Environmental Science & Technology Letters

pubs.acs.org/journal/estlcu

Letter

Aged and Obscured Wildfire Smoke Associated with Downwind Health Risks

Published as part of Environmental Science & Technology Letters special issue "Wildland Fires: Emissions, Chemistry, Contamination, Climate, and Human Health".

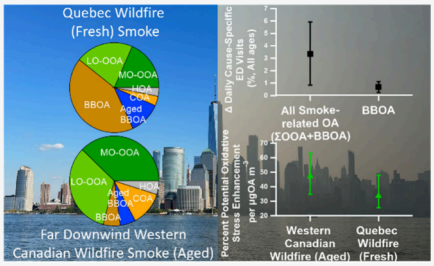
Taekyu Joo, Mitchell J. Rogers, Catelynn Soong, Tori Hass-Mitchell, Seulkee Heo, Michelle L. Bell, Nga L. Ng, and Drew R. Gentner*

Cite This: *Environ. Sci. Technol. Lett.* 2024, 11, 1340−1347

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Fine-mode particulate matter ($PM_{2.5}$) is a highly detrimental air pollutant, regulated without regard for chemical composition and a chief component of wildfire smoke. As wildfire activity increases with climate change, its growing continental influence necessitates multidisciplinary research to examine smoke's evolving chemical composition far downwind and connect chemical composition-based source apportionment to potential health effects. Leveraging advanced real-time speciated $PM_{2.5}$ measurements, including an aerosol chemical speciation monitor in conjunction with source apportionment and health risk assessments, we quantified the stark pollution enhancements during peak Canadian wildfire smoke transport to New York City over June 6−9, 2023. Interestingly, we also observed lower-intensity, but frequent, multiday wildfire smoke episodes during May−June 2023, which risk exposure misclassification as generic aged organic $PM_{2.5}$ via aerosol mass spectrometry given its extensive chemical transformations during 1 to 6+ days of transport. Total smoke-related organic $PM_{2.5}$ showed significant associations with asthma exacerbations, and estimates of in-lung oxidative stress were enhanced with chemical aging, collectively demonstrating elevated health risks with increasingly frequent smoke episodes. These results show that avoiding underestimated aged biomass burning $PM_{2.5}$ contributions, especially outside of peak episodes, necessitates real-time chemically resolved $PM_{2.5}$ monitoring to enable next-generation health studies, models, and policy under far-reaching wildfire impacts in the 21st century.



KEYWORDS: *wildland fires, organic aerosol, biomass burning, oxidative stress, long-range transport, health effects, source apportionment, potassium*

INTRODUCTION

Air quality has substantially improved in the United States (U.S.) over 50+ years of policies targeting anthropogenic sources.[1] Among air pollutants, fine particulate matter ($PM_{2.5}$) has the largest effects on premature mortality with contributions from both direct emissions and secondary production following the oxidation of gas- and particle-phase precursors.[2,3] Given its health effects, the U.S. $PM_{2.5}$ annual standard was recently lowered to 9 $\mu g\ m^{-3}$ but remains above the World Health Organization guideline of 5 $\mu g\ m^{-3}$. Simultaneously, exacerbated by climate change, wildfires have become increasingly prevalent sources of $PM_{2.5}$ and other air pollutants in the U.S.[4,5] The composition of wildfire and other biomass burning smoke has been increasingly investigated through multiple methods, including laboratory combustion experiments,[6,7] oxidation chamber studies,[8−11] and aircraft-based measurements of emissions and their downwind evolution.[12−15] These methods ranged from bulk characterization of chemical and physical properties to detailed chemical speciation.[16−18]

Wildfires have increased in intensity and burned acreage over the past four decades, with projected climate scenarios heightening the risk of more frequent and larger scale fires.[4,19] The impacts of biomass burning events, such as wildfires, are more often exerting continental influence, with evident, but poorly constrained, public health risks.[20−22] The June 6−9, 2023, wildfire transport event brought record-setting $PM_{2.5}$ levels to New York City (NYC), the U.S.'s largest city. These studies, focused on $PM_{2.5}$ enhancements during these days, showed associations with higher asthma-related health risks in NYC.[23−25] Chen et al.[23] reported 1.44 times higher asthma-related emergency department (ED) visits during these wildfire smoke days compared to the reference nonsmoke days.

Received: September 20, 2024
Revised: October 29, 2024
Accepted: October 29, 2024
Published: November 4, 2024

