

Chapter 6

Smoke Chemistry



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Abstract Smoke chemistry (i.e., chemical transformations taking place within smoke plumes) can alter the composition and toxicity of smoke on time scales from minutes to days. Air quality agencies need better information on and better models of smoke chemistry to more accurately characterize the contributions of smoke to ambient ozone and particulate matter, and to better predict good windows for prescribed burning. The ability of these agencies to quantify the contributions of wildland fires to air pollutants and the ability of forest and burn managers to both predict and mitigate these impacts are limited by how current models represent smoke chemistry. This limitation is interconnected with uncertainties in smoke emissions, plume dynamics, and long-range transport. Improving predictive models will require a combination of laboratory, field, and modeling studies focused on enhancing our knowledge of smoke chemistry, including when smoke interacts with anthropogenic emissions and enters indoors.

Keywords Chemical transport models • Ozone • Secondary organic aerosol • Statistical models

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6.1 Introduction

Better understanding and improved model representation of the coupled chemical and physical transformations occurring in wildland fire smoke plumes will be critical to improving predictions of the contribution of wildland fires to ozone (O_3), particulate matter $<2.5 \mu\text{m}$ ($PM_{2.5}$), and other air pollutants at local and regional scales. This includes understanding this chemistry as a function of fuel type (Chap. 2) and burn characteristics (Chap. 3). Air quality (AQ) agencies need better information and better models to achieve and maintain compliance with National Ambient Air Quality Standards (NAAQS) (including exceptional events demonstrations; USEPA 2016) and to maintain progress toward the visibility goals set for Class I areas in the Regional Haze Rule. The ability of these AQ agencies to quantify the contributions of wildland fires to air pollutants and the ability of forest and burn managers to predict these impacts are limited by the ability of current models to capture the chemical complexities, which are interconnected to uncertainties in smoke emissions (Chap. 5), plume dynamics, and long-range transport (Chap. 4). Improving predictive models will require a combination of laboratory, field, and modeling studies focused on improving our knowledge of the chemical and physical transformations taking place within smoke plumes, including when smoke interacts with anthropogenic emissions.

6.1.1 Overview and Context of the Issues

The chemically diverse mixture of pollutants in smoke emitted from wildland fires is not inert. Complex and interconnected chemical and physical transformations take place in smoke plumes at time scales from minutes to days (e.g., Hobbs et al. 2003; Baylon et al. 2015), altering the composition of smoke and its effects on human health and climate. As one example, nitrogen oxides ($NO_x = NO + NO_2$) and volatile organic compounds (VOCs) emitted by fires can lead to in-plume production of O_3 , a U.S. Environmental Protection Agency (USEPA) criteria pollutant, on a time scale of hours (e.g., Jaffe and Wigder 2012). Smoke can also contribute to O_3 formation at much longer temporal and spatial scales, either through (1) near-source formation of peroxy nitrates (PNs) like peroxyacetyl nitrate (PAN), which can serve as a NO_x reservoir and ultimately a NO_x source (e.g., Alvarado et al. 2010) (Fig. 6.1), or (2) transport of smoke-derived VOCs to NO_x -rich urban areas (e.g., Brey and Fischer 2016). Although these general pathways of O_3 formation from wildland fire smoke are well known, the amount of O_3 formed in each fire event is highly variable (Jaffe and Wigder 2012), and the causes of this variability are not well understood or well represented in current AQ models (Baker et al. 2016).

$PM_{2.5}$ emitted by fires also undergoes chemical and physical transformations, such that the organic component of $PM_{2.5}$ (~80–90% of total $PM_{2.5}$ mass; Akagi et al. 2011) becomes more oxidized during plume transport (e.g., Garofalo et al. 2019). Observed increases in the oxidation state of organic $PM_{2.5}$ can be driven

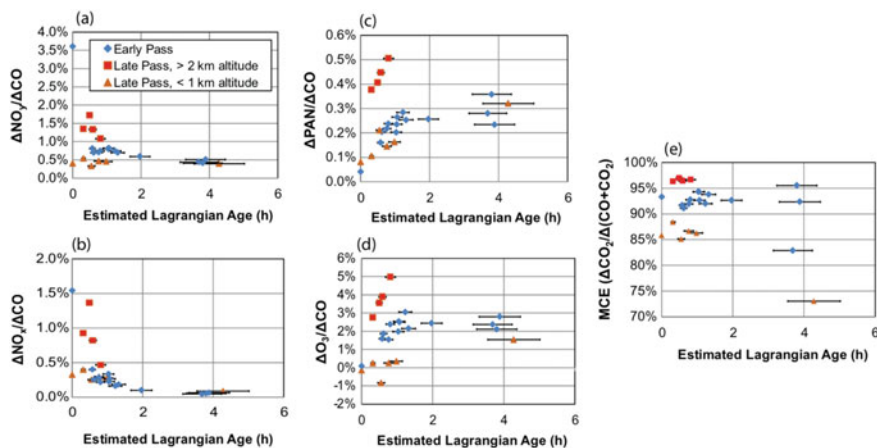


Fig. 6.1 Enhancement ratios of **a** NO_y , **b** NO_x , **c** PAN, and **d** O_3 and **e** modified combustion efficiency (MCE) versus estimated Lagrangian age for a smoke plume from the Lake McKay wildfire (Saskatchewan, Canada; 56.5° N , 106.8° W) sampled during a 1 July 2008 flight of the NASA DC8 during the Arctic Research of the Composition of the Troposphere from Aircraft and Satellites (ARCTAS-B) field campaign. Blue diamonds are for samples taken during the early pass (13:00–15:00 LT), red squares and orange triangles are for samples taken during the late pass (18:20–19:40 LT) above 2 km and below 1 km in altitude, respectively [From Alvarado et al. (2010)]

by physics or chemistry, which also can increase or decrease the total $\text{PM}_{2.5}$ mass relative to what was directly emitted. Directly emitted $\text{PM}_{2.5}$ can be rapidly diluted as a smoke plume disperses, leading to evaporation of the more volatile organic constituents; this decreases the total $\text{PM}_{2.5}$ mass and can lead to an increase in the oxidation state of the remaining organic fraction (May et al. 2013).

