and spatial coverage of existing sampling networks are sparse compared to air quality data. By contrast, it is much easier to collect local water quality data in burned watersheds, likely explaining in part why the preponderance of the scientific literature has focused on local effects to date.⁸⁵ Nevertheless, other studies, especially in coastal systems, are suggestive of a mechanistic linkage between smoke from fires and primary production, even without water quality data.^{14,15,39,122} Here, the drop in dissolved oxygen (Figure S7, Figure S8) likely indicates a preceding algal bloom. The monthly nitrate data also show that nutrient concentrations in the water column can be low in late summer relative to the rest of the

year. This suggests that nutrients delivered to the water surface could help contribute to an algal response. Otherwise, however, the monthly data do not have the temporal resolution to confirm whether or not a depositional effect from the fire occurred. Given that the blooms occurred days after the fire, any depositional changes in monthly chemistry data are likely to be masked by biological uptake. Thus, there were relatively high nutrient concentrations in smoke from these fires, the smoke intercepted the lakes, and there were algal blooms subsequent to smoke exposure, but we cannot quantify nutrient concentration changes in the water column in response to the smoke. Perhaps, as this potential relationship becomes more well known, rapid response water quality sampling could be conducted downwind of fires to help fill in this data gap.

There were similarities across all cyanobacteria blooms described herein following the intersection with wildfire smoke. The average increase in CIcyano for all lakes investigated was 73.0, though this was highly variable (range 0.8 - 409.8). An increase in CIcyano was observed two to seven days after intersection with high nutrient wildfire smoke concentrations. Most blooms persisted for 7–14 days, with the exception of the Mystic Lake bloom that lasted over 21 days. No precipitation was recorded during or immediately after the case study fires. In the absence of precipitation or runoff, dry deposition is the hypothesized route of transport for nutrients to lakes.^{91,112} Air mass trajectories support the atmospheric transport of nutrients to the selected lakes.

We investigated the change in CIcyano for all lakes associated with case study fires as a function of lake surface area, depth, and volume, yet the conclusions that can be drawn are fairly limited given the small number of lakes analyzed. Surface area may have had some influence on CIcyano. For example, the change in CIcyano was similar for both West Valley Reservoir and Mystic Lake when accounting for surface area, though Mystic Lake had a significantly higher CIcyano (436.4 and 224.8, respectively; Figure S9). For the La Brea fire, the change in CIcyano at Lake Cachuma was higher than Lake Casitas (5.7 and 0.8, respectively), and was likely influenced by the larger surface area for nutrient deposition, closer proximity to the fire, and shallower lake depth allowing for sunlight penetration and mixing that promotes cyanobacteria growth (Table S6, Figure 1).^{48,126}

For cases where depth could be determined, lakes with shallow depths generally experienced more severe blooms. Mystic Lake experienced the most severe bloom of all lakes examined during the Zaca Fire, likely due to the shallow depth (2 m) of the lake (Table S6). The most notable bloom following the Carr Fire occurred at West Valley Reservoir; the shallow depth of this lake (1–3 m) also likely contributed to the intense increase in CI observed (Table S6). By contrast, there was not an observable relationship between CIcyano and lake volume for the lakes examined in this study.

In addition to lake properties, we also considered the distance from fire boundaries to AQS stations and lakes. Previous studies have observed correlations between proximity of monitoring stations to burned areas and high species concentrations.³³ In both the La Brea and Williams fire examples, AQS stations were present 15–25 kilometers from the fire burn boundaries. In contrast, the Zaca and Carr fires were much farther from their associated AQS stations (~140 kilometers). Though these fires burned significantly more acreage (Table 1),

they were not associated with higher nutrient concentrations than the La Brea and Williams fires. For the La Brea fire, the lake closest to the fire burn boundary experienced higher cyanobacteria activity. However, this trend was not observed for the lakes associated with the Carr and Zaca fire events. Given the small sample size of case study fires used in this study, the conclusions regarding distance are fairly limited.