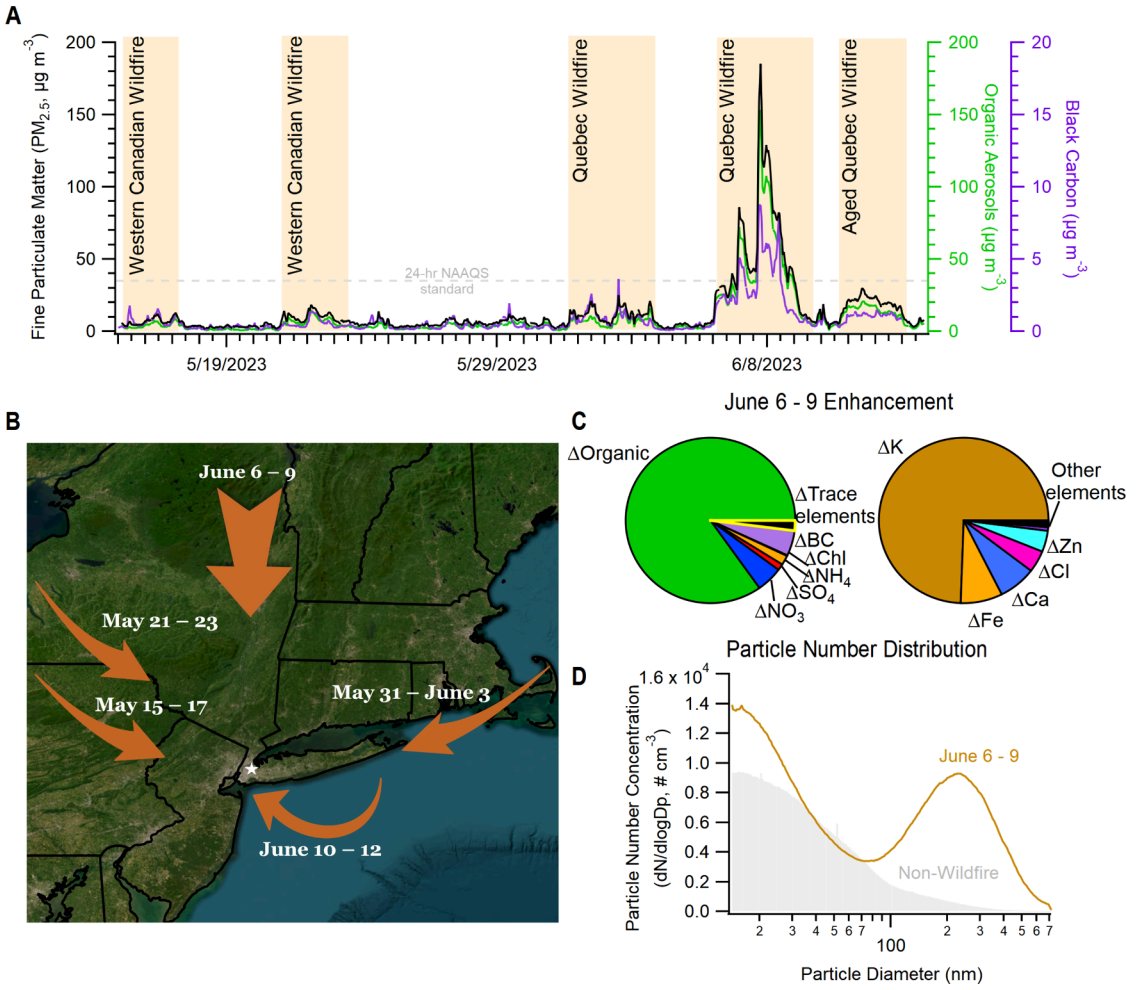


Figure 1. Air quality impacts from smoke transport to New York City. (A) Hourly fine particulate matter ($PM_{2.5}$) concentrations (i.e., sum of OA, inorganic aerosols, BC, and trace elements), with OA and BC concentrations shown across five major smoke transport events, including the June 6–9, 2023, transport of Quebec wildfire smoke. (B) Summary of plumes from May 15 to June 13, 2023, with more detailed descriptions of each episode's origin, arrival, and wind roses in Figures S2–S3. (C) June 6–9, 2023, enhancements of organic and inorganic (i.e., nitrate (NO_3), sulfate (SO_4), ammonium (NH_4), BC) PM components and associated trace elements, relative to nonfire influenced periods (note: total mass fraction in yellow wedge of left pie chart is speciated in the right pie chart). (D) Submicrometer size distributions of particle number concentrations during June 6–9, 2023, compared to nonwildfire periods.

Asthma ED visits were 1.03 times higher per 10 μg m^{-3} increase in daily wildfire-related $PM_{2.5}$ enhancements in Thurston et al.[25] However, the stark nature of the June 6–9 wildfire transport event overshadowed other more frequent, though less dramatic, wildfire smoke episodes.

To better understand the extent of wildfire smoke transport and its impact on public health, we use real-time data on PM composition to examine a series of five wildfire smoke episodes that influenced air quality in the eastern U.S. during May–June 2023. This combines chemically resolved PM data from multiple instruments to better identify and quantify the impacts of such events and avoid exposure misclassification. We then compare our source apportionment results to asthma-related hospital admission rates across the study period while also evaluating key metrics of PM composition that may modify its health effects to inform critical avenues of inquiry at the intersection of atmospheric and public health sciences.

METHODS AND MATERIALS

Using in situ $PM_{2.5}$ chemical composition data from the newly installed ASCENT (Atmospheric Science and Chemistry mEasurement NeTwork (Section S1)) site in Queens, NY (40.74 N, 73.82 W, 16 m a.s.l.), we examined five different major smoke transport events of varying intensity and chemical composition from May 15 to June 13, 2023. Wildfire influences (and origins) during this period were confirmed for each episode, along with background periods for comparison, via 144-h air-mass trajectories and satellite observations of fire activity (Section S2).[26] PM analysis occurred in real-time with 3–60 min resolution measurements of organic and inorganic aerosol components via mass spectrometry (Aerodyne aerosol chemical speciation monitor; ACSM), spectroscopy (Magee Scientific AE33 aethalometer), metals via energy dispersive X-ray fluorescence (Sailbri Cooper Xact 625i), and aerosol sizing via a scanning particle mobility sizer (TSI SMPS), with complementary gas-phase pollutant and meteorological measurements.

Source apportionment was conducted via positive matrix factorization (PMF; PET v.3.08) on organic aerosol (OA) spectra (m/z 12–100) obtained from the ACSM data while leveraging online metals data, as well as black/brown carbon (BC/BrC) data, to quantify the contributions of transported

https://doi.org/10.1021/acs.estlett.4c00785
Environ. Sci. Technol. Lett. 2024, 11, 1340–1347

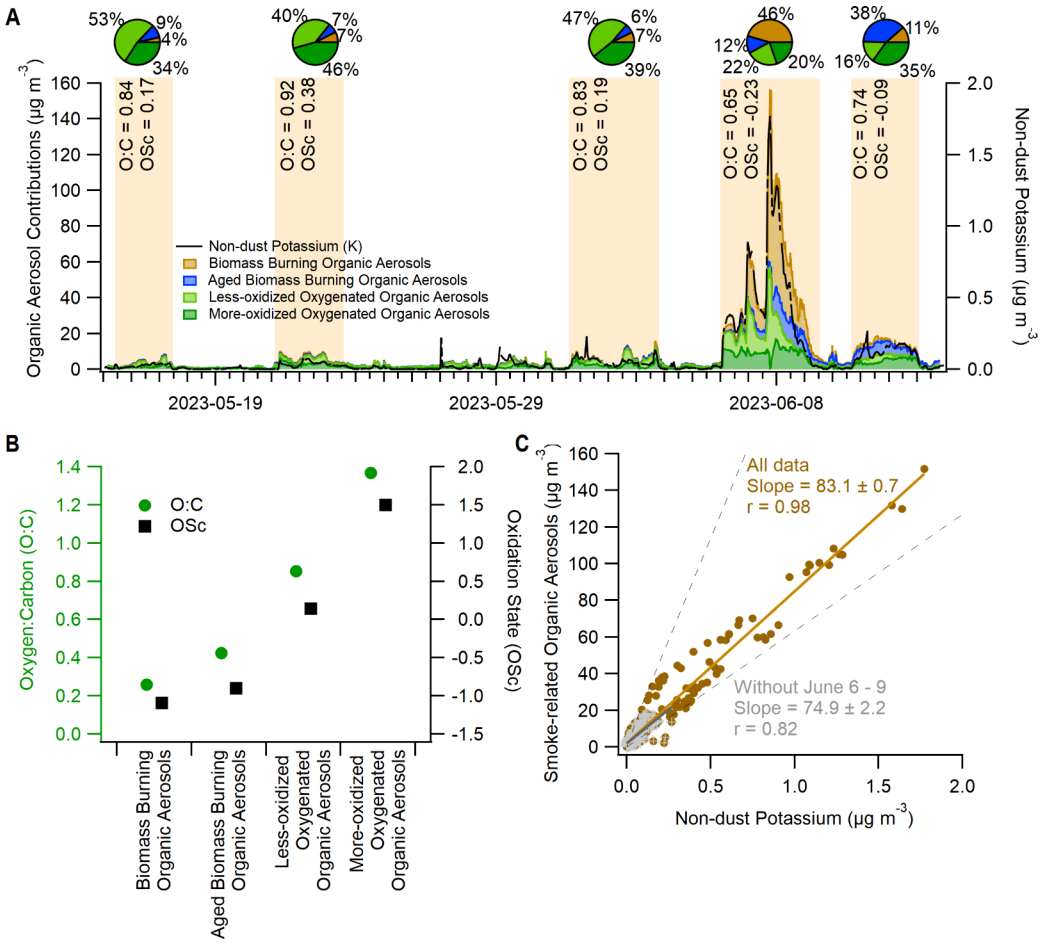


Figure 2. Transported smoke observed predominantly as OOA with the fraction of evident biomass burning-related OA varying between fire events. (A) The influence of transported smoke detected across different aerosol types (i.e., factors) observed as BBOA, aged-BBOA, and OOA factors with (B) increasing average oxygen-to-carbon ratios (O:C) and oxidation states (OSc), which together capture the contributions of OA from transported smoke during the study period. (C) The sums of smoke-related enhancements in these four OA types were best correlated with nondust potassium, during June 6–9, 2023, and across the other smoke events. Black dashed lines signify the 2σ range of μg μgK^{-1} ratios during all wildfire smoke transport episodes. Contributions of cooking- and hydrocarbon-related OA can be found in Figure S5.