At the same time, gas-phase organic compounds (including those partitioned from the particle to the gas phase upon dilution) can be oxidized in plumes. These oxidation reactions can increase functionalization and the tendency of organic compounds to condense (i.e., form secondary organic aerosol [SOA]), increase total $\text{PM}_{2.5}$ mass, and increase the oxidation state of the organic $\text{PM}_{2.5}$. The extent of SOA formation can differ greatly between laboratory fires, even among similar fuel types (Tkacik et al. 2017), and the relative importance of evaporation versus condensation can vary greatly between smoke plumes (Hodshire et al. 2019a).

The chemical and physical transformations of gases and particles in wildland fire smoke may also change the overall toxicity of smoke, which may also affect human health impacts. For example, air toxics within smoke, such as aldehydes (e.g., formaldehyde and acrolein) and isocyanic acid (HNCO), can be formed or destroyed by in-plume chemistry. In addition, recent studies with mice have indicated that the mutagenicity and toxicity of fresh smoke are a function of the type of fuel burned and burn conditions (Kim et al. 2018, 2019), suggesting that the health impact of smoke differs with the chemical composition of the smoke.

6.1.2 *Need for Decision Support*

In order to provide better information to the public about ambient AQ and reduce human health impacts of wildland fire, we need better information on the spatial and temporal distributions of the primary (directly emitted) and secondary (formed by chemistry after source emission) pollutants from smoke. Such information can be used by health studies to further elucidate which chemical compounds and/or chemical properties of smoke cause adverse health outcomes and improve the development of relevant multi-pollutant air quality indices (AQIs) for smoke.

State and local agencies need better forecasting of pollutant concentrations from smoke to prepare the appropriate public alerts. Fire and natural resource managers also need better forecast models to inform prescribed burning decisions. Current smoke forecast models have uncertainties related to smoke emissions and transport. In addition, these forecast models either ignore smoke chemistry entirely (Stein et al. 2009), approximate smoke chemistry with simplified (lumped) mechanisms developed for anthropogenic air pollution (Baker et al. 2016), and/or have difficulty handling the changes in the spatial scale of the chemistry as smoke disperses and is transported over long distances (Alvarado et al. 2010). These current approaches are insufficient to accurately estimate the effects of wildfires and prescribed burns on O_3 , $PM_{2.5}$, and other air toxics, whose formation and loss rates can differ significantly between smoke plumes. Improved models or statistical approaches are needed to determine whether a specific fire led to non-compliance with an O_3 or $PM_{2.5}$ standard (NAAQS) and to accurately model $PM_{2.5}$ composition and optical properties to determine fire contributions to regional haze.

In addition, we need information on how different prescribed burning methods affect the subsequent chemistry of the smoke. Methods used to start prescribed burns can have significant effects on the plume dynamics, transport, and emissions. These changes will also affect smoke chemistry, but there have been no studies about how ignition methods affect subsequent chemistry in the smoke plume.

6.1.3 *Scientific Challenges*

6.1.3.1 **Ozone Formation in Isolated Plumes**

O_3 is a secondary pollutant that is formed from the oxidation of VOCs in the presence of NO_x and UV light. Because fires emit NO_x and VOCs in variable amounts, O_3 may be formed in a smoke plume at varying concentrations depending on the emissions, temperature, UV light, and many complex interactions within the plume. Under warmer conditions, O_3 can form fairly rapidly (hours; Akagi et al. 2013) (Fig. 6.2), whereas in cooler environments, O_3 production takes longer and may not be apparent (Alvarado et al. 2010). An important control on O_3 production is the amount of NO_x emitted and then subsequently removed by chemistry (Mauzerall et al. 1998). NO_x is

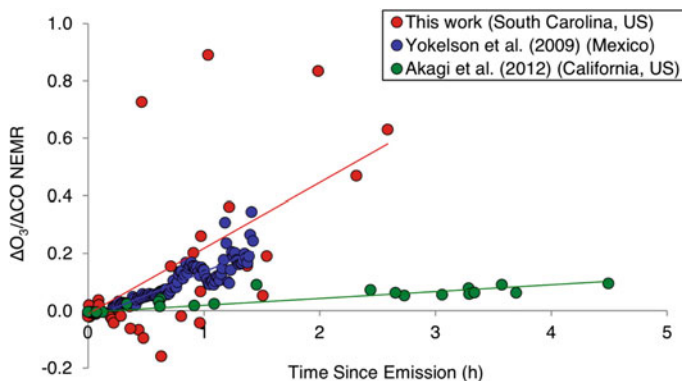


Fig. 6.2 Ozone enhancement ratios ($\Delta\text{O}_3/\Delta\text{CO}$) versus time since emission from Akagi et al. (2013) (red), Yokelson et al. (2009) (blue), and Akagi et al. (2012) (green) [From Akagi et al. (2013)]

rapidly sequestered as peroxyacetyl nitrate (PAN) in boreal smoke plumes (Alvarado et al. 2010) (Fig. 6.1). A similar result was found for smoke plumes at the Mt. Bachelor Observatory in central Oregon at 2.8 km above sea level (Baylon et al. 2015).

