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Beyond particulate matter mass: heightened levels of lead and other pollutants associated with destructive fire events in California

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Abstract

As the climate warms, wildfire activity is increasing, posing a risk to human health. Studies have reported on particulate matter (PM) in wildfire smoke, yet the chemicals associated with PM have received considerably less attention. Here, we analyzed 13 years (2006–2018) of PM_{2.5} chemical composition data from monitors in California on smoke-impacted days. Select chemicals (e.g., aluminum and sulfate) were statistically elevated on smoke-impacted days in over half of the years studied. Other chemicals, mostly trace metals harmful to human health (e.g., copper and lead), were elevated during particular fires only. For instance, in 2018, lead was more than 40 times higher on smoke days on average at the Point Reyes monitoring station due mostly to the Camp Fire, burning approximately 200 kilometers away. There was an association between these metals and the combustion of anthropogenic material (e.g., the burning of houses and vehicles). Although still currently rare, these infrastructure fires are likely becoming more common, and can mobilize trace metals in smoke far downwind, at levels generally unseen except in the most polluted areas of the country. We hope a better understanding of the chemicals in wildfire smoke will assist in the communication and reduction of public health risks.

Keywords

wildfire; Camp Fire; particulate matter; smoke; air quality; metals; lead; Pb

1. Introduction

The annual area burned by wildfires, total number of large fires, and fire season length have all been increasing in the western United States in recent decades.^{1, 2} Warmer average temperatures, reduced snowpack, and reduced warm-season precipitation contribute

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Supporting Information.

Figures and tables labeled “Supplementary” in the text found in the Supporting Information section

to greater wildfire activity, with climate change amplifying these trends.³ Beyond loss of life and destruction of property, wildfires profoundly affect air quality, even in relatively far downwind communities. The 2020 fire season, for instance, blanketed the entire West Coast of the United States (U.S.) in a thick layer of smoke for multiple days, and in some areas, for weeks (Figure 1a). These smoke events are becoming longer and more widespread as wildfires burn more acres.

Fires impact air quality through the generation of a mixture of gaseous and particulate pollutants, with negative impacts to human health.⁴ The most well-studied pollutants are particulate matter (PM), ozone, and carbon monoxide.^{5–9} These criteria air pollutants (CAPs), as defined by the U.S. Environmental Protection Agency (EPA), are emitted in high quantities during wildfires, with important implications for human health.^{10–12} In contrast, less is known about the concentrations of specific chemicals found within wildfire smoke. Organic compounds can make up >90% of the PM in wildfire smoke.⁴ Beyond these compounds, however, PM from wildfires can contain traces of many chemicals, from toxic metals to nutrients. Even in small quantities, these chemicals can pose a threat to human health and impact ecosystems. There are studies reporting emission factors of these toxic chemicals, as well as studies looking at concentrations in post-fire ash,^{13–20} yet there are fewer studies focused on the actual concentrations in air quality samples associated with fire.^{21–24} Moreover, often studies reporting downwind air concentrations of these chemicals do so for only a handful of fires.^{21, 22} Long-term studies of these trace chemicals in smoke are lacking.

In addition to chemicals mobilized from natural fuels, there is an increasing concern that chemicals from burning infrastructure (e.g., vehicles, structures, etc.) will mobilize into the atmosphere or waterways as fires burn into urban areas. Wildfires burning into urban areas are likely becoming more common because of an increase in large fire frequency and an expansion of the wildland-urban interface (WUI).^{25, 26} The WUI is the intersection between the wildland vegetation and the urban housing. From 1990–2010, the WUI experienced a 41% growth in new houses and 33% growth in land area in the U.S., with the vast majority due to new housing.²⁵ Fires are difficult to fight and often ignited by humans in the WUI.^{27, 28} These fires risk mobilization of a suite of pollutants from burning plastics, metals, and other human-made materials, in addition to property destruction and loss of life. There is very little information on emissions from fires in the urban environment,⁴ with studies generally limited to vehicle and tire fires showing elevated levels of select chemicals (e.g., fluoride, calcium, sodium, lead, and zinc).^{29, 30} There is more information on structure fires derived from firefighter exposure measurements, where crustal elements (e.g., aluminum, calcium, iron, zinc) and antimony, chromium, copper, and nickel were most frequently observed in air samples.³¹ However, firefighter exposure measurements may include emissions from other sources (e.g., resuspended dust, diesel exhaust) in addition to the fire emissions.

To better understand the chemicals mobilized from fires, we analyzed over a decade of fire and air quality data from the U.S. state of California between 2006 and 2018. During this period, California experienced many destructive fires, especially in the last few years. In 2017 and 2018, for example, over 3.5 million hectares burned in California, with 34,506

structures destroyed.^{32, 33} Moreover, California has one of the most extensive networks of PM_{2.5} speciation stations in the U.S., facilitating a detailed analysis of smoke composition. We focused on individual chemicals in PM_{2.5} since this size class poses the greatest risk to human health.^{11, 34} Thus, using over a decade of extensive data from California, we posed the following questions:

1. Beyond organic compounds, what chemicals in PM_{2.5} air quality samples are associated with smoke plumes from fires?
2. How much do these PM_{2.5} chemicals increase on smoke days versus non-smoke days?
3. Does distance between fires and monitors or total PM_{2.5} concentrations explain the potential variation in these chemicals in smoke?
4. Is there a unique air quality signature associated with fires burning infrastructure in the WUI?

Addressing these questions will help inform potential air quality risks posed by fire beyond that of PM mass, ozone, and carbon monoxide. It will also provide more information on chemicals emitted during infrastructure destroying fires and, if, and how, the smoke from these fires differs from that of natural fuels.

2. Data and Methods

a. Smoke plume identification

To answer Questions 1 and 2, we compared PM_{2.5} speciation air quality data inside and outside of smoke plumes. For smoke plume identification, we employed the Hazard Mapping System (HMS) fire and smoke product provided by the National Oceanic and Atmospheric Administration (NOAA).^{35, 36} This product uses multiple satellites to detect fire and smoke presence daily, with resolutions ranging from 2 kilometers (GOES-16 East and West geostationary satellites) down to 375 meters (S-NPP and NOAA-20 polar-orbiting satellites). The system operates year-round, and the automated fire detections utilize multi-spectral imagery, apply a form of temperature threshold, and evaluate each hotspot. The detected hotspots are then analyzed manually for validity by fire analysts, with the final daily smoke polygon and fire detection data made available to the public.