smoke on OA. Following the approach of Zhang et al.,[27] six OA factors (i.e., hydrocarbon-like OA, cooking OA, biomass burning OA (BBOA), aged-BBOA, less-oxidized oxygenated OA (LO-OOA), and more-oxidized OOA (MO-OOA)) were identified from the PMF analysis, and the uncertainties were examined via 100 bootstrapping runs (Section S3). We note that the study period enabled us to examine smoke-related contributions to LO-OOA and MO-OOA components before hotter summertime temperatures brought temperature-dependent OOA enhancements from other sources.[28] Nondust potassium associated with smoke transport was determined by subtracting dust-related potassium determined from five other mineral dust species (Ca, Fe, Ti, Cu, Ba) using linear regression equations obtained during background periods (Section S4).[29,30]

Our epidemiological analysis examined associations between PM components and daily emergency department (ED) visits for asthma-related symptoms, including asthma, wheezing, complaints in the airway, or chronic obstructive pulmonary disorder, using EpiQuery–Syndromic Surveillance data for NYC.[31] We focused on asthma-related symptoms as wildfire smoke has been associated with asthma hospitalization and asthma emergency department (ED) visits in previous studies including those focusing on the recent Canadian wildfire (Section S5).[23,32] Separately, potential oxidative stress enhancements were estimated for each smoke event via a Monte Carlo approach utilizing prior studies with assay-based observations of oxidative stress associated with OA oxidation state and PMF-derived source factors (Section S6).[33−38] Additional methods details are described in Supporting Information Sections S1–S6.

RESULTS

June 6–9, 2023, Smoke Transport from the Quebec Wildfire. Smoke transport from the Quebec wildfire was greatest during June 6–9, 2023, when smoke brought stark regional changes in visibility extending well beyond the metro NYC area and record-setting,[39] reported peak $PM_{2.5}$ concentrations (previous daily $PM_{2.5}$ record: 86 μg m^{-3}). These exceeded 24-h EPA standards in NYC (Figure 1A, B) and even approached the prior wildfire-induced daily averaged $PM_{2.5}$ levels in major California cities over the 21st century (Figure S1), where wildfire influence on $PM_{2.5}$ has been more severe than the northeastern U.S.[4] This 3-day concentrated plume with $PM_{2.5}$ reaching an hourly maximum of 185 μg m^{-3} increased levels of many, but not all air pollutants, including 2500%, 2000%, 1140%, 686%, and 511% increases in average

https://doi.org/10.1021/acs.estlett.4c00785
Environ. Sci. Technol. Lett. 2024, 11, 1340−1347

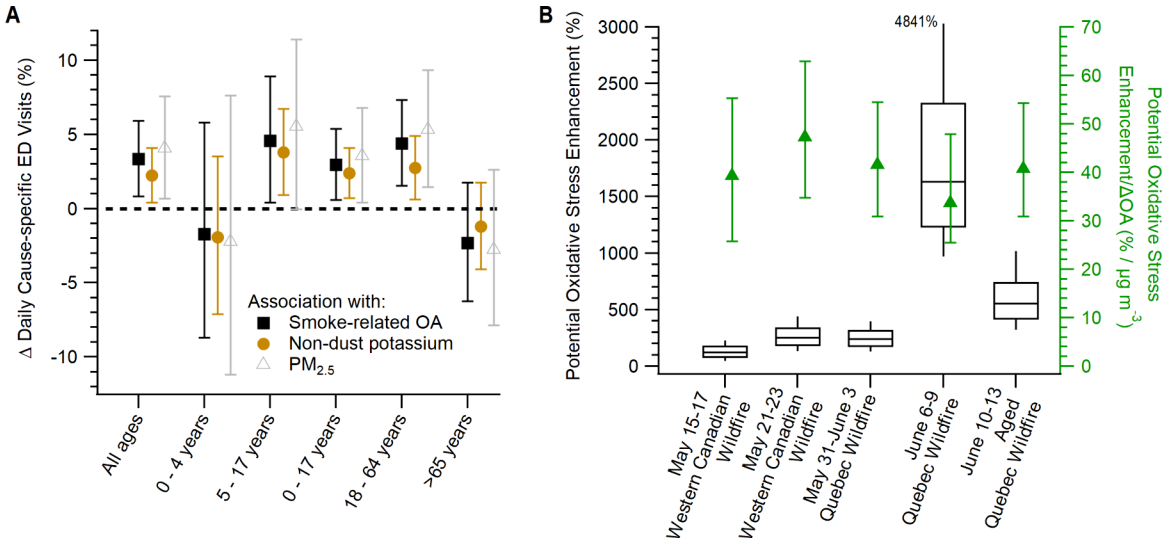


Figure 3. Observed health effects associated with smoke transport and potential oxidative stress enhancements across study period. (A) Observed association between asthma emergency department (ED) visits and smoke-related OA (i.e., sum of four factors) over May 15 to June 13, 2023, as well as nondust potassium as a confirmational marker of both "fresh" and aged smoke. Epidemiological results are shown as the % change in ED visits for an interquartile range (IQR) increase in concentrations with vertical lines displaying 95% confidence intervals (CI). It also shows the association of ED visits with $PM_{2.5}$, which is in line with prior studies summarized in Table S6, confirming that our epidemiologic model was valid to assess exposure−response associations for chemical components of PM during the study period. (B) Estimates of potential oxidative stress enhancements (left axis) for each of the five smoke transport events compared to background conditions (May 25−26 and June 4−5), determined via Monte Carlo analysis ($N = 1 \times 10^6$) using available studies. Shown alongside the concentration-normalized potential oxidative stress enhancement (right axis, error bar refers to 25 and 75 percentile values calculated based on box-whisker plot results), more-aged smoke shows greater potential oxidative stress per OA mass, on average, for the episodes outside of June 6−9.

$PM_{2.5}$, OA, BC, formaldehyde, and trace elements concentrations, respectively (Figure 1A−C, Table S1), relative to nonsmoke periods (May 25−26 and June 4−5). The $PM_{2.5}$ in the plume was predominantly composed of OA (85%) with varying enhancements in noncarbonaceous inorganic aerosol components (215%−2240%; Figure 1C, Table S1) and a pronounced bimodal particle diameter distribution (Figure 1D), including sizes that enable deep lung penetration.[40]

Capturing the Broader Influence of Aged Wildfire Smoke. While the June 6−9 smoke transport event brought the most striking deterioration in air quality, our high temporal resolution observations show that there were several other pollution episodes attributed to smoke transport, with average $PM_{2.5}$ concentrations ranging 7.9−20 $\mu g\ m^{-3}$ (Figures 1A; Table S1). The location of these wildfires spanned from northwestern Canada to Quebec with average transport times (i.e., atmospheric ages) ranging from 2 to 4 days (Figures S2 and S4; Table S2).