In a review of more than 100 different studies, Jaffe and Wigder (2012) found that O_3 is commonly enhanced downwind from fire plumes, and the production increases with plume age. Tropical and subtropical fires generally produce more O_3 and at a faster rate than temperate and boreal fires, because tropical/subtropical fires emit more NO_x per unit of fuel, and the higher temperatures discourage PAN formation (Jaffe and Wigder 2012). Nonetheless, PAN is only a temporary reservoir; subsequent thermal decomposition will regenerate the original NO_x back and distribute O_3 production further downwind (Val Martin et al. 2006). Rapid O_3 production is likely driven by several sources of oxidants, including OH from HONO (nitrous acid) photolysis. HONO can be either emitted directly (Burling et al. 2011) or produced from heterogeneous reactions (Ye et al. 2017).

6.1.3.2 Ozone Formation When Smoke Mixes in Urban Areas

When a smoke plume enters an urban area, it will mix with all the existing pollutants and change the local photochemical environment. Thus, the presence of smoke can increase urban O_3 either by increasing O_3 production upwind of the city center or by increasing O_3 production in the urban environment. Optimum O_3 production occurs at a VOC/NO_x molar ratio of around 8. Ratios for most urban areas are near this or lower. Fire emissions typically have high VOC/NO_x molar ratios, e.g., $\sim 10\text{--}30$ (Akagi et al. 2011), so when smoke mixes into an urban area it can facilitate even more O_3 production. Buysse et al. (2019) show that enhanced O_3 in urban areas due to wildland fires is most pronounced at $\text{PM}_{2.5}$ concentrations below $60 \mu\text{g m}^{-3}$. At higher $\text{PM}_{2.5}$ concentrations, O_3 levels appear to be suppressed due to reduced

photolysis rates, insufficient reaction times, or heterogeneous chemistry on smoke particles. Photolysis can be complex; there can be multiple scattering influences and photolysis rates will depend on the location within the plume (Alvarado et al. 2015). At moderate smoke levels and with high scattering amounts, photolysis may or may not be significantly reduced inside a smoke plume (Baylon et al. 2018).

Many studies have examined O_3 production in smoke plumes by comparing concentrations in the plume to concentrations outside a plume, defined as the “enhancement.” Enhancement of a chemically active compound (e.g., O_3) can be ratioed to a relatively inert compound (e.g., CO_2 or CO) to give an enhancement ratio that shows the chemical production or loss of the species after accounting for plume dilution. Lindaas et al. (2017) documented enhancements in O_3 associated with transported smoke plumes of around 15 ppb in Colorado.

Significant impacts on surface O_3 via intercontinental transport of wildfire emissions can also occur, such as from Siberian smoke reaching the western USA (Teakles et al. 2017; Jaffe et al. 2004) or Alaskan smoke reaching the North Atlantic (Real et al. 2007). Canadian wildfires have been shown to enhance O_3 in the southeastern USA (McKeen et al. 2002), Maryland (Dreessen et al. 2016), and New England (DeBell et al. 2004). Smoke from wildland fires raised the maximum daily 8-h average (MDA8) O_3 levels by 3–6 ppb on average, with a maximum enhancement of up to 40 ppb for six cities in the western USA (Gong et al. 2017). During an especially smoky summer in Boise, Idaho, smoke increased the O_3 MDA8 by an average of ~15 ppb and significantly increased the number of days over the 70 ppb MDA8 AQ threshold (McClure and Jaffe 2018).

The details of nighttime chemistry are poorly understood and are therefore not well represented in models. Although O_3 production is driven by UV photolysis in the daytime, chemical processing can still occur at night, though few studies on this nocturnal chemistry of smoke have been done. From other (non-smoke) studies, we know that NO_2 and O_3 will react to form the NO_3 radical, which can oxidize many organic species and further react to form N_2O_5 . Several nighttime reactions, mostly with the NO_3 radical, can significantly modify the reactivity of smoke, aerosols, and O_3 (Finewax et al. 2018; Decker et al. 2019). Nighttime chemical processing in smoke generates both N_2O_5 and $ClNO_2$, both of which regenerate NO_2 through photolysis (Ahern et al. 2018). $ClNO_2$ can also generate reactive Cl radicals that can increase oxidation of VOCs.

6.1.3.3 Secondary Organic Aerosol Formation and Organic Aerosol Dilution/Oxidation

Organic aerosol (OA) composes a significant fraction of the total $PM_{2.5}$ measured in smoke plumes and in smoke-impacted regions. OA includes compounds that are directly emitted, as well as compounds that are formed in-plume during chemical transformations of the smoke. The OA formed by chemical transformations of gas-phase compounds is known as secondary organic aerosol (SOA). Although the fundamental understanding of SOA formation is well developed, there are uncertainties

about the gas-phase and particle-phase chemistry of SOA precursors emitted from wildland fires. This limits accurate representation of SOA formation from wildland fires in models and predictions of the contribution of wildland fires to SOA and $PM_{2.5}$.

Field measurements and laboratory experiments have been conducted to understand the aging of PM mass and composition in biomass-burning plumes, as well as to provide bottom-up estimates of biomass-burning PM (Hodshire et al. 2019b). Markers of OA oxidation (e.g., O:C ratios) increase with smoke aging, indicating that chemical reactions are taking place within the smoke plumes and/or there is preferential loss of more volatile, lower O:C containing compounds. However, this aging does not always lead to a net increase in $PM_{2.5}$ mass, and there is significant variability in the observed change of $PM_{2.5}$ mass among studies. In the field, increases in $PM_{2.5}$ mass have occurred at shorter transport ages (<5 h) and have been relatively small (mean increases <10%). In the laboratory, larger increases in $PM_{2.5}$ mass (mean increases of ~70%) have been observed, but these estimates are sensitive to methods used to correct for particle loss on smog chamber walls. Variability within and between field and laboratory studies currently inhibits a unified framework for predicting the mass and composition of wildland fire-derived $PM_{2.5}$ as a function of aging.