The HMS has been tested and validated by multiple studies.^{37, 38} After upgrades made to the system in 2006/2007, Schroeder, Ruminski, Csiszar, Giglio, Prins, Schmidt and Morisette³⁸ compared the HMS fire detections to 30-m spatial resolution ASTER satellite data. They found an average 2% false positive rate, with a reduction in omission errors as additional fire locations were added by fire analysts. Commission errors, with true fires being automatically deleted from the HMS data accidentally, are more common. Additionally, satellite fire detection is typically best for detecting larger wildfires.³⁹ Finally, the smoke plumes from the product are representative of smoke throughout the entire atmospheric column, not just at the surface. Yet, despite these inherent limitations, the HMS data provide a robust method for identifying daily smoke-plume impacts.

b. Particulate matter (PM_{2.5}) measurements

In addition to the smoke plumes, we obtained PM_{2.5} 24-hour concentration data for California from the EPA's Air Quality System (AQS), specifically data from the PM_{2.5} Chemical Speciation Network (CSN) and the Interagency Monitoring of Protected Visual Environments (IMPROVE) network (Figure 1b).^{40, 41} The CSN stations are in more urban locations, generally higher in PM, while the IMPROVE network operates in National Parks and wilderness areas to track changes in visibility and typically record lower ambient PM_{2.5} concentrations. Depending upon the network and station, PM_{2.5} measurements are taken once every three to six days. Data from 2006–2018 were employed since these were the years with both complete HMS smoke polygon data and AQS PM_{2.5} speciation measurements.

Finally, we defined a fire season and cut down our data accordingly. To identify a fire season, we plotted the number of stations within a smoke plume each day from 2006–2018 in R version 4.0.3 using the *sf* and *tidyverse* packages. April 1 through December 31st contained ~99% of smoke plume measurements, so we used that to define our fire season, capturing both early and late season fires (Supplementary Figure 2).⁴²

c. PM_{2.5} chemistry on smoke-impacted vs. non-smoke days

Using these input data, we compared PM_{2.5} chemical concentrations within and outside of the HMS plume for all years from 2006–2018 at each station. PM_{2.5} measurements were labeled as smoke-impacted if the monitor location fell within an HMS smoke plume on the day of the measurement. For each station, we calculated the difference between the average PM_{2.5} chemical concentration on smoke-impacted days vs non-smoke impacted days. Comparing station-specific differences allowed us to control for non-smoke variation between stations (e.g., urban stations are often higher in certain PM_{2.5} chemicals than rural stations). We performed a permutation test for each PM_{2.5} chemical for each year grouped by station to test if differences between smoke and non-smoke days were significant.⁴³ We used a non-parametric test to avoid the issues in our data violating the assumptions of a parametric test, including a skewed distribution and unequal sample sizes (i.e., the sample size of treatment 'smoke days' was smaller than the control 'non-smoke days').⁴⁴

d. Chemical associations with distance and total PM_{2.5} concentrations

To explore the potential variation in PM_{2.5} chemical concentrations in smoke (Question 3), we compared chemical concentrations with distance to the closest fire and total PM_{2.5} concentrations within the smoke plume. For the distance analysis, we employed the fire source point HMS data. The fire points correspond to any fire burning during the 24-hour period of detection, and are not directly linked to the smoke polygons. We measured the distance between each AQS monitor site impacted by a smoke plume and the nearest HMS-detected fire point location. Days without any fires detected in the HMS fire point dataset were excluded from this analysis as there were no fires in which to measure distance.

The relationships between PM_{2.5} chemical concentrations within HMS smoke plumes and distance were investigated using a quantile regression model. We normalized the chemical concentration data through a robust scalar method, whereby we subtracted the median

concentration for each chemical at every monitoring location for every year from its respective data and scaled the concentration distribution to the interquartile range. This accounted for variability in average PM_{2.5} composition across monitoring locations and time, while preserving the signature of extreme events in the data. A quantile regression model was fit to the normalized PM speciation data as a function of distance to the nearest HMS-detected fire point location,⁴⁵ implemented in the Statsmodels Python package.⁴⁶

Further, we tested the correlation between chemical concentrations and total PM_{2.5} concentrations by plotting the normalized concentrations of both on smoke-impacted days. Total PM_{2.5} was used as an index for smoke severity. If chemical concentrations were a function of higher smoke severity, we would expect a positive linear relationship with PM_{2.5}, whereas if the concentrations did not follow PM_{2.5}, this could be interpreted as a shift in the composition of the smoke. Both variables were normalized across all years and stations using the same robust scaling method, and the relationship was analyzed using linear regression.

e. Destructive fire air quality signature

Finally, we sought to identify any air quality signature associated with destructive fires. Here we define “destructive” as fires that burn infrastructure, for example, vehicles and houses (Question 4). Given the limited number of data points, we chose to use a case study approach to identify differences between a few fires of varying levels of destruction. The most destructive fire event we explored was the Camp Fire, which burned in November of 2018 and destroyed approximately 18,000 structures over two weeks. We also explored the Tubbs/Atlas/Nuns Fire complex, the Butte and Valley Fires, the Carr Fire, and the fires of June-July 2008, which destroyed approximately 7,000, 3,000, 1,500 and minimal structures (less than 100), respectively. We compared the chemical profiles of these fires along this spectrum of destructive fires to determine any patterns in concentrations of PM_{2.5} chemicals. We chose stations downwind of each fire event. The amount of smoke across the stations varied, but all sites fell within a smoke plume. For each station in the analysis, we subtracted the station-specific, non-fire average concentration for each chemical for the year (from April 1st through December 31st) from the concentration measured during each case study fire, in order to better characterize the chemistry of the smoke only.

All data processing and statistics were conducted in Python version 3.8.3, unless otherwise specifically noted. Results of all analyses were considered significant at a p-value of 0.05.

3. Results

Our results show that many chemicals (e.g., bromine, calcium, aluminum, iron, silicon, manganese, potassium, sulfate, and titanium) were statistically elevated on smoke-impacted days. In contrast, other chemicals were elevated only during select fires, mostly trace metals particularly toxic to humans and ecosystems (e.g., lead and copper). We used two different methods to analyze the monitoring data and both supported this conclusion. This section describes those analyses and findings in detail.

a. Chemical composition on smoke-impacted vs. non-smoke impacted days

Comparing smoke and non-smoke days for Questions 1 and 2, a third of the chemicals were consistently higher on smoke days for all the data combined when considering the median percent change across all stations averaged across all years (Supplementary Table 1; Figure 2). Thirteen of the 39 chemicals had a median percent change above 10% when comparing smoke to non-smoke days (bromine, potassium, manganese, calcium, titanium, silicon, sulfate, aluminum, iron, sulfur, copper, sodium, and zinc). The results from the permutation test similarly show a group of PM_{2.5} chemicals consistently elevated on smoke days (Supplementary Table 2). Bromine, calcium, aluminum, iron, silicon, manganese, potassium, sulfate, sulfur, and titanium were all significantly higher on smoke days for 8+ years in our 13-year study (Supplementary Table 1). Conversely, ammonium was significantly lower on smoke days for 7 of the 10 years, and on average across all the years (Supplementary Table 1; Figure 2). Nitrate was significantly lower on smoke impacted days for 9 of the 10 years, yet was slightly higher on average on smoke days across all years (ca. 6% higher) because of a few extremely high values on particular smoke days (Supplementary Table 1; Figure 2).