Given the complex mix of sources and chemical processes influencing urban air, accurately estimating the contributions of biomass burning is a critical challenge for research and policy to protect public health. Source apportionment of aerosol mass spectrometry data is frequently used to quantify contributions from BBOA and other OA source types (Figure S5).[28,41−43] However, in this study, outside of the major Quebec smoke transport episode, aerosol mass spectrometry alone loses its ability to identify the extent of wildfire smoke after long-distance oxidative aging diminishes the characteristic spectral peaks of BBOA (i.e., m/z 60, 73; levoglucosan fragments), rendering it less distinguishable from other-source originated OOA with elevated m/z 44 abundance (Figure S6).[16,44,45]

Smoke transport to NYC was observed across four OA types—two BBOA-like factors and two OOA factors, with the majority of $PM_{2.5}$ [i.e., 70.4% (42−87%)] appearing as OOA (Figure 2A, B). Concentration enhancements in the sum of these four factors was, on average, 13.9 $\mu g\ m^{-3}$ ± 6.0 $\mu g\ m^{-3}$ (3.7−40.6 $\mu g\ m^{-3}$) during the five smoke events relative to the background periods. Enhancements in LO-OOA and MO-OOA ranged 160−237% and 112−592%, respectively, across the four relatively smaller smoke transport events, and their chemical composition varied with plume age (Figure 2A, Table S3). Only the June 6−9 episode primarily consisted of "typical" BBOA (46%) and had shorter transport times compared to the other identified smoke events (48 h on average). Several days later, meteorological conditions brought more-aged Quebec wildfire smoke from over the ocean with a greater extent of aged-BBOA and OOA (Figure 2, Figures S2 and S4; average transport time of 100 h). A comparison of the smoke events studied here demonstrates that the smoke episodes which were more diluted during transit (i.e., first−third events; average transport times of 67, 86, 71 h) had a greater extent of oxidation despite having a similar range of transport times as the less-oxidized fifth event (Figure 2A, Figure S4; Table S2). This is consistent with studies showing photochemical aging can accelerate with wildfire plume dilution, enhancing exposure to atmospheric radicals,[12] and diminishing semi-volatile biomass burning tracers in OA.[44]

Due to the photochemically aged features of smoke reaching NYC, our real-time trace element measurements were key to identifying and constraining wildfire influences, especially for low-intensity or long-range aged smoke.[45] While other elements were also enhanced during wildfire events (e.g., Cl, Mn, Zn) (Figure 1C, Table S4), potassium is typically abundant in biomass burning aerosol emissions[46] and has been used to ascribe $PM_{2.5}$ to wildfires.[45,47−49] Nondust potassium concentrations calculated for this study exhibited the strongest correlations with smoke-related OA (r = 0.98)

https://doi.org/10.1021/acs.estlett.4c00785
Environ. Sci. Technol. Lett. 2024, 11, 1340−1347

(Figure 2C) compared to other biomass burning-related pollutants (e.g., BC, CO, NO_x; Figure S7A−C) and demonstrated consistent enhancements during periods when air-mass trajectories confirmed wildfire influences. While other pollutants are also associated with wildfire smoke, the results of this study exemplify dust-corrected potassium's pronounced utility as a reliable indicator of transported smoke across diverse spatial scales, combustion conditions, and age. This is not only due to the loss of key BBOA mass spectral features with aging, but also since BC/BrC, CO, or NO_x can be biased by urban source contributions or incur losses due to photobleaching (i.e., for BrC), which varies with plume age.[50]

The composition of wildfire smoke has been shown to vary with fuel type, fire size, temperature, combustion efficiency (e.g., smoldering vs flaming), and interactions with background aerosols.[51−54] Yet, nondust potassium captures contributions from both fresh biomass burning-related OA and highly oxidized biomass burning-related OA, exhibiting stronger correlations ($r \geq 0.82$) compared to the other wildfire-related pollutants (Figure S7A−C) with a slope of 83.1 ± 0.7 $\mu g\ \mu g\ K^{-1}$ and a 2σ range of 63.5−253.3 $\mu g\ \mu g\ K^{-1}$ (Figure 2C). Thus, real-time metals data provide powerful opportunities to identify, validate, and quantify less-evident biomass burning transport events, yet other sources (e.g., mineral dust, coal combustion) must be considered when quantifying wildfire influence.

Downwind Health Risks of Dilute and Aged Wildfire Smoke. Over the 1 to 6+ days of oxidative aging during transport (Figure S4, Table S2), the OA underwent considerable transformations (Figure 2, Figure S6), and this can have important implications for its health risks. First, the depletion of BBOA's molecular signatures outside of the major June 6−9 episode poses the risk of exposure misclassification of far downwind smoke as indistinct OOA without valuable nonreactive covariate data, specifically nondust potassium. Epidemiological analysis spanning the repeated wildfire smoke episodes identified statistically significant associations between daily emergency department (ED) visits for asthma and concentrations of total smoke-related OA, and also with nondust potassium (Figures 3A, Table S5). For example, an interquartile (IQR) increase in smoke-related OA and nondust potassium was associated with a 3.35% and 2.23% increase in risk of asthma ED visits (95% confidence intervals (CI): 0.83%−5.93% and 0.40%−4.08%), respectively, similar in magnitude to relative risks increases from prior $PM_{2.5}$ assessments.[55,56] If such health risks are evaluated based on the average ED visit numbers (203 visits day^{-1}) during the analysis period (May 15−June 13, 2023), approximately 6.9 (95% CI: 1.6, 11.7) more cause-specific ED visits day^{-1} and 2068 (95% CI: 49.0, 350.3) more cause-specific ED visits throughout the study period were estimated for an IQR increase in smoke-related OA (e.g., 4.74). Given the prominence of smoke-related OA during the study period and its covariance with $PM_{2.5}$, total $PM_{2.5}$ mass concentrations were similarly strongly associated with daily asthma ED visits (Figure 3a). The consistency with prior studies validates the robustness of our epidemiologic model (Table S6, Section S5).[23−25,32] Though, we note that prior analyses were focused on the major smoke event (i.e., June 6−8) and examined $PM_{2.5}$ alone. Here, we now associate health effects specifically with the sum of smoke-related OA as well as nondust potassium as a well-correlated independent marker of biomass burning (Figure 3A), regardless of plume age. Moreover, the sum of smoke-associated OA had a greater estimated health effect than that of BBOA alone (Table S5). We note that the epidemiologic analysis in this study was performed within a relatively shorter period than typical studies with limited considerations for lagged effects, causing uncertainties in some age groups.[57]