6.1.3.4 Modeling Challenges

The chemical mechanisms used in most three-dimensional (3D) photochemical transport models were derived to simulate atmospheric chemistry in polluted urban regions, and as a result the representation of organic species within these models is focused on species common in emissions from cars, trucks, power plants, and other anthropogenic sources. This means that the models are potentially missing or misrepresenting the chemistry of the NMOCs from wildland fires, which can lead to errors in the predicted chemical formation of O_3 and $PM_{2.5}$ from wildland fire smoke. For example, furan compounds (containing a 4-carbon, 1-oxygen aromatic ring) are a significant part of the NMOC emissions from biomass burning, accounting for ~25% of the OH reactivity of fresh smoke (Koss et al. 2018). However, few atmospheric chemistry models account for the distinctive chemistry of these aromatic compounds, either ignoring them or lumping them with other aromatic or alkane species. For many of the recently identified compounds that are potential SOA precursors, few data exist on reaction mechanisms and SOA formation potentials (Hatch et al. 2017).

The chemistry of smoke plumes presents scale challenges as they can start out with a small horizontal extent (~1 km or less) but can rapidly disperse to the continental scale. Most 3D AQ models have a minimum horizontal resolution of 4–12 km for regional models and hundreds of km for global models. They are not able to correctly represent the near-source chemistry of smoke plumes, as they automatically dilute the plumes into large-scale grid boxes, which when combined with the nonlinear chemical processes, can lead to significant errors in model predictions (Sakamoto et al. 2016). For example, the 3D Eulerian model CMAQ overestimates the effect of

biomass burning on individual hourly O_3 measurements at CASTNET monitoring sites near fires by up to 40 ppb, underestimating the impact downwind by up to 20 ppb (Baker 2015), possibly due to mistreatment of photolysis rates and peroxy acyl nitrate (PAN) formation.

Plume-scale process models allow examination of chemical and physical transformations of trace gases and aerosols within smoke plumes (Chap. 4) and are used to develop parameterizations for the aging process in coarser grid-scale models (Alvarado et al. 2015). For example, McDonald-Buller et al. (2015) used a subset of the parameterization of Lonsdale et al. (2017) to adjust the chemistry of biomass burning in 3D Eulerian model CAMx, concluding that this approach reduced the median impact of biomass burning on MDA8 O_3 by 0.3 ppb, or 15%.

6.2 Current State of the Science

6.2.1 Well-Understood Aspects of Smoke Chemistry

O_3 production from wildfires is a complex process involving numerous variables including fire emissions, chemical and photochemical reactions, aerosol effects on chemistry and radiation, and local and downwind meteorological patterns (Jaffe and Wigder 2012). Although O_3 production requires both NO_x and NMOCs, wildfire smoke tends to be NO_x -limited. Nitrogen emissions from wildfires are a function of fuel nitrogen content (0.2–4.0%) and the efficiency of combustion, which correlates with NO_x emissions. Modified combustion efficiency (MCE), a unitless ratio, can be used to quantify combustion efficiency; typical MCE values for individual fires range between 0.80 and 1.00. Chemical and photochemical reactions also significantly affect O_3 production in wildfire plumes. Thermal decomposition of downwind PAN, up to two weeks after being emitted, has been linked to O_3 production. The colder temperatures of high latitudes favor sequestration of NO_x in the form of PAN, although tropical wildfire plumes also show evidence of this.

Wildfires generate substantial emissions of O_3 precursors (Akagi et al. 2011), and most observations suggest some degree of O_3 production from wildfires (e.g., Jaffe and Wigder 2012). However, a smaller number of studies, mainly in boreal regions, have found that O_3 is minimally enhanced or even depleted downwind of some smoke plumes (Alvarado et al. 2010). The low O_3 production in these plumes was likely caused by low mixing ratios of NO_x due to low emissions, sequestration of NO_x as PAN, and/or a reduction in photochemical reactions (especially due to aerosol effects on radiation).

Most studies show that O_3 is produced in wildfire smoke, and that typical O_3 -to-CO enhancement ratios ($\Delta O_3/\Delta CO$) range from nearly 0 to 0.7 (Jaffe and Wigder 2012). The $\Delta O_3/\Delta CO$ ratio increases with plume age and is higher in tropical regions, which is consistent with higher NO_x emissions per unit of fuel consumed, likely due to higher fuel N content and combustion efficiency. Species that produce HO_x radicals

by photolysis (e.g., HONO and formaldehyde) can accelerate O_3 production in smoke plumes.

Mixing of wildfire plumes with air masses containing natural and anthropogenic O_3 precursors has been shown to enhance O_3 production. Smoke-influenced O_3 mixing ratios are highest in locations with the highest emissions of NO_x (Brey and Fischer 2016) (Fig. 6.3). The northeastern US corridor, Dallas, Houston, Atlanta,