The maximum differences at individual stations for smoke and non-smoke days were much more variable, indicating that particular fires produce high levels of certain chemicals. For example, arsenic, chromium, copper, lead, nickel, and zinc all had maximum percent changes over 2,000% (Supplementary Table 1; Figure 2). Thus, concentrations on select smoke days were much higher than the highest concentrations on non-smoke days. Additionally, chemicals had multiple outlier events on smoke days (Figure 2).

As a result of this outlier pattern, we observed a second group of chemicals that were not higher on average on smoke days and only higher in a few of the years in the permutation test, yet still exhibited very high concentrations during select fire events. These chemicals include lead, copper, arsenic, and chromium (Supplementary Table 1). The magnitude of the chemical concentration of these episodically elevated individual events generally exceeded that of the chemicals almost always elevated. For example, comparing aluminum and lead, aluminum was consistently higher on smoke days with percent differences consistently above zero for all years (Figure 3a and b). By contrast, concentrations and percentages of lead were typically the same or lower on smoke days, on average, with only a few exceptions (Figure 3c). These exceptions were driven, however, by very high events, with the largest over 4,000% higher (Figure 3d).

b. Chemical associations with distance and total PM_{2.5} concentrations

In answering Question 3, we found that PM_{2.5} chemical concentrations generally had significant relationships with distance at the highest concentrations or quantiles but with relatively low goodness of fit (R^2). High concentrations (defined as the 80th percentile or above) declined rapidly with distance for a group of chemicals, including aluminum, bromine, calcium, chloride, chlorine, iron, lead, magnesium, nickel, potassium, rubidium, selenium, strontium, total nitrate, vanadium, and zinc. (Supplementary Figure 4a, 4b). The remaining chemicals did not have a relationship significantly different from zero with distance at high concentrations (i.e., the 80th percentile) (Supplementary Table 4). At lower

concentrations, declines with distance were either not significant or small compared to those at higher concentrations (Supplementary Table 4).

Similarly, we observed a significant relationship, but with low goodness of fit, between normalized chemical concentrations and normalized total PM_{2.5} for most of the chemicals consistently elevated on smoke days (i.e., chemicals consistently higher 8 years or more; Supplementary Table 1). Normalized bromine concentrations, for example, had a significant relationship with normalized total PM_{2.5}, with a low goodness of fit, (Supplementary Figure 5a). Likewise, normalized concentrations of nitrate and ammonium, consistently lower on smoke days, were also significantly related to normalized total PM_{2.5}. For the remaining 27 chemicals (i.e., those not consistently higher or lower most years), slightly under half (12) had a significant relationship with normalized PM_{2.5}, yet with extremely low R² values (Supplementary Table 1); whereas, the other chemicals, such as sodium (Supplementary Figure 5b), did not have a significant relationship with normalized PM_{2.5} at all.

c. Chemical profile of destructive fires

Finally, for Question 4, we found distinct chemical profiles for destructive fires, burning structures and vehicles, especially in the production of trace metals (Figure 4 & Figure 5). The June 2008 fires (Figures 4a), burning minimal structures, exhibited relatively high sodium concentrations, followed by calcium and aluminum, the latter commonly elevated chemicals on smoke days (Supplementary Table 1). The Carr Fire (Figure 4b, c) burned a substantial area, but a small number of structures (~1,500). Its chemical profile mostly consisted of iron, calcium, and aluminum, commonly elevated chemicals (Supplementary Table 1), with a smaller fraction of zinc. Zinc was a metal only episodically elevated on smoke days, statistically significant in only four of the 10 years studied (Supplementary Table 1). The most destructive fire, the Camp Fire, produced these same chemicals, but the concentrations of zinc were relatively high compared to the other fires (Figure 4f). This occurred despite similar or lower total PM during the Camp Fire at several of the monitors relative to that measured during the Carr Fire (e.g., the Modesto vs. the Lava Beds monitors).

The distinct profile of more destructive fires was most evident in the trace chemicals, particularly lead and copper (totaling < 0.5 ug/m³; Figure 5). The 2008 Fire (Figure 5a), the least destructive, produced almost exclusively magnesium, while the Carr Fire (Figure 5b, c), the second least destructive, produced mainly manganese and titanium, with small amounts of lead and copper. The 2015 Fires (Figure 5d), intermediately destructive, produced mostly magnesium and titanium, with small concentrations of lead and copper. Lead and copper were only statistically elevated on smoke vs non-smoke days in one and four of the 10 years studied, respectively—the former in 2018 corresponding the Camp Fire. Indeed, the most destructive fires, the October 2017 and Camp Fires (Figure 5e, f), produced lead and copper in much higher concentrations compared to the other fires. The fires further mobilized additional chemicals such as arsenic, chromium, and nickel. This again was not driven by total PM. The Point Reyes station for example, during the Camp Fire, reported much higher concentrations of lead and copper than the Lassen station during the Carr Fire, despite similar PM values (Figure 5b, f).

As a potential indicator of destructive fires, we employed two chemicals found in destructive fires, lead and copper, divided by potassium, a typical marker of smoke. This ratio was lower during less destructive fires and a higher when more infrastructure was burning (Supplementary Figure 6).

4. Discussion

a. Chemical composition on smoke vs. non-smoke days

Overall, in answer to Question 1, a wide range of chemicals were associated with PM_{2.5} in smoke plumes from fires, including heavy metals. Our results echo the findings from a recent California state report⁴⁷ raising this as an issue of concern. Exposure to PM_{2.5} is already associated with increased respiratory problems, such as asthma, reduced lung function and lung cancer, and cardiovascular disease, especially in pediatric patients.¹¹ Further, there are likely ecosystem effects of mobilization of these chemicals, including the potential for bioaccumulation of metals or the eutrophication of terrestrial and aquatic systems from nutrient deposition.⁴⁸

In general, there were two broad categories of these PM_{2.5}-associated chemicals: those chemicals, like aluminum, consistently elevated on smoke vs. non-smoke days; and those chemicals, such as lead or copper, episodically elevated only during specific circumstances aligned with structural burning (e.g., houses, vehicles). As implied, this finding is likely influenced primarily by fuel source. Chemicals such as aluminum, calcium, iron, silicon, and potassium were found to be elevated for eight or more years out of the 13-years studied. Most of these chemicals are typically found in soil. These chemicals have been found to be elevated after fires in various mediums such as ash and air measurements.^{13, 14, 21, 23, 24, 49} Mobilized dust is one hypothesized reason for elevated soil-derived chemicals during wildfire events, since wildfires burn the most area during windy conditions, likely leading to the entrainment of dust into smoke plumes.