Second, while total $PM_{2.5}$ mass concentrations remain important for evaluating health risks, multiple laboratory and epidemiological studies have observed greater health effects for SOA compared to other aerosol components (e.g., $(NH_4)_2SO_4$, NH_4NO_3, and primary OA). This includes cardiovascular premature mortality risks and enhanced oxidative stress via cellular and acellular assays.[3,33−38] There is also evidence for increased oxidative stress from more-aged, oxidized aerosols with greater reactive oxygen species production in the respiratory track.[33] Across the five major smoke transport episodes studied here, our Monte Carlo analysis consistently showed pronounced increases in potential oxidative stress of 124−1631% (median enhancements) with variations constrained using the available literature while considering uncertainties (Figure 3B, Figure S8). This enhancement in potential oxidative stress was recently confirmed in Europe by Vasilakopoulou et al.[45] who observed 470−3730% enhancements in dithiothreitol assays concurrent with downwind wildfire-associated enhancements in OOA and potassium in Europe. Additionally, while the smoke transported to NYC often lost its molecular signatures, the more-aged aerosols present a greater potential oxidative stress per unit mass on average (Figure 3B), which could be further exacerbated by coincident wildfire- and dust-related enhancements of redox-active metals (i.e., Mn, Fe, Cu) across the smoke transport events (Table S4).[33,38,58]

DISCUSSION

Increased wildfire activity is anticipated to worsen air quality under a changing climate, contributing an increasing fraction of ambient $PM_{2.5}$. However, its human health effects remain uncertain and potentially underestimated, which is further complicated by multiday downwind transformations and potential exposure misclassification of less-evident $PM_{2.5}$ enhancements. Acute effects were observed in epidemiological associations (Figure 3A). Yet, chronic effects of increasingly frequent low-level exposures to more-aged, dilute smoke represent a major concern and research priority given the enhanced potential oxidative stress with highly aged smoke (Figure 3B) and repeated exposures, even far downwind.

Cross-disciplinary research linking atmospheric sciences and public health communities is necessary to address pressing issues. This includes accurately categorizing pollutant contributions, especially $PM_{2.5}$, from wildfires and other sources to empower next-generation epidemiological studies that advance our understanding of source-specific and speciated PM-specific health effects. The $PM_{2.5}$ source apportionment strategies employed here avoid undercounting biomass burning contributions across the continuum of plume ages and serve as key inputs to epidemiological studies. These future studies should also examine the health effects of different fire types (e.g., fuel type and combustion conditions), downwind plume transformations (e.g., oxidation conditions and SOA formation), associated hazardous volatile−semivolatile gas-phase pollutants (e.g., formaldehyde), the health impacts of multiple stressors (i.e., repeated exposure to wildfire smoke over multiple events), and different lag times. Doing so necessitates real-

https://doi.org/10.1021/acs.estlett.4c00785
Environ. Sci. Technol. Lett. 2024, 11, 1340−1347

time trace metal measurements with corrections for other source types (e.g., dust) to effectively attribute otherwise indistinct wildfire influences. This will also facilitate model validation, especially with greater biomass burning contributions to background aerosol levels,[45] which are increasingly important to accurately constrain with recent revisions to the U.S. $PM_{2.5}$ standard.

Epidemiological research demonstrates that PM's chemical composition influences its health risks and specific effects.[59] However, the most harmful PM characteristics are not well established, though more-oxidized secondary aerosols present likely exacerbating factors.[3,33,36] Epidemiological studies to date generally lack chemical or spatiotemporal complexity and are typically limited to total $PM_{2.5}$ measurements with additional filter-based speciation, which has sparse temporal resolution (weekly or semiweekly), following existing monitoring network procedures. In other cases, health studies instead use modeled exposure estimates, though a lack of sufficient speciated measurements hinders their validation. Although a growing number of health studies instead use modeled exposure estimates, a lack of sufficient speciated measurements hinders their validation. While previous health studies examined individual source-specific events via total $PM_{2.5}$ concentration changes (e.g., Table S6), here, routine chemical speciation allowed us to target wildfire-related OA and evaluate source-based health effects. This can be furthered by long-term, continuous, and accurate monitoring of speciated $PM_{2.5}$, possibly supplemented by routine potential oxidative stress measurements to enable multipollutant epidemiological studies across different populations and health outcomes. The ensuing scientific evidence on which sources and chemical/physical particle characteristics (e.g., age, oxidation) are most harmful could aid effective decision-making to protect public health, especially as $PM_{2.5}$ reductions have largely stagnated at levels with continued health risks.[28,60]

Summer 2023 established a prominent role for transported wildfire smoke exposure in NYC and other populous areas typically insulated from wildfire's worst air quality impacts—raising timely questions about effectively achieving cobenefits for air, health, and climate. The path forward necessitates multidisciplinary science employing next-generation approaches to develop policies that address the public health burden of both peak and unapparent smoke episodes expected over the coming decades.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made publicly available via the ASCENT data repository (https://ascent.research.gatech.edu/database) and are also available by contacting the corresponding author..

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.4c00785.

Additional details on measurements, methods, and results, including supplemental figures and tables to support the main text (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Drew R. Gentner − *Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States*; Email: drew.gentner@yale.edu

Authors

Taekyu Joo − *Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States; Department of Earth and Environmental Sciences, Korea University, Seoul 02841, South Korea*; orcid.org/0000-0002-8252-4232

Mitchell J. Rogers − *Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States*

Catelynn Soong − *Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States;* Present Address: Department of Earth System Science, University of California, Irvine, California 92697, United States

Tori Hass-Mitchell − *Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06511, United States*; orcid.org/0000-0002-8588-0769

Seulkee Heo − *School of the Environment, Yale University, New Haven, Connecticut 06511, United States*; orcid.org/0000-0002-0786-5002

Michelle L. Bell − *School of the Environment, Yale University, New Haven, Connecticut 06511, United States; Interdisciplinary Program in Precision Public Health, Department of Public Health Sciences, Graduate School of Korea University, Seoul 02841, South Korea*

Nga L. Ng − *School of Chemical and Biomolecular Engineering, School of Earth and Atmospheric Sciences, and School of Civil and Environmental Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States*; orcid.org/0000-0001-8460-4765

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.estlett.4c00785

Notes

This paper has been previously published to Chemrxiv, an archive service for unpublished preprints in chemistry and related areas. The preprint can be cited as Joo, T.; Rogers, M. J.; Soong, C.; Hass-Mitchell, T.; Heo, S.; Bell, M. L.; Ng, N. L.; Gentner, D. R. Aged and obscured wildfire smoke associated with downwind health risks. ChemRxiv Preprint, 2024. DOI: 10.26434/chemrxiv-2024-6zb16/ This content is a preprint and has not been peer-reviewed.

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the National Science Foundation (AGS-2131914) and New York State Research and Development Authority (NYSERDA; Agreement No. 183866) for financial support. Any opinions expressed in this article do not necessarily reflect those of NYSERDA or the State of New York. We also thank the ASCENT steering committee and research team for their assistance with establishing the instrumentation at the site, and the New York State Department of Environmental Conservation for site access, support, and supporting data, including gaseous formaldehyde. The meteorology data from the Queens College site was made possible by the New York State (NYS) Mesonet. Original funding for the NYS Mesonet was provided by Federal Emergency Management Agency Grant FEMA-4085-DR-NY, with the continued support of the

NYS Division of Homeland Security and Emergency Services; the State of New York; the Research Foundation for the State University of New York (SUNY); the University at Albany; the Atmospheric Sciences Research Center (ASRC) at the University at Albany; and the Department of Atmospheric and Environmental Sciences (DAES) at the University at Albany.