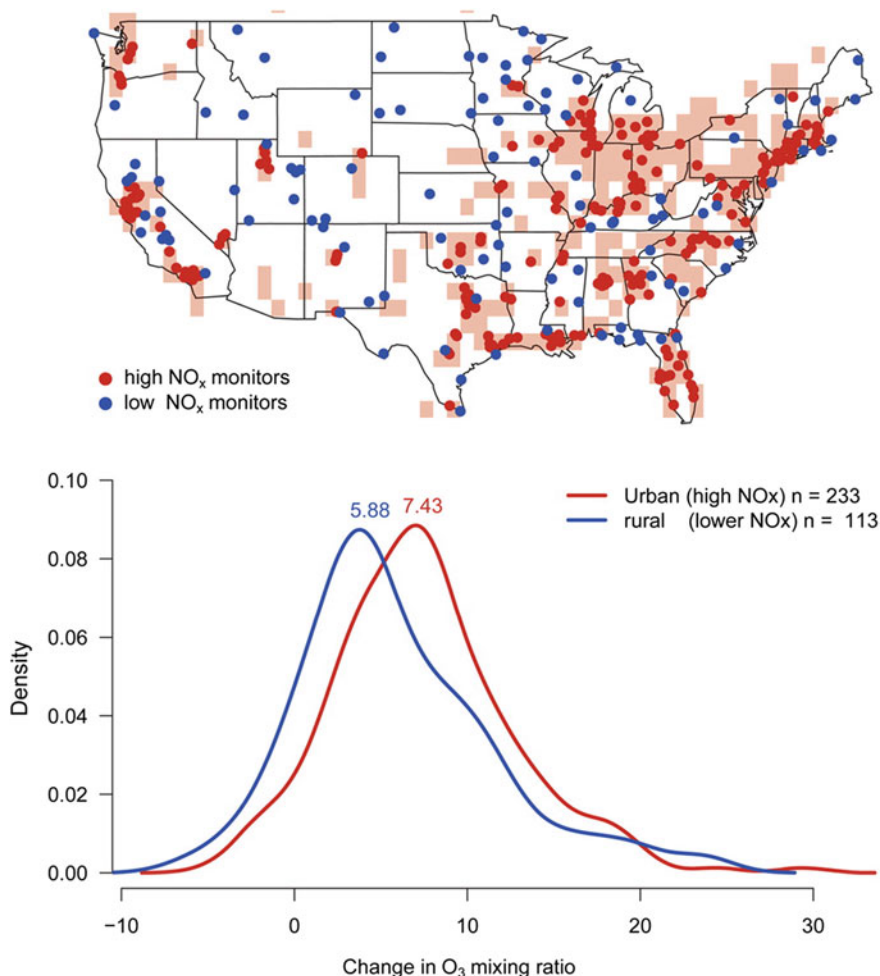


Fig. 6.3 Top panel: locations of urban and rural monitors as defined by NO_x emission rates in the 2008 National Emissions Inventory. Bottom panel: probability distribution of the difference between mean smoke-impacted MDA8 value and smoke-free MDA8 value for urban and rural monitors. Smoke-free days are required to have temperatures that exceed the mean -0.5 standard deviation of the smoke-impacted days temperature values to reduce the impact of varying temperatures on the comparison [From Brey and Fischer (2016)]

Birmingham, and Kansas City stand out as having smoke present 10–20% of the days when 8-h average O₃ mixing ratios exceed 75 ppbv.

The mass, composition, and properties of biomass-burning vapors and particles evolve as smoke ages due to complex chemical and physical processes (Hodshire et al. 2019a). The vapors and particles are composed of thousands of chemical compounds with a range in volatility (vapor pressures), reactivity, and other properties (Shiraiwa et al. 2014). Volatility governs the partitioning of compounds between the gas and particle phases (Pankow 1994) and is often reported as the effective saturation concentration in $\mu\text{g m}^{-3}$ (Donahue et al. 2006). Organic compounds are often grouped into five volatility categories (Murphy et al. 2014):

- Volatile organic compounds (VOCs; $C^* \geq \sim 10^7$),
- Intermediate-volatility organic compounds (IVOCs, $C^* \sim 10^3\text{--}10^6$),
- Semivolatile organic compounds (SVOCs, $C^* \sim 10^0\text{--}10^2$),
- Low-volatility organic compounds (LVOCs, $C^* \sim 10^{-3}\text{--}10^{-1}$),
- Extremely low-volatility organic compounds (ELVOCs, $C \leq \sim 10^{-4}$).

The higher the OA concentrations, the larger the portion of SVOCs that is partitioned in the particle phase. IVOCs are in the gas phase under dilute OA conditions, but some will partition in the particle phase under very high OA concentrations. In general, higher molecular weight and more oxygenated molecules have lower volatility.

During chemical aging within plumes, the volatility of compounds may both decrease—primarily through functionalization or oligomerization reactions—and increase, primarily through fragmentation (Kroll et al. 2009). Gas-phase compounds that decrease in volatility may partition to the particle phase through condensation, forming SOA and thereby adding to aerosol mass. Conversely, semivolatile condensed compounds may evaporate upon dilution of the smoke plume, thereby decreasing aerosol mass. These evaporated compounds may act as SOA precursors that can undergo volatility-lowering reactions and then condense with continued aging of the plume. The time scales for evaporation may differ based on the particle-phase state, and evaporation may also be modified by particle-phase and surface reactions (Zaveri et al. 2014). The net amount of OA or PM that exists as a function of time represents the balance of primary PM mass lost due to evaporation and secondary PM formation.

6.2.2 Existing Data, Tools, Models, and Other Technology

6.2.2.1 Improved Emission Speciation Data

The most comprehensive speciation data have come from laboratory studies. Until recently, IVOCs emitted from biomass burning were poorly characterized (and

nearly entirely unaccounted for in models). Hatch et al. (2017) combined FLAME-IV data collected using multiple measurement techniques into the most comprehensive biomass-burning gas-phase organic emissions inventory to date. Over 500 compounds were identified using multiple measurement techniques, and ~90% of the gaseous NMOC mass was accounted for; 6–11% of the gaseous NMOC mass was associated with IVOCs. These compounds are largely missing in existing emissions inventories, with only a few in the USEPA SPECIATE database.