If indeed contributing to algal bloom formation as suggested here, the mobilization and deposition of nutrients from wildfire has implications for communities and waterbodies far downwind and even upslope, like alpine systems. Cyanobacteria blooms can produce cyanotoxins, such as microcystins¹²⁷ and cylindrospermopsin,¹²⁸ both of which have recommended levels for safe consumption in drinking water (1.6 µg/L for microcystin¹²⁹ and 3 µg/L for cylindrospermopsin).¹³⁰ These toxins require purification, often by oxidation¹³¹ or ozonolysis,¹³² when present in drinking water supplies. For example, toxic algae blooms in Oregon's Detroit Lake contained cylindrospermopsin and microcystin, which impacted drinking water for 200,000 people in the surrounding communities in 2018.^{133,134} Cyanobacteria blooms can also affect secondary drinking water standards, such as taste and odor.¹³⁵ Overall, cyanobacteria blooms are becoming a threat to inland water quality and aquatic ecosystems.¹³⁶

In addition to health impacts, cyanobacteria blooms can lead to decreased dissolved oxygen levels,^{137–139} altered light and heat transport in water bodies,¹³⁹ and negative impacts on biota.^{116,139} Aquatic light reduction may affect the vertical distribution and productivity of primary producers, thus altering the food-web structure.¹³⁹ Several studies have noted a reduction in abundance or diversity of macroinvertebrates^{17,140–143} and fish^{144,145} following fire-related eutrophication and increased cyanobacteria. These, in turn, can lead to negative impacts on fishing industries, recreation, and tourism.¹⁴⁶ There is some evidence to suggest eutrophic lakes are increasing across the United States, with increases in lake and stream phosphorus most exacerbated in the western United States.¹¹⁴ An increase in phosphorus deposition from fires could impact downwind lakes and the detriment of their aquatic life.

Another potential link between wildfires and cyanobacteria bloom formation is the use of phosphorus-based fire retardants, which have been shown to stimulate algae growth at concentrations <1 mg/L.¹⁴⁷ While fire retardant usage was not quantified in this study, the use of phosphorus-based fire retardants is increasing¹⁴⁸ and expected to promote algal growth near fire boundaries. Similarly, wildfire-driven deforestation has been linked to enhanced nutrient loadings of nitrogen and phosphorus, leading to eutrophication to downstream water bodies.¹⁴⁹ Our results suggest a systematic study linking fires to cyanobacteria growth is warranted.

Limitations

Our study contains limitations that should be considered when interpreting results. First, the use of remote-sensing data for both smoke plume detection and cyanobacteria abundance contains inherent limitations. The smoke plumes from HMS are representative of smoke throughout the entire atmospheric column, not just at the surface. This may have decreased the difference between smoke and non-smoke nutrient concentrations if the smoke plume

was high in the atmospheric column but not measured by ground-based monitors. Other studies have identified increased PM_{2.5} on days before and after HMS-identified smoke events when using daily measurements.¹⁵⁰ With the measurements used herein taken less frequently (every 3 - 6 days depending on the station) we expect a minimal effect on the results of this study. However, accounting for these two limitations would likely increase the magnitude of our fire-mobilized nutrient estimates. Additionally, HMS satellite products could potentially miss smoke due to cloud coverage, hereby mislabeling smoke and non-smoke days. Similarly, the MERIS and OCLI satellite sensors have interference with smoke, glint, clouds, and cloud shadows. This could reduce the magnitude of cyanobacteria measurements if smoke was consistently over a given lake during image acquisition. The lakes analyzed herein were at least 300m x 300m to be resolvable by MERIS and OCLI, so results may be different for smaller aquatic systems. Pixels along the land-water interface were excluded automatically with the satellite algorithms, though this can be where bloom biomass accumulates due to wind advection. Lastly, the satellites only measure the surface of the water column and may under-represent cyanobacteria in well-mixed lakes. Taken together, all of these limitations suggest we may be under-reporting cyanobacteria abundances in these bodies of water.

Next, the AQS data contained varying numbers of measurements for each type of chemical. Of the 15 years of data analyzed for this study, measurements ranged from as high as 1,931 for potassium, manganese, zinc, silicon, and iron, but were as few as 620 for ammonium. The significantly fewer data points for ammonium could explain why there was not a strong correlation with fire activity. Similarly, each species measured contained a portion of measurements at 0 (Table S1), which likely resulted in lower average concentrations and smaller differences between smoke and non-smoke days. The highest phosphorus measurement on smoke days ($0.08 \ \mu g/m^3$ associated with the La Brea fire) resulted in a very high (~86,000%) percent above average for the year 2012 at that station. This percent calculation was based on just two non-zero measurements and highlights episodically high concentrations that may not always be consistently observed.