By contrast, ammonium and nitrate concentrations were generally lower on smoky days. This is likely because concentrations of ammonium nitrate in PM are typically higher on colder versus warmer days due to enhanced partitioning of ammonium nitrate into the particle phase.⁵⁰ The enhanced partitioning is favored by lower temperatures and higher relative humidity.⁵⁰ For example, Hasheminassab, Daher, Saffari, Wang, Ostro and Sioutas⁵⁰ reported that seasonal contributions of ammonium nitrate to PM averaged over eight sites in California was 8.4 µg/m³ in winter and 3.2 µg/m³ in summer, and Hand, et al.⁵¹ also reported wintertime peaks of ammonium nitrate at both urban and rural monitors for nearly every region in the U.S., including California. We limited our analysis to smoky and non-smoky days for the period of April 1st through December 31st, and most of the high values for ammonium and nitrate occurred in November and December (Supplementary Figure 1). These months are relatively colder with higher relative humidity compared to the other months included and had fewer fires (Supplementary Figure 2), a combination likely explaining the generally higher ammonium and nitrate values on non-smoky days.

We also observed some chemicals only episodically elevated, such as lead, copper arsenic, nickel, chromium, and zinc (Supplementary Table 1). These are chemicals elevated for

four years or less, especially in 2018. A few studies have shown the presence of remobilized lead from both natural and legacy sources in ash from wildfires in Australia and California.^{15, 16, 18, 52, 53} Thus, wildfire burning in the WUI or along roadways could remobilize lead deposited before the phase out of leaded gasoline.^{54, 55} Although this could have contributed to the signal we observed in this study, we found that episodic chemicals were most associated with destructive fires, particularly structural burning. The wildfire season of 2018 burned approximately 24,000 structures, with select destructive fires, like the Camp Fire, producing comparatively high amounts of lead, copper, zinc, and other metals relative to other fires (see part c below for more discussion on this topic).

In answer to Question 2, fires caused high concentration events for most chemicals measured. This was evident in the average values across all stations and all years, but even more so in the individual fire data, with “super-emitting” fires leading to extremely high average values at individual stations (Figure 3; Supplementary Figure 3). Averaging all stations for each chemical for each year, the chemicals that were statistically higher on smoke days in at least eight of the 13 years had median concentrations ranging around 20–50% higher on smoke days compared to non-smoke days (Figure 2). Comparatively, the remaining chemicals had median concentrations ranging from lower on smoke days to around 15% higher (Figure 2). Despite the lower average values, these chemicals had extremely high outliers, much higher than the elevated group, up to 150 times higher on smoke days at a given station and year (Figures 2 and 3; Supplementary Figure 3).

This was certainly the case, for example, at the Point Reyes monitoring station, where smoke days were more than 40 times higher in lead concentrations compared to non-smoke days on average because of the Camp Fire in 2018. This substantially increased the annual averages for lead at that station, located near the Pacific Ocean north of the San Francisco Bay area. The average for lead across all smoke and non-smoke days (from April 1st through December 31st) was almost 10 times higher than the average on non-smoke days alone at Point Reyes (0.00147 vs. 0.000157 ug/m³, respectively). Using our methods, we could not separate PM_{2.5} from wildfire vs. those from other sources, since non-fire sources often remain present on smoky days. Nonetheless, it has been estimated that almost half of PM_{2.5} originates from wildfires annually in the western U.S.⁵⁶ This, plus the high percent increases shown here, suggests that fire can be a relatively large source of PM_{2.5}-associated chemicals, such as lead, annually. This is likely particularly the case for areas like Point Reyes away from more traditional sources, such as utilities or industrial centers. Indeed, our results here indicate an episodic event, a wildfire burning WUI infrastructure, may mobilize a substantial proportion of lead measured in certain locations for the entire year in just a few days.

b. Chemical associations with distance and total PM_{2.5} concentration

In answering Question 3, we found that chemicals showed only a small decline with distance or no-relationship at all with distance at lower concentrations (below the 80th percentile). Even at higher concentrations where results with distance were generally significant, the relationships had low goodness of fit, meaning other factors, besides our measure of distance, explained the variation in concentrations. This finding may be explained, in part, by other fires, besides the nearest one by distance, influencing a measurement at

a monitoring station. Identified fire points were often abundant, raising the prospect of other fires affecting a given measurement. Moreover, there were cases where monitors were covered by multiple smoke plumes, suggesting an influence of multiple fires. Furthermore, chemicals can also undergo atmospheric chemistry alterations downwind of fires, potentially affecting their relationship with distance.⁵⁷ Despite this weak or lack of a relationship with distance, however, the very highest concentrations of most chemicals did decline rapidly with distance. This has implications for air quality managers and public health professionals since population centers, varying in distance from fire epicenters, would thus be impacted differently.

As for PM, we observed that chemicals almost always elevated (or lower in the case of nitrate and ammonium) on smoke days tended to have significant relationships with normalized total PM_{2.5}, albeit with relatively low goodness of fit. By contrast, chemicals only episodically elevated tended to be more mixed in their relationship with normalized PM_{2.5}, and even if significant, had extremely low R² values. These results are perhaps unsurprising, given that we conducted the regression analysis on all smoke days, and if chemicals are not affected on most smoke days, then a relationship with normalized PM_{2.5} on those days is unlikely. Additionally, as in the distance analysis, the generally weak goodness-of-fit values also suggest that factors other than total PM_{2.5} affected chemical concentrations (Supplementary Table 1). This finding is consistent with the results from the destructive fires, where the amount of lead and other metals did not necessarily scale with total PM_{2.5} (Figure 5).

c. Burning of infrastructure

Finally, in answer to our fourth question, fires burning infrastructure do appear to have a unique air quality signature. Overall, both fires burning natural fuels and fires burning these fuels plus structures produce certain chemicals, such as magnesium, aluminum, and calcium. However, fires burning infrastructure in the WUI also produce other chemicals, such as copper lead and zinc, in significant quantities generally not observed from fires occurring where fewer structures were burned. Notably, these results are relatively rare. Most studies have examined measurements of metals in ash after fires, or emissions factors of pollutants from certain fuel types, and there are only a handful of papers that have examined concentrations of metals in air quality samples and linked them directly back to infrastructure-destroying wildfires.^{21–24} One study in Ottawa, Canada, did observe elevated lead and antimony resulting from structure fires, consistent with our findings for lead.⁵⁸ Further, Sparks and Wagner⁵⁹ focused on air emissions from the Camp Fire and found elevated levels of manganese, tin, copper, zinc, nickel, and lead, mostly in the PM₁₀ size fraction, in wildfire smoke from that event. We observed similar results, with elevated lead, copper, zinc, and, to a lesser extent, nickel in the PM_{2.5} size fraction.