REFERENCES

(1) Parrish, D. D.; Singh, H. B.; Molina, L.; Madronich, S. Air quality progress in North American megacities: A review. *Atmos. Environ.* **2011**, *45* (39), 7015−7025.
(2) Murray, C. J. L.; Aravkin, A. Y.; Zheng, P.; Abbafati, C.; Abbas, K. M.; Abbasi-Kangevari, M.; Abd-Allah, F.; Abdelalim, A.; Abdollahi, M.; Abdollahpour, I.; et al. Global burden of 87 risk factors in 204 countries and territories, 1990−2019: a systematic analysis for the Global Burden of Disease Study 2019. *Lancet* **2020**, *396* (10258), 1223−1249.
(3) Pye, H. O. T.; Ward-Caviness, C. K.; Murphy, B. N.; Appel, K. W.; Seltzer, K. M. Secondary organic aerosol association with cardiorespiratory disease mortality in the United States. *Nat. Commun.* **2021**, *12* (1), 7215.
(4) Burke, M.; Childs, M. L.; de la Cuesta, B.; Qiu, M.; Li, J.; Gould, C. F.; Heft-Neal, S.; Wara, M. The contribution of wildfire to PM2.5 trends in the USA. *Nature* **2023**, *622* (7984), 761−766.
(5) Bourgeois, I.; Peischl, J.; Neuman, J. A.; Brown, S. S.; Thompson, C. R.; Aikin, K. C.; Allen, H. M.; Angot, H.; Apel, E. C.; Baublitz, C. B.; et al. Large contribution of biomass burning emissions to ozone throughout the global remote troposphere. *Proc. Natl. Acad. Sci. U. S. A.* **2021**, *118* (52), No. e2109628118.
(6) Koss, A. R.; Sekimoto, K.; Gilman, J. B.; Selimovic, V.; Coggon, M. M.; Zarzana, K. J.; Yuan, B.; Lerner, B. M.; Brown, S. S.; Jimenez, J. L.; et al. Non-methane organic gas emissions from biomass burning: identification, quantification, and emission factors from PTR-ToF during the FIREX 2016 laboratory experiment. *Atmos. Chem. Phys.* **2018**, *18* (5), 3299−3319.
(7) Hatch, L. E.; Luo, W.; Pankow, J. F.; Yokelson, R. J.; Stockwell, C. E.; Barsanti, K. C. Identification and quantification of gaseous organic compounds emitted from biomass burning using two-dimensional gas chromatography−time-of-flight mass spectrometry. *Atmos. Chem. Phys.* **2015**, *15* (4), 1865−1899.
(8) Coggon, M. M.; Lim, C. Y.; Koss, A. R.; Sekimoto, K.; Yuan, B.; Gilman, J. B.; Hagan, D. H.; Selimovic, V.; Zarzana, K. J.; Brown, S. S.; et al. OH chemistry of non-methane organic gases (NMOGs) emitted from laboratory and ambient biomass burning smoke: evaluating the influence of furans and oxygenated aromatics on ozone and secondary NMOG formation. *Atmos. Chem. Phys.* **2019**, *19* (23), 14875−14899.
(9) Lim, C. Y.; Hagan, D. H.; Coggon, M. M.; Koss, A. R.; Sekimoto, K.; de Gouw, J.; Warneke, C.; Cappa, C. D.; Kroll, J. H. Secondary organic aerosol formation from the laboratory oxidation of biomass burning emissions. *Atmos. Chem. Phys.* **2019**, *19* (19), 12797−12809.
(10) Joo, T.; Rivera-Rios, J. C.; Takeuchi, M.; Alvarado, M. J.; Ng, N. L. Secondary Organic Aerosol Formation from Reaction of 3-Methylfuran with Nitrate Radicals. *ACS Earth and Space Chemistry* **2019**, *3* (6), 922−934.
(11) Joo, T.; Machesky, J. E.; Zeng, L.; Hass-Mitchell, T.; Weber, R. J.; Gentner, D. R.; Ng, N. L. Secondary Brown Carbon Formation From Photooxidation of Furans From Biomass Burning. *Geophys. Res. Lett.* **2024**, *51* (1), No. e2023GL104900.
(12) Xu, L.; Crounse, J. D.; Vasquez, K. T.; Allen, H.; Wennberg, P. O.; Bourgeois, I.; Brown, S. S.; Campuzano-Jost, P.; Coggon, M. M.; Crawford, J. H.; et al. Ozone chemistry in western U.S. wildfire plumes. *Science Advances* **2021**, *7* (50), No. eabl3648.
(13) Hayden, K. L.; Li, S. M.; Liggio, J.; Wheeler, M. J.; Wentzell, J. J. B.; Leithead, A.; Brickell, P.; Mittermeier, R. L.; Oldham, Z.; Mihele, C. M.; et al. Reconciling the total carbon budget for boreal forest wildfire emissions using airborne observations. *Atmos. Chem. Phys.* **2022**, *22* (18), 12493−12523.
(14) Jolleys, M. D.; Coe, H.; McFiggans, G.; Capes, G.; Allan, J. D.; Crosier, J.; Williams, P. I.; Allen, G.; Bower, K. N.; Jimenez, J. L.; et al. Characterizing the Aging of Biomass Burning Organic Aerosol by Use of Mixing Ratios: A Meta-analysis of Four Regions. *Environ. Sci. Technol.* **2012**, *46* (24), 13093−13102.
(15) Permar, W.; Wang, Q.; Selimovic, V.; Wielgasz, C.; Yokelson, R. J.; Hornbrook, R. S.; Hills, A. J.; Apel, E. C.; Ku, I. T.; Zhou, Y.; et al. Emissions of Trace Organic Gases From Western U.S. Wildfires Based on WE-CAN Aircraft Measurements. *Journal of Geophysical Research: Atmospheres* **2021**, *126* (11), No. e2020JD033838.
(16) Hodshire, A. L.; Akherati, A.; Alvarado, M. J.; Brown-Steiner, B.; Jathar, S. H.; Jimenez, J. L.; Kreidenweis, S. M.; Lonsdale, C. R.; Onasch, T. B.; Ortega, A. M.; et al. Aging Effects on Biomass Burning Aerosol Mass and Composition: A Critical Review of Field and Laboratory Studies. *Environ. Sci. Technol.* **2019**, *53* (17), 10007−10022.
(17) Liang, Y.; Weber, R. J.; Misztal, P. K.; Jen, C. N.; Goldstein, A. H. Aging of Volatile Organic Compounds in October 2017 Northern California Wildfire Plumes. *Environ. Sci. Technol.* **2022**, *56* (3), 1557−1567.
(18) Palm, B. B.; Peng, Q.; Fredrickson, C. D.; Lee, B. H.; Garofalo, L. A.; Pothier, M. A.; Kreidenweis, S. M.; Farmer, D. K.; Pokhrel, R. P.; Shen, Y.; et al. Quantification of organic aerosol and brown carbon evolution in fresh wildfire plumes. *Proc. Natl. Acad. Sci. U. S. A.* **2020**, *117*, No. 202012218.
(19) Abatzoglou, J. T.; Williams, A. P. Impact of anthropogenic climate change on wildfire across western US forests. *Proc. Natl. Acad. Sci. U. S. A.* **2016**, *113* (42), 11770−11775.
(20) Rogers, H. M.; Ditto, J. C.; Gentner, D. R. Evidence for impacts on surface-level air quality in the northeastern US from long-distance transport of smoke from North American fires during the Long Island Sound Tropospheric Ozone Study (LISTOS) 2018. *Atmos. Chem. Phys.* **2020**, *20* (2), 671−682.
(21) Wu, Y.; Arapi, A.; Huang, J.; Gross, B.; Moshary, F. Intra-continental wildfire smoke transport and impact on local air quality observed by ground-based and satellite remote sensing in New York City. *Atmos. Environ.* **2018**, *187*, 266−281.
(22) O'Dell, K.; Bilsback, K.; Ford, B.; Martenies, S. E.; Magzamen, S.; Fischer, E. V.; Pierce, J. R. Estimated Mortality and Morbidity Attributable to Smoke Plumes in the United States: Not Just a Western US Problem. *GeoHealth* **2021**, *5* (9), No. e2021GH000457.
(23) Chen, K.; Ma, Y.; Bell, M. L.; Yang, W. Canadian Wildfire Smoke and Asthma Syndrome Emergency Department Visits in New York City. *JAMA* **2023**, *330* (14), 1385−1387.
(24) McArdle, C. E.; Dowling, T. C.; Carey, K.; DeVies, J.; Johns, D.; Gates, A. L.; Stein, Z.; Santen, K. L. v.; Radhakrishnan, L.; Kite-Powell, A., et al.. *Asthma-Associated Emergency Department Visits During the Canadian Wildfire Smoke Episodes — United States, April−August 2023*; MMWR and Morbidity and Mortality Weekly Report; U.S. Department of Health and Human Services, 2023; pp 926−9352.
(25) Thurston, G.; Yu, W.; Luglio, D. An Evaluation of the Asthma Impact of the June 2023 New York City Wildfire Air Pollution Episode. *American Journal of Respiratory and Critical Care Medicine* **2023**, *208* (8), 898−900.
(26) Stein, A. F.; Draxler, R. R.; Rolph, G. D.; Stunder, B. J. B.; Cohen, M. D.; Ngan, F. NOAA's HYSPLIT Atmospheric Transport and Dispersion Modeling System. *Bulletin of the American Meteorological Society* **2015**, *96* (12), 2059−2077.
(27) Zhang, Q.; Jimenez, J. L.; Canagaratna, M. R.; Ulbrich, I. M.; Ng, N. L.; Worsnop, D. R.; Sun, Y. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. *Anal. Bioanal. Chem.* **2011**, *401* (10), 3045−3067.
(28) Hass-Mitchell, T.; Joo, T.; Rogers, M.; Nault, B. A.; Soong, C.; Tran, M.; Seo, M.; Machesky, J. E.; Canagaratna, M.; Roscioli, J.; et al. Increasing Contributions of Temperature-Dependent Oxygenated Organic Aerosol to Summertime Particulate Matter in New York City. *ACS ES&T Air* **2024**, *1* (2), 113−128.