Sekimoto et al. (2018) showed that only two emission profiles (each being a mass spectral representation of the relative abundance of emitted VOCs) explained 85% of the VOC emissions across various fuel mixtures representative of the western USA. The two profiles are related to low- and high-temperature pyrolysis and are quantitatively similar between different fuel types. The two profiles can represent previously reported VOC data for laboratory and field burns ($r \geq 0.92$), suggesting that these two profiles could be used to determine emissions of VOCs not measured in other studies.

6.2.2.2 Ozone Data

Current data on wildland fire effects on O₃ come from: laboratory studies where smoke from small fires is oxidized within smog chambers (e.g., Bian et al. 2017), surface monitoring (e.g., Brey and Fischer 2016), and field campaigns (e.g., Hobbs et al. 2003). These studies show that O₃ production in smoke is generally NO_x-limited, and thus boreal forest smoke on average forms less O₃ than savannah and grassland smoke on average (Jaffe and Wigder 2012). These studies also show high variability in O₃ production between smoke plumes, for which the causes are not fully understood.

6.2.2.3 SOA Data

There are no direct long-term measurements of SOA. Long-term measurement networks such as IMPROVE and CSN measure the mass of total organic carbon in PM_{2.5}. These total carbon measurements do not provide enough chemical composition information to distinguish between primary and secondary components. Although some studies have approximated secondary versus primary components of organics based on emission ratios of particulate OA to black (or elemental) carbon (Yu et al. 2017), this methodology does not apply if there is evaporative loss of organic compounds from the aerosol after emissions (Sect. 6.2.1).

Data on wildland fire effects on secondary formation of OA are mostly from laboratory (Cubison et al. 2011) or intensive field studies (Garofalo et al. 2019). Quantifying the contribution of chemistry to OA is challenging due to complex chemistry and gas–particle partitioning processes, resulting in variability among studies in contribution of SOA to PM mass (Hodshire et al. 2019b).

Enhancement in total OA relative to CO (i.e., increase in normalized excess mixing ratio $\Delta\text{OA}/\Delta\text{CO}$) provides evidence of SOA formation. However, the SOA amount cannot be quantified simply from $\Delta\text{OA}/\Delta\text{CO}$, because ΔOA includes changes in OA concentrations due to evaporation of more semivolatile constituents of primary OA as well as SOA formation. Field studies show OA becoming more oxidized with plume age, suggesting formation of SOA; but again quantification of SOA is potentially complicated by evaporative loss of semivolatile organic compounds with low O:C ratio. Zhou et al. (2017) applied positive matrix factorization (PMF) to HR-AMS mass spectra data measured at Mt. Bachelor Observatory (Oregon) in 2013, identifying three biomass-burning aerosol factors, two of which represent SOA.

6.2.2.4 Smoke Plume Models

Accurate modeling of O_3 and SOA production from wildland fire emissions is needed to understand chemical processing and impacts on human health (Brown et al. 2014; Chap. 7). Here we describe three different approaches that have been used to model O_3 and SOA production: Eulerian gridded chemical transport models (CTMs), Lagrangian plume or box models, and statistical methods.

Chemical Transport Models

Chemical transport models (CTMs) characterize the chemical environment in three dimensions plus time. Modeling O_3 and SOA production in a CTM depends on accurately knowing the flux, timing, and location of the primary emissions (PM, NO_x , CO, VOCs, etc.). Modeling the resulting concentrations requires spatial and temporal knowledge of injection heights, 3D wind fields, and other meteorological parameters (temperature, relative humidity, etc.) (Kopplitz et al. 2018). Modeling O_3 and SOA also requires a detailed reaction mechanism and accurate UV radiation fields.

Grid resolution is a key component in CTMs. Smaller grid size means greater spatial resolution but increases computational demands. Grid size is especially important for understanding wildfire O_3 production, since this is nonlinear with NO_x and VOCs (Jaffe and Wigder 2012). For a primary pollutant, even if the spatial distribution is not well described, the integrated flux downstream will still reflect the emission flux, assuming no loss or additional production. This is not true for O_3 due to the nonlinearity in production rates. Wildland fires have large emissions of the PAN precursor acetaldehyde, which can result in rapid sequestration of NO_x into PAN (as described above). The degree to which a model captures this process depends on its spatial resolution and accuracy of emissions. Models that overpredict NO_x emissions and/or underpredict acetaldehyde will probably overpredict O_3 near fires (Zhang et al. 2014; Baker et al. 2016).

An additional challenge for CTMs is the large number of VOCs and oxygenated VOCs that are emitted by wildland fires, most of which are not included in standard

chemical mechanisms. For example, furans (5-carbon aromatic compounds) can be responsible for 10% of the O₃ production in smoke plumes (Coggon et al. 2019), but these reactions are not included in most chemical mechanisms. Given that over 500 VOCs have been identified in biomass-burning plumes (Hatch et al. 2017), it is necessary to simplify the reaction scheme for CTMs. Despite the challenges in modeling O₃ from wildland fires, an advantage of CTMs is that all sources (multiple fires, industrial emissions, etc.) can be modeled simultaneously for all receptor locations, and the contribution from each source can be determined from the results (e.g., Baker et al. 2016).

Many studies have also examined the production of SOA from biomass-burning emissions using CTMs (Shrivastava et al. 2015). However, there is disagreement about the global production of SOA from biomass-burning emissions due to high uncertainty in precursor emissions and chemistry.

Lagrangian Plume Models

Box models have been used to overcome the challenges of grid resolution and accurately simulate transport (Wolfe et al. 2016). In this approach, a hypothetical box (or air mass) is identified, whereby detailed chemistry is simulated in the box as it moves downwind (with the prevailing wind) in a Lagrangian framework. The concentrations in the box can be initialized with observations, emission factors, and dilution rates. There are several variations in this approach, but it generally outperforms CTMs in simulating O₃ production (Alvarado et al. 2015) (Fig. 6.4).