Since it can be difficult to link particular fires with downwind effects, as indicated by our distance analysis, an indicator may be helpful for smoke from destructive fires. More data are needed, but the ratio of lead and copper combined over potassium appears to be useful as an indicator, or tracer, of smoke from destructive fires (Supplementary Figure 6). The ratio roughly increases with number of structures burned. Ideally, we would regress

this ratio against number of structures/vehicles burned, but we lacked sufficient data on structures/vehicles burned for most fires to perform this analysis. Further research on more individual fires is needed to determine whether this ratio is broadly indicative of destructive fires.

d. Limitations

As in any study, our results have limitations caused by the data and methods we employed. Both the NOAA HMS smoke and fire data and the AQS monitoring system measurements are subject to assumptions. First, the HMS data has a few limitations, consistent with satellite-based fire products. As noted in the methods, the HMS plumes are representative of smoke throughout the entire atmospheric column, not just at the surface. This likely reduced the magnitude of the smoke day versus non-smoke day results since the chemical concentration measurements of a given smoke plume high in the atmosphere would be low at the surface, even though it would be counted as a day with smoke. Thus, if this was accounted for, concentrations on smoke days for most chemicals would have been even more pronounced. Also, satellite products can miss smoke due to cloud coverage, which could mislabel some true smoke days as non-smoke days. Additionally, each smoke plume is labeled with a density of smoke (i.e., low, medium, or high density). We did not preserve this labeling system in our analysis when we treated all smoke plumes as equal. In our study, we considered using organic carbon as an indicator of smoke (along with the smoke plumes), but chose to use smoke plumes alone, as has been done in other studies.³⁷ To attempt to account for these limitations, we compared chemical concentrations with total PM_{2.5} as a proxy for smoke at the surface. The HMS fire points impose limitations as well since a fire point is any detection of fire on the satellite image. This could be a misdetection or a small fire, which could end up being the closest fire to a station even if that fire is not producing the smoke above the station. This resulted in assumptions during the distance analysis, as discussed above.

The AQS data also have limitations. We chose to focus on PM_{2.5}, but it must be noted that metals have been measured in PM size fractions larger than PM_{2.5} (i.e. PM_{2.5-10}). Because PM_{10-2.5} is known to be inhalable, the total metal exposure impacts from wildfire events may be more extensive than those evaluated herein. Notably, the amount of data for each chemical also varied, with the number of non-zero smoke measurements ranging from 180 to 3356 in the chemicals analyzed (Supplementary Table 3). Thus, conclusions for certain chemicals were based on less data than others. However, despite this limitation, the ratio of non-zero smoke days to non-smoke days stayed relatively consistent, ranging from 7.9–12.9% of the available data for each chemical. This suggests our use of the ratio of smoke days to non-smoke days provided a valid comparison across all chemicals.

Finally, across the different chemicals and 13 years, the detection limit at monitoring sites varied due to measurement system changes and varying systems at different stations and is often not clearly reported in the AQS data. Additionally, there are differences in both detection limits and measurements around detection limits between the IMPROVE and CSN monitoring systems.⁶⁰ Values below zero were set to zero, while positive values below the detection limit were retained and included in the analysis. The retention of low values

below the detection limit likely predominantly affects chemicals with consistently low concentration measurements near or below the detection limit and few values (e.g., silver). This, however, likely does not impact the main results of this study because we focused almost entirely on median and the highest, outlier measurements even for trace chemicals.

e. Implications

Overall, this study has implications for both downwind communities and ecosystems. The difference in PM_{2.5} chemical composition breakdown in smoke observed in this study, specifically an increase in toxic metals due to structural burning, could have potential public health implications. As the WUI continues to grow into fire-prone wildlands,²⁵ and as wildfire activity also increases, populations may suffer exposures to wildfire smoke that contains elevated concentrations of these metals. This has the potential to create additional health risks for fire-affected populations in general, and especially for more vulnerable populations, such as children. To date, studies of ambient PM_{2.5} exposure have not indicated that any individual chemical is more strongly related to health effects than PM_{2.5} mass, and less is known about whether combinations of specific chemicals could elicit greater health responses or differential risk¹¹. While some epidemiologic studies have attempted to examine whether there are differences in the toxicity of wildfire-specific PM_{2.5} compared to ambient PM_{2.5}, this is challenging and has been studied most extensively in experimental settings. In addition, studies of differences in toxicity have typically focused on natural fuel sources, with more limited data from fire burning human-made structures.^{61, 62} This research gap is significant considering the results of this study.

Also implied by this study is that fires are eroding past air quality gains from lowering anthropogenic emissions (e.g., from smokestacks and tailpipes). For example, we observed elevated lead and other metals from the Camp Fire at multiple sites despite measures to phase lead out from the environment.⁴⁰ Since our results suggest that these extremely high concentrations decline with distance, these data may be able to be used for setting distance limits for exceptional event designations. Moreover, our findings suggest that emissions inventories may need to account for variable emission factors depending on fire type – for example, destructive versus non-destructive fires.⁶³

Our study also shows that stationary monitors can be a powerful tool in understanding the chemistry of wildfire smoke. There has been an emphasis on more mobile monitors, particularly for PM, ozone, and CO, but the role of stationary monitors should not be overlooked. To better understand the impacts of smoke from different fires, full chemical speciation measurements are essential. These data have been routinely collected at stationary monitors over many years, both increasing the time frame of study and decreasing the need for additional expense. Moreover, wildfire-targeted and mobile studies tend to be limited by the availability of comparable non-fire data, required for demonstrating fire impacts. We suggest that future research could use stationary monitors to characterize PM composition on smoke days across the entire western U.S. to compare to the results found here for California.

Beyond human health, downwind ecosystems are also likely being impacted. Chemicals from fires can move into—and concentrate in—the ecological food chain, and nutrients

can cause eutrophication. For example, we observed a high increase in PM_{2.5} phosphorus on smoke days. Thus, fires could be contributing to observed increases in lake phosphorus concentrations, particularly in the West.⁶⁴ Likewise, a recent modeling paper by Koplitz, Nolte, Sabo, Clark, Horn, Thomas and Newcomer-Johnson⁴⁸ found wildland fire emissions contributed up to 30% of total deposition for N and S in some areas, leading to levels of N that may affect tree survival and growth rates.