https://doi.org/10.1021/acs.estlett.4c00785
Environ. Sci. Technol. Lett. 2024, 11, 1340−1347

(29) Liu, X.; Turner, J. R.; Hand, J. L.; Schichtel, B. A.; Martin, R. V. A Global-Scale Mineral Dust Equation. *J. Geophys Res. Atmos* **2022**, *127* (18), No. e2022JD036937.
(30) Pachon, J. E.; Weber, R. J.; Zhang, X.; Mulholland, J. A.; Russell, A. G. Revising the use of potassium (K) in the source apportionment of PM2.5. *Atmospheric Pollution Research* **2013**, *4* (1), 14−21.
(31) New York City Department of Health and Mental Hygiene. *EpiQuery - Syndromic Surveillance Data 2023*. https://nyc.gov/health/epiquery (accessed on 2023−09−26).
(32) Meek, H. C.; Aydin-Ghormoz, H.; Bush, K.; Muscatiello, N.; McArdle, C. E.; Weng, C. X.; Hoefer, D.; Hsu, W.-H.; Rosenberg, E. S. *Notes from the Field: Asthma-Associated Emergency Department Visits During a Wildfire Smoke Event — New York, June 2023*; MMWR and Morbidity and Mortality Weekly Report; U.S. Department of Health and Human Services, 2023; pp 933−935.
(33) Liu, F.; Joo, T.; Ditto, J. C.; Saavedra, M. G.; Takeuchi, M.; Boris, A. J.; Yang, Y.; Weber, R. J.; Dillner, A. M.; Gentner, D. R.; et al. Oxidized and Unsaturated: Key Organic Aerosol Traits Associated with Cellular Reactive Oxygen Species Production in the Southeastern United States. *Environ. Sci. Technol.* **2023**, *57* (38), 14150−14161.
(34) Daellenbach, K. R.; Uzu, G.; Jiang, J.; Cassagnes, L.-E.; Leni, Z.; Vlachou, A.; Stefenelli, G.; Canonaco, F.; Weber, S.; Segers, A.; et al. Sources of particulate-matter air pollution and its oxidative potential in Europe. *Nature* **2020**, *587* (7834), 414−419.
(35) Zhou, J.; Elser, M.; Huang, R. J.; Krapf, M.; Fröhlich, R.; Bhattu, D.; Stefenelli, G.; Zotter, P.; Bruns, E. A.; Pieber, S. M.; et al. Predominance of secondary organic aerosol to particle-bound reactive oxygen species activity in fine ambient aerosol. *Atmos. Chem. Phys.* **2019**, *19* (23), 14703−14720.
(36) Tuet, W. Y.; Chen, Y.; Fok, S.; Champion, J. A.; Ng, N. L. Inflammatory responses to secondary organic aerosols (SOA) generated from biogenic and anthropogenic precursors. *Atmos. Chem. Phys.* **2017**, *17* (18), 11423−11440.
(37) Yu, Q.; Chen, J.; Qin, W.; Ahmad, M.; Zhang, Y.; Sun, Y.; Xin, K.; Ai, J. Oxidative potential associated with water-soluble components of PM2.5 in Beijing: The important role of anthropogenic organic aerosols. *Journal of Hazardous Materials* **2022**, *433*, No. 128839.
(38) Verma, V.; Fang, T.; Xu, L.; Peltier, R. E.; Russell, A. G.; Ng, N. L.; Weber, R. J. Organic Aerosols Associated with the Generation of Reactive Oxygen Species (ROS) by Water-Soluble PM2.5. *Environ. Sci. Technol.* **2015**, *49* (7), 4646−4656.
(39) *US EPA Air Quality System Data Mart*. https://www.epa.gov/outdoor-air-quality-data (accessed 2023−10−17).
(40) Hinds, W. C. *Aerosol Technology: Properties, Behavior, and Measurement of Airborne Particles*; John Wiley & Sons, 1999.
(41) Joo, T.; Chen, Y.; Xu, W.; Croteau, P.; Canagaratna, M. R.; Gao, D.; Guo, H.; Saavedra, G.; Kim, S. S.; Sun, Y.; et al. Evaluation of a New Aerosol Chemical Speciation Monitor (ACSM) System at an Urban Site in Atlanta, GA: The Use of Capture Vaporizer and PM2.5 Inlet. *ACS Earth and Space Chemistry* **2021**, *5* (10), 2565−2576.
(42) Jimenez, J. L.; Canagaratna, M. R.; Donahue, N. M.; Prevot, A. S. H.; Zhang, Q.; Kroll, J. H.; DeCarlo, P. F.; Allan, J. D.; Coe, H.; Ng, N. L.; et al. Evolution of Organic Aerosols in the Atmosphere. *Science* **2009**, *326* (5959), 1525−1529.
(43) Ng, N. L.; Canagaratna, M. R.; Zhang, Q.; Jimenez, J. L.; Tian, J.; Ulbrich, I. M.; Kroll, J. H.; Docherty, K. S.; Chhabra, P. S.; Bahreini, R.; et al. Organic aerosol components observed in Northern Hemispheric datasets from Aerosol Mass Spectrometry. *Atmos. Chem. Phys.* **2010**, *10* (10), 4625−4641.
(44) Cubison, M. J.; Ortega, A. M.; Hayes, P. L.; Farmer, D. K.; Day, D.; Lechner, M. J.; Brune, W. H.; Apel, E.; Diskin, G. S.; Fisher, J. A.; et al. Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. *Atmos. Chem. Phys.* **2011**, *11* (23), 12049−12064.