Box models can allow for a complex chemical scheme, as only one grid cell needs to be simulated. By simulating emissions from a single fire plume, more accurate representation of the emissions can be incorporated, and transport is removed as an uncertainty (the box follows the prevailing plume direction). In the future, box models for individual plumes could be embedded in CTMs to carry out higher-resolution chemistry simulations.

Statistical Modeling

Statistical models attempt to model or “predict” O₃ concentrations (hourly or 8-h average) using a variety of meteorological indicators (daily maximum temperature, vector winds, 24-h backward trajectories, relative humidity, 500-mb geopotential height, etc.). Typical approaches use either multiple linear regression (Jaffe et al. 2013) or generalized additive models (Gong et al. 2017). The data are split into a non-smoke training dataset, an evaluation or cross-validation dataset, and a smoke dataset. The difference between the prediction from the non-smoke training set and the actual observation indicates the contribution to O₃ due to fire emissions. In practice, these models can predict the O₃ MDA8 for non-smoke days with R² values of 0.5–0.8. This suggests that for urban environments, the average contribution on smoke days to the MDA8 is 3–10 ppb, with a maximum contribution in extreme

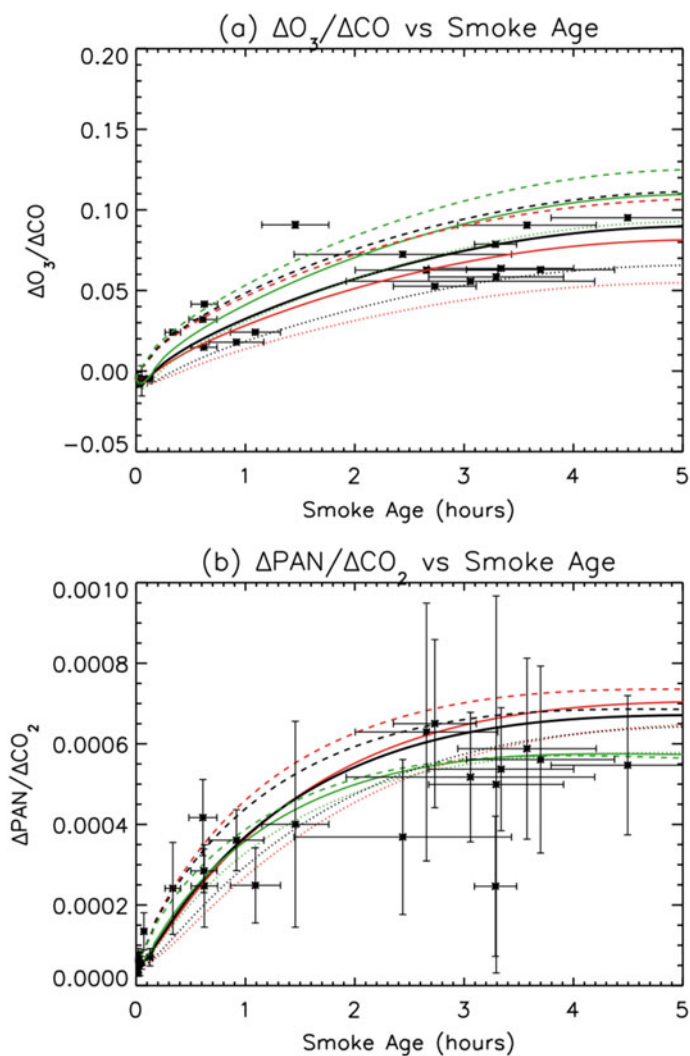


Fig. 6.4 Enhancement ratios (mol mol^{-1}) of **a** O_3 to CO and **b** PAN to CO_2 versus estimated smoke age, when the chemistry of the unidentified SVOCs is included in the model. Asterisks are measured mixing ratios; horizontal error bars show uncertainty in estimated age; vertical error bars show uncertainty in measurement. Red, black, and green are Aerosol Simulation Program results for the slow, best fit (medium), and fast plume dilution rates. Dashed lines are for above-plume photolysis rates; solid lines are for the middle of the plume; dotted lines are for the bottom of the plume [From Alvarado et al. (2015)]

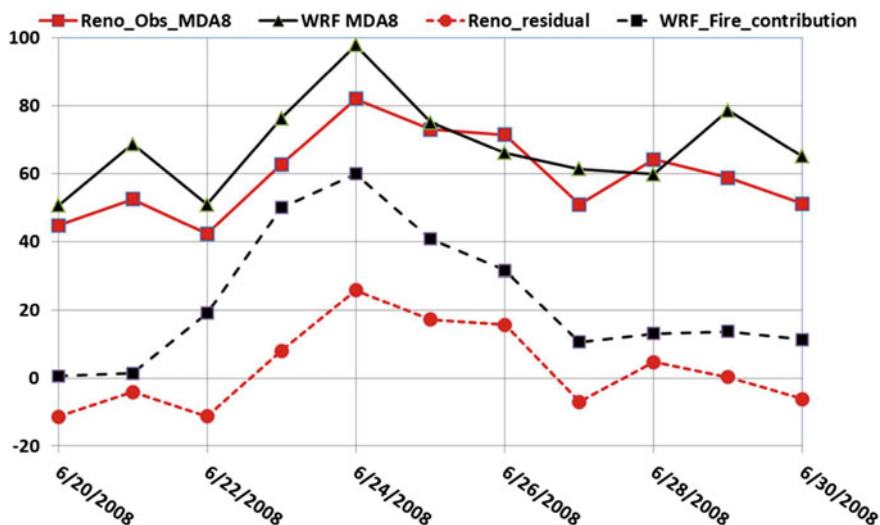


Fig. 6.5 Upper two lines: observed MDA8 (solid red line and squares) and calculated MDA8 from the WRF-Chem model (solid black line and triangles). Bottom two lines: the residual (difference of observed value from predicted value) from the statistical model for Reno, Nevada (dashed red line and circles) and the WRF-Chem model calculated contribution from fires (dashed black line and squares) [From Jaffe et al. (2013)]

cases of up to 50 ppb (Fig. 6.5). These models are simpler to apply than the CTM approach and give statistically robust predictions. However, a statistical approach does not clearly indicate cause and effect.