Overall, we analyzed over a decade of air chemistry data on smoke vs. non-smoke days for the state of California in this study. Certain chemicals are routinely found in higher concentrations in smoke, while some are only episodically elevated. In particular, we conclude that infrastructure-destroying fires in the WUI can mobilize chemicals, especially metals such as lead, at concentrations far exceeding those typically observed and reaching a couple hundred kilometers or more from the fire center. With climate change increasing fire frequency, combined with the expansion of urban areas in fire-prone regions, it is even more urgent to understand how pollutants in smoke affect human health and downwind ecosystems. These findings emphasize the need for further studies of the health and environmental effects of fires, especially those burning infrastructure.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Data Availability Statement.

Data analyzed in this study were a re-analysis of existing data, which are openly available at locations cited in the reference section. Further documentation about data processing is available at <https://edg.epa.gov/metadata/catalog/main/home.page>.

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SYNOPSIS

This study finds elevated concentrations of metals mobilized by wildfires destroying infrastructure in California over the last decade, raising potential health concerns for downwind communities.

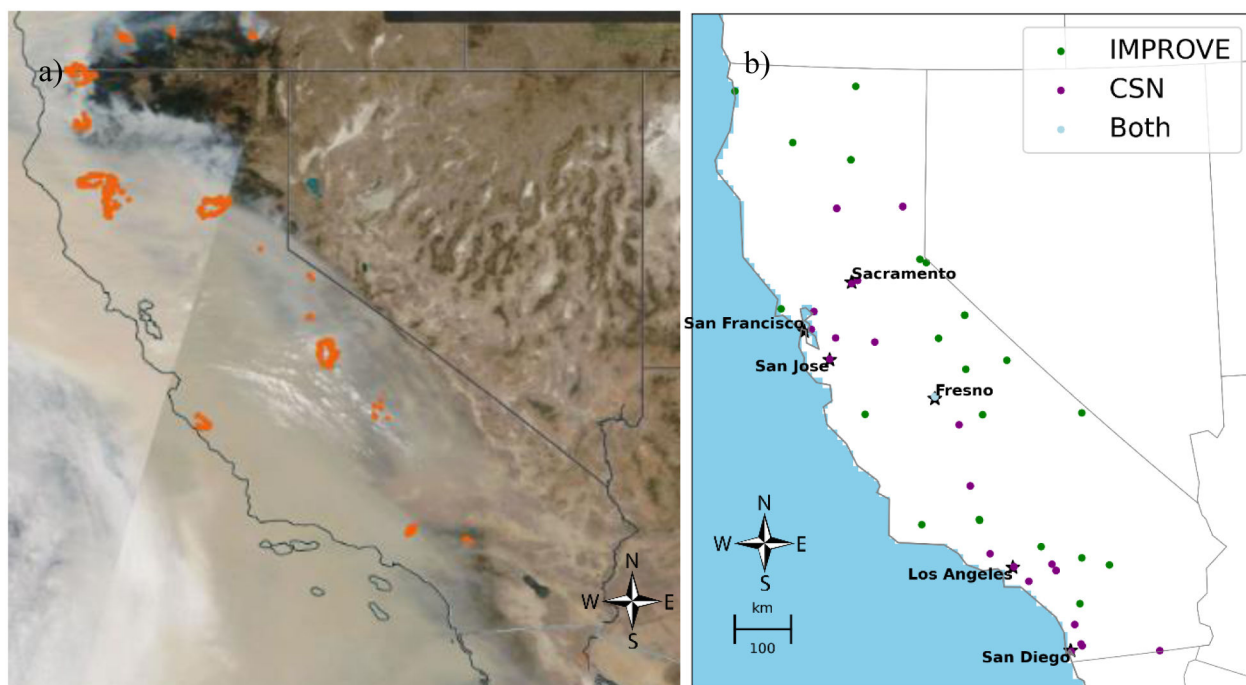


Fig. 1. A satellite image of smoke covering California on September 10, 2020, with the orange dots of active fires superimposed (a); and a map of Air Quality System PM_{2.5} speciation network monitors (both the Interagency Monitoring of Protected Visual Environments (IMPROVE) (29 monitors) and Chemical Speciation Network (CSN) (35 monitors)) active at some point during 2006–2018 (b).

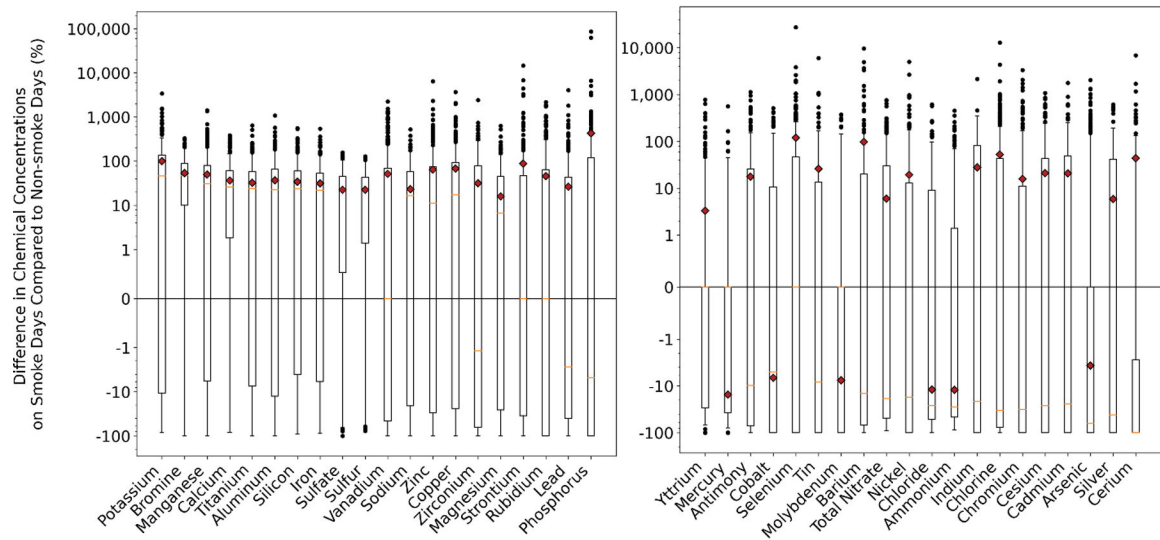


Fig. 2. Percent differences in chemical concentrations on smoke days compared to non-smoke days at each monitoring station, for each chemical, across all years (2006–2018). Each black dot represents a single monitoring station for one year. The red diamonds are the average values across all stations, all years. The red horizontal lines are the median values across all monitoring stations, all years.