Finally, in contrast to the 15 years of airborne nutrient data, we were limited in the number of fires we could investigate for a potential linkage between wildfire smoke and algal blooms. Using four high phosphorus fires, we identified 10 total lakes near each fire boundary with increases in cyanobacteria abundance. Further studies should consider expanding the spatial extent to find more fires with accompanying cyanobacteria measurements, if available. We were also limited by the paucity of water quality data in most cases. Lastly, deposition flux estimates were not attainable in the current work but represent an important next question in determining a relationship between fire emissions and aquatic ecosystem effects. Future modeling work may be necessary to determine wildfire-influenced nutrient fluxes to water surfaces.

Conclusions

In this study, we examined the mobilization of nutrients by wildfire smoke over a 15 year period in the western United States, and observed increased airborne concentrations of phosphorus, nitrate, potassium, manganese, copper, zinc, aluminum, silicon, calcium,

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iron, magnesium, and sodium in wildfire-influenced PM_{2.5}. Of all nutrients, phosphorus increased the most on smoke days (averaged 226% higher on smoke days compared to non-smoke days, with a percent change of approximately 86,000% at its maximum). In four high phosphorus case study fires, we further observed a potential link between high nutrients in smoke and an increase in cyanobacteria abundance in multiple downwind lakes. Cyanobacteria blooms occur naturally from a multitude of stressors, particularly increased temperature and nutrient loading. We propose that fire-driven nutrient mobilization could be an additional stressor contributing to the formation of blooms given the proper antecedent conditions, like elevated water temperatures.

With climate change expected to increase both fire and cyanobacteria bloom activity in the continental United States in the coming years, it is vital to further understand if a link exists between these two environmental trends. The findings presented herein warrant the need for future studies systematically investigating the relationship between wildfire emissions and downwind lake eutrophication, including in regions outside of the western United States.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Environmental Significance Statement

Wildfire activity is increasing with a warming climate. Wildfires mobilize chemicals in smoke with potential impacts to communities and ecosystems far downwind. In this study, particulate matter ($PM_{2.5}$) nutrients were elevated on wildfire smoke days compared to non-smoke days, with the exception of ammonium. For example, phosphorus concentrations in smoke from one fire were ~86,000% higher than days without smoke and reached a maximum value of 0.08 µg/m³. Downwind of several high nutrient fires, remotely sensed cyanobacteria abundances increased in the days following intersection with smoke. This is suggestive of a relationship between nutrients from wildfire smoke and cyanobacteria bloom formation, with potential to impact drinking water and aquatic ecosystems in the western United States and other fire-prone regions.

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Figure 1.

Air Quality System (AQS) speciation network monitors for $PM_{2.5}$ locations active at some point during 2006–2020.

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Figure 2.

A) Absolute change in concentration (μ g/m³) and B) percent change in concentration on smoke days compared to non-smoke days at each monitoring station, for phosphorus and nitrogen-containing chemicals, across all years (2006–2020). Each black dot represents a single monitoring station for one year. The diamonds represent the average values across all stations and years, while the orange horizonal lines symbolize the median values. Median values are higher on smoke days for phosphorus and nitrate, but lower for ammonium. The number of measurements (n) is listed after each species. Boxes represent 25–75th quartiles while whiskers represent 5–95th quartiles. Concentrations for all species investigated are shown in Figure S1. C) Median percentage change in concentration for phosphorus and nitrogen-containing chemicals on smoke days compared to non-smoke days, separated by year.

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Figure 3.

The chemical species profile for the A) Zaca, B) La Brea, C) Williams, and D) Carr fire events in California. Species were plotted on different concentration axes for easier visualization. Ammonium was not measured during the selected fire events. No Fire dates were chosen as the nearest date preceding the fire with no visible smoke observed in the atmospheric column. Relative abundance of each species is shown in Figure S4; percent differences in chemical species during case study fires compared to the nearest no-fire date at the same location are shown in Table S5.