(45) Vasilakopoulou, C. N.; Matrali, A.; Skyllakou, K.; Georgopoulou, M.; Aktypis, A.; Florou, K.; Kaltsonoudis, C.; Siouti, E.; Kostenidou, E.; Błaziak, A.; et al. Rapid transformation of wildfire emissions to harmful background aerosol. *npj Climate and Atmospheric Science* **2023**, *6* (1), 218.
(46) Reid, J. S.; Koppmann, R.; Eck, T. F.; Eleuterio, D. P. A review of biomass burning emissions part II: intensive physical properties of biomass burning particles. *Atmos. Chem. Phys.* **2005**, *5* (3), 799−825.
(47) Andreae, M. O. Soot Carbon and Excess Fine Potassium: Long-Range Transport of Combustion-Derived Aerosols. *Science* **1983**, *220* (4602), 1148−1151.
(48) Li, J.; Pósfai, M.; Hobbs, P. V.; Buseck, P. R. Individual aerosol particles from biomass burning in southern Africa: 2, Compositions and aging of inorganic particles. *Journal of Geophysical Research: Atmospheres* **2003**, *108* (D13), na DOI: 10.1029/2002JD002310.
(49) Park, R. J.; Jacob, D. J.; Logan, J. A. Fire and biofuel contributions to annual mean aerosol mass concentrations in the United States. *Atmos. Environ.* **2007**, *41* (35), 7389−7400.
(50) Hems, R. F.; Schnitzler, E. G.; Liu-Kang, C.; Cappa, C. D.; Abbatt, J. P. D. Aging of Atmospheric Brown Carbon Aerosol. *ACS Earth and Space Chemistry* **2021**, *5* (4), 722−748.
(51) Hecobian, A.; Liu, Z.; Hennigan, C. J.; Huey, L. G.; Jimenez, J. L.; Cubison, M. J.; Vay, S.; Diskin, G. S.; Sachse, G. W.; Wisthaler, A.; et al. Comparison of chemical characteristics of 495 biomass burning plumes intercepted by the NASA DC-8 aircraft during the ARCTAS/CARB-2008 field campaign. *Atmos. Chem. Phys.* **2011**, *11* (24), 13325−13337.
(52) Sekimoto, K.; Koss, A. R.; Gilman, J. B.; Selimovic, V.; Coggon, M. M.; Zarzana, K. J.; Yuan, B.; Lerner, B. M.; Brown, S. S.; Warneke, C.; et al. High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels. *Atmospheric Chemistry and Physics* **2018**, *18* (13), 9263−9281.
(53) Hodshire, A. L.; Bian, Q.; Ramnarine, E.; Lonsdale, C. R.; Alvarado, M. J.; Kreidenweis, S. M.; Jathar, S. H.; Pierce, J. R. More Than Emissions and Chemistry: Fire Size, Dilution, and Background Aerosol Also Greatly Influence Near-Field Biomass Burning Aerosol Aging. *Journal of Geophysical Research: Atmospheres* **2019**, *124* (10), 5589−5611.
(54) Jen, C. N.; Hatch, L. E.; Selimovic, V.; Yokelson, R. J.; Weber, R.; Fernandez, A. E.; Kreisberg, N. M.; Barsanti, K. C.; Goldstein, A. H. Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency. *Atmos. Chem. Phys.* **2019**, *19* (2), 1013−1026.
(55) Ye, T.; Guo, Y.; Chen, G.; Yue, X.; Xu, R.; Coêlho, M. d. S. Z. S.; Saldiva, P. H. N.; Zhao, Q.; Li, S. Risk and burden of hospital admissions associated with wildfire-related PM2·5 in Brazil, 2000−15: a nationwide time-series study. *Lancet Planetary Health* **2021**, *5* (9), e599−e607.
(56) Heaney, A.; Stowell, J. D.; Liu, J. C.; Basu, R.; Marlier, M.; Kinney, P. Impacts of Fine Particulate Matter From Wildfire Smoke on Respiratory and Cardiovascular Health in California. *GeoHealth* **2022**, *6* (6), No. e2021GH000578.
(57) Halonen, J. I.; Lanki, T.; Yli-Tuomi, T.; Kulmala, M.; Tiittanen, P.; Pekkanen, J. Urban air pollution, and asthma and COPD hospital emergency room visits. *Thorax* **2008**, *63* (7), 635.
(58) Lakey, P. S. J.; Berkemeier, T.; Tong, H.; Arangio, A. M.; Lucas, K.; Pöschl, U.; Shiraiwa, M. Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract. *Sci. Rep.* **2016**, *6* (1), No. 32916.
(59) Masselot, P.; Sera, F.; Schneider, R.; Kan, H.; Lavigne, É.; Stafoggia, M.; Tobias, A.; Chen, H.; Burnett, R. T.; Schwartz, J. Differential Mortality Risks Associated With PM2.5 Components: A Multi-Country, Multi-City Study. *Epidemiology* **2022**, *33* (2), 167.
(60) Weichenthal, S.; Pinault, L.; Christidis, T.; Burnett, R. T.; Brook, J. R.; Chu, Y.; Crouse, D. L.; Erickson, A. C.; Hystad, P.; Li, C.; et al. How low can you go? Air pollution affects mortality at very low levels. *Science Advances* **2022**, *8* (39), No. eabo3381.