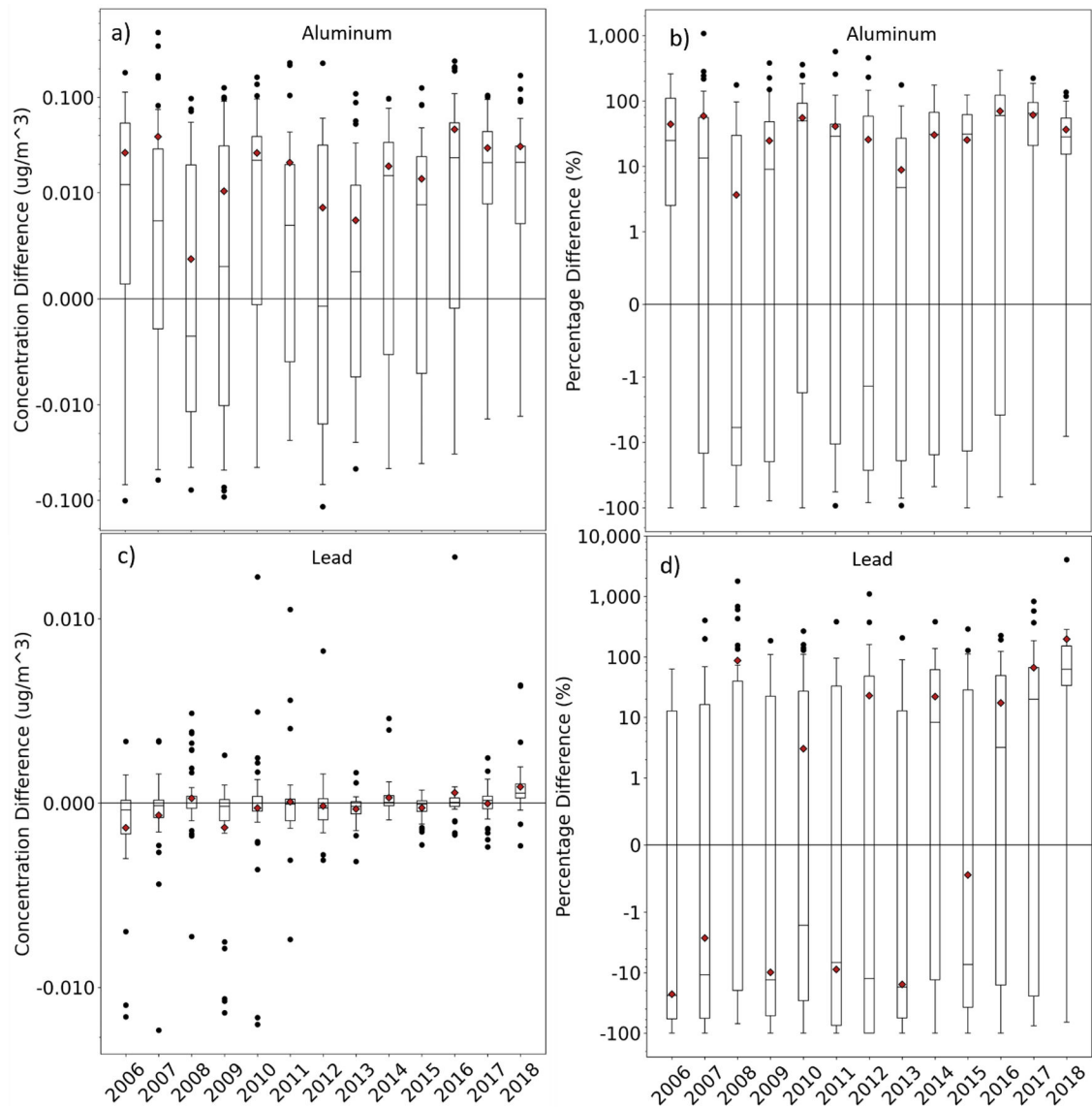


Fig. 3.

Absolute and percentage concentration differences on smoke days compared to non-smoke days at each monitoring station for aluminum (a and b) and lead (c and d). The red diamonds are the average differences across all stations for each year. The red lines are the average median differences across all stations for each year. The black dots are outliers beyond the 5th and 95th percentiles.