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Figure 4.

HYSPLIT backward (top row) and forward (bottom row) trajectory plots corresponding to the Zaca Fire, La Brea Fire, Williams Fire, and Carr Fire. Backward trajectories were initiated at the corresponding Air Quality System (AQS) station for 24 h at 10 m above ground level, with markers labeling the location of the air mass every 1 h starting at the AQS station and working towards the fire boundary. Representative backward trajectories were overlaid with the burn boundary for the corresponding fire to verify plumes traveled over/near fire locations before sampling at AQS stations. Forward trajectories were initiated from the corresponding AQS station every 3 h at 10 m above ground level. The contours represent the percentage of trajectory endpoints in each grid cell divided by the total number of trajectories calculated. Forward trajectories were used to identify lakes downwind of high nutrient measurements.

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Figure 5.

A) Satellite images of cyanobacteria concentrations in the Santa Barbara area of California on August 19, 2009, five days after high nutrient concentrations in smoke from the La Brea Fire. The red star on the map marks the nearest Air Quality System (AQS) station and the orange area on the map represents the La Brea Fire burn boundary. Satellite imagery showing pre- and post-fire cyanobacteria abundances for each lake are shown in the bottom left and Figure S5. B) One month and C) annual April-December time series of cyanobacteria indices (CIcyano) for Lakes Cachuma and Casitas. The orange shaded regions represent smoke coverage over the lakes.

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Figure 6.

A) Satellite images of cyanobacteria concentrations in the Santa Barbara area of California on August 19, 2007, five days after high phosphorus concentrations in smoke from the Zaca Fire. Lakes with observed increased in cyanobacteria index (CIcyano) are circled and shown in detail on the top right with comparison to satellite images captured pre-fire. The red star on the map marks the nearest Air Quality System (AQS) station and the orange area on the map represents the Zaca Fire burn boundary. B) One month and C) annual April-December time series of CIcyano for Mystic Lake, Pyramid Lake, and Perris Reservoir. Plots are colored based on the circled locations on the maps. The orange shaded regions represent smoke coverage over the lakes.

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Figure 7.

A) Satellite images of cyanobacteria concentrations in Northern California on August 27, 2018, twelve days after high nutrient concentrations in smoke from the Carr Fire. Lakes with observed increased in cyanobacteria index (CIcyano) are circled and shown in detail on the bottom left with comparison to satellite images captured pre-fire. The red star on the map marks the nearest Air Quality System (AQS) station and the orange area on the map represents the Carr Fire burn boundary. B) Annual April-December time series of CIcyano for all lakes circled. Plots are colored based on the circled locations on the maps. The orange shaded region represents smoke coverage over the lakes. Monthly CIcyano plots for these lakes are shown in Figure S6.

Table 1.

Case study fires with area burned, airborne phosphorus and nitrogen concentrations, downwind lakes, lake distance from fire and Air Quality System (AQS) station, and pre- and post-fire cyanobacteria index (CIcyano) values. Pre-fire CIcyano were taken 5 days before the start of the fire. Post-fire CIcyano represent the maximum value detected 5–12 days after each corresponding fire. CIcyano values correspond to the dates and images shown in Figure S5.

Fire	Area burned (hectares)	P,N at AQS station (µg/m ³)	Downwind lakes	Lake distance from fire (km)	Lake distance from AQS station (km)	Pre-fire CI (cyanobacteria index)	Post-fire CI (cyanobacteria index)
La Brea	36,215	.08, 4.5	Lake Cachuma	31	15	1.0	6.7
			Lake Casitas	89	60	1.0	1.8
Zaca	97,208	.01, 1.7	Pyramid Lake	56	72	10.7	46.5
			Perris Reservoir	230	160	1.0	39.4
			Mystic Lake	230	160	26.6	436.4
Carr	92,936	.01, 1.6	Eagle Lake	140	133	1.4	2.4
			Tule Lake	140	19	1.4	2.7
			Honey Lake	170	180	5.1	14.6
			Red Rock Lake	185	132	9.9	13.8
			West Valley Reservoir	175	105	1.1	224.8