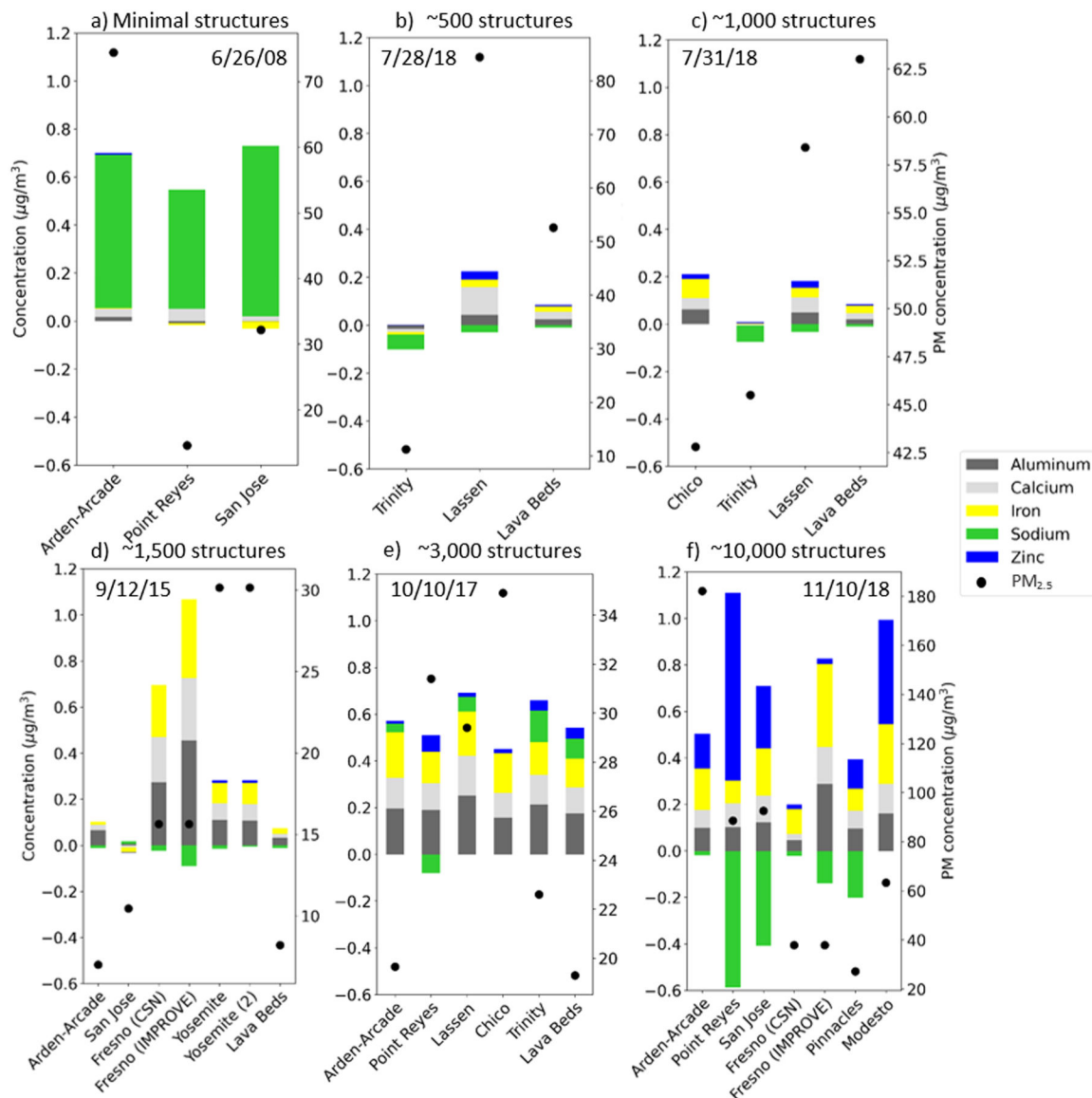


Fig. 4. Chemical concentrations (in $\mu\text{g}/\text{m}^3$) at smoke-impacted monitoring stations for six fire events in California: June 2008 Fires (a), the Carr Fire (b and c), the 2015 September Fires (Valley and Butte) (d), the October 2017 Fires (Tubbs, Atlas, Nuns, and Redwood Complex) (e), and the Camp Fire (f). Presented are the concentrations measured at each monitor on the fire event date noted in each panel minus the non-smoke day average concentration for each chemical at the corresponding station and year (April 1st through December 31st). Values are negative where the fire event concentration was exceeded by the corresponding non-smoke day average. Structures listed are approximate structures burned at time of measurement. The black dots are total $\text{PM}_{2.5}$ concentration (in $\mu\text{g}/\text{m}^3$) at each monitoring station.

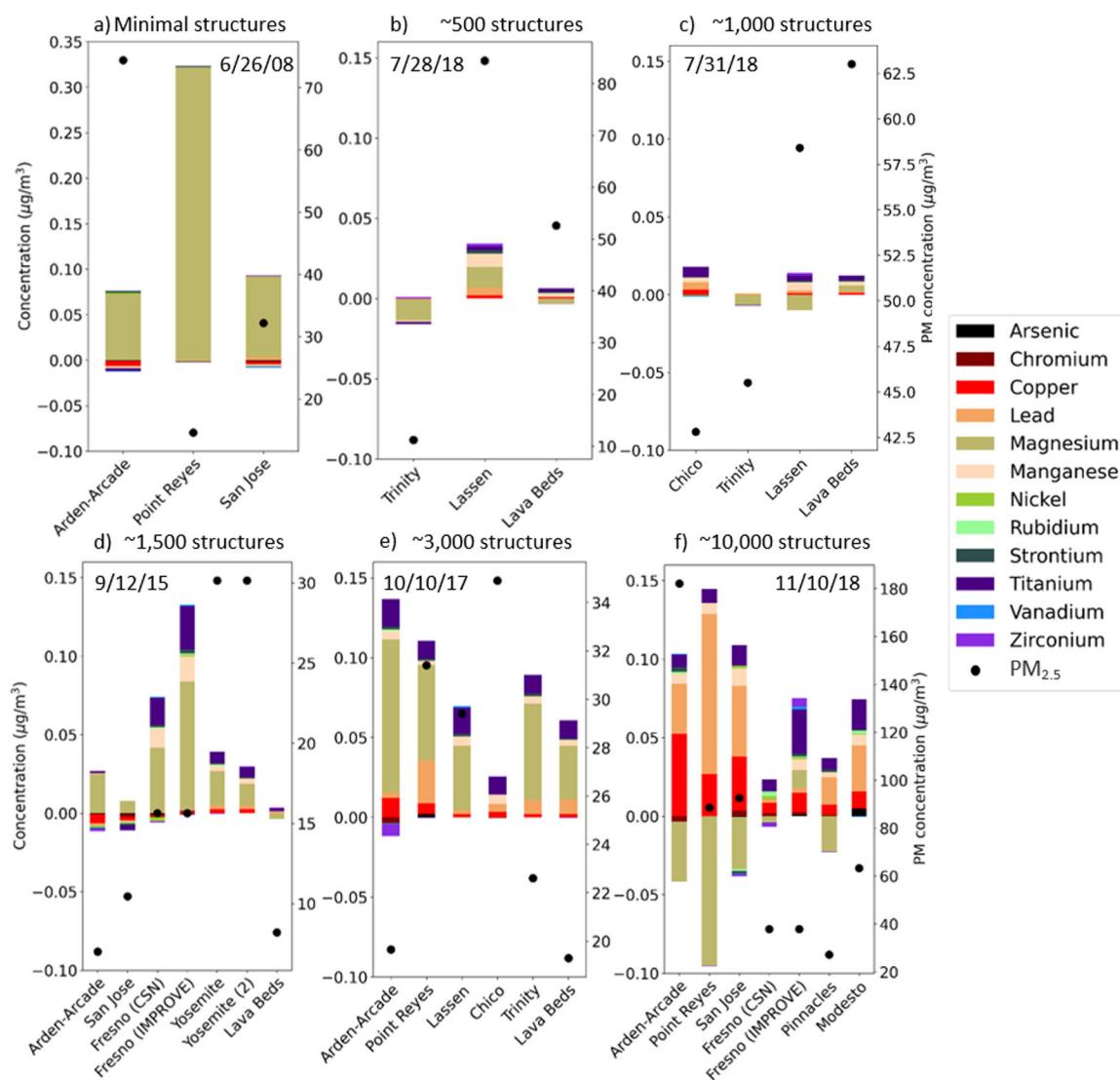


Fig. 5. Profile of trace chemical concentrations (in $\mu\text{g}/\text{m}^3$; totaling less than $0.5 \mu\text{g}/\text{m}^3$) at smoke-impacted monitoring stations for six fire events in California: June 2008 Fires (a), the Carr Fire (b and c), the 2015 September Fires (Valley and Butte) (d), the October 2017 Fires (Tubbs, Atlas, Nuns, and Redwood Complex) (e), and the Camp Fire (f). Presented are the concentrations measured at each monitor on the fire event date noted in each panel minus the non-smoke day average concentration for each chemical at the corresponding station and year (April 1st through December 31st). Values are negative where the fire event concentration was exceeded by the corresponding non-smoke day average. Structures listed are approximate structures burned at time of measurement. The black dots are total $\text{PM}_{2.5}$ concentration (in $\mu\text{g}/\text{m}^3$) at each monitoring station.