6.3 Gaps in Data, Understanding, and Tools/Technology

6.3.1 Ozone Data Gaps

More data from laboratory studies, field studies, and long-term monitoring are needed to improve our understanding of the effects of wildland fire smoke on O_3 . Although several laboratory studies have examined the chemistry of biomass-burning in smog chambers (Bian et al. 2017), these studies lack measurements needed to close the reactive nitrogen budget and understand how variation in emissions of organics affects O_3 and PAN formation. Thus, smog chamber studies of wildland fire smoke need a more complete set of observations, especially for highly reactive VOCs (alkenes and aldehydes), oxidized nitrogen species (NO_x , HONO, PAN, etc.), HO_x radicals, and measurements of total OH reactivity.

Until the recent Western Wildfire Experiment for Cloud Chemistry, Aerosol Absorption, and Nitrogen (WE-CAN) study, most field experiments did not include

enough measurements to close the reactive nitrogen budget. More field observations of this type are needed to understand the sources of the variability in O_3 production in smoke plumes. Better information is also needed on how smoke aerosol radiative effects alter O_3 and SOA chemistry within optically thick smoke plumes, as well as how this chemistry varies horizontally and vertically within smoke plumes.

There are few O_3 and $PM_{2.5}$ monitors in rural areas, so insufficient data are available to help communities in these areas predict and respond to O_3 and $PM_{2.5}$ produced by smoke. Although many urban areas have long-term monitoring of O_3 and $PM_{2.5}$, few have measurements of biomass-burning tracer species (e.g., CO, HCN) that allow easy identification of smoke-influenced days. Multi-channel aethalometers that can help separate $PM_{2.5}$ contributions from OA and BC can also be used to identify smoke. This limits our ability to confidently attribute the formed O_3 to smoke, or to understand how the interaction of smoke with urban emissions affects urban AQ.

6.3.2 Secondary Organic Aerosol Data Gaps

A large number of IVOCs from the FLAME-IV laboratory experiments have been identified as potential SOA precursors, using reactivity with OH and carbon number scaling approach (Hatch et al. 2017). However, many of these newly identified compounds are not represented in current models, and few data exist on their reaction mechanisms and SOA formation potentials. Fifty-five to 77% of the reactive carbon was associated with compounds for which SOA yields are unknown or understudied. They also identified best-candidate compounds (furan derivatives and polyunsaturated aliphatic hydrocarbons) for future smog chamber experiments. However, the technique used by Hatch et al. (2017) may not identify all potential SOA precursors, and other studies have suggested that biogenic compounds are an important precursor (Ahern et al. 2019).

There is significant variability among studies regarding the enhancement of OA (or PM) mass due to aging. Differences in prescribed burning ignition procedure, fuel characteristics (species, composition, moisture), and burn conditions (e.g., combustion efficiency) lead to differences in absolute and relative emission rates of various gaseous organic compounds that are SOA precursors. These precursors produce chemical reaction products with different volatility distributions and SOA yields. Oxidant concentrations (affected by the amount NO_x emitted from burning), amount of sunlight, and relative humidity also affect the distribution of reaction products and SOA yields. Differences in dilution/entrainment, losses in experimental chambers and lines, and differences in the baseline from which changes are estimated also contribute to the variability among studies (Hodshire et al. 2019b).

Nighttime oxidation of wildland fire emissions by NO_3 radicals and O_3 is expected to lead to SOA formation. For example, Decker et al. (2019) reported that, during the 2013 Southeast Nexus (SENEX) campaign, nighttime oxidation for rice straw and ponderosa pine (*Pinus ponderosa*) emissions was dominated by NO_3 (72% and 53%, respectively), but O_3 oxidation (25% and 43%) was also significant. Vakkari

et al. (2014) observed lower production of OA in nighttime biomass-burning plumes compared to daytime plumes in South Africa. Vakkari et al. (2018) observed no net increase in total PM₁ mass concentrations at night but did see net increases in aged mass during the day. In a study at Mt. Bachelor Observatory in Oregon, wildfire plumes transported primarily at night versus day showed little difference in mass enhancement, but the OA was less oxidized in the nighttime plumes (Zhou et al. 2017).

6.3.3 *Model Gaps*

Although understanding O₃ production in smoke plumes is critical for policy and health studies, in situations where wildland fires cause ambient concentrations to exceed the NAAQS, the Clean Air Act allows for exclusion of these data based on the “exceptional event” rule (USEPA 2016). Statistical models have been used to support exceptional-event cases, showing concentrations that would be expected for the prevailing meteorological conditions (USEPA 2016).

There have been few comparisons of the three modeling methods (CTM, Lagrangian plume or box, and statistical) used to quantify O₃ from fire emissions. A statistical and CTM approach was compared to estimate the O₃ contribution due to transported smoke into Salt Lake City in August 2012 (Jaffe et al. 2013) (Fig. 6.5). Significant differences found between the two approaches were large enough to complicate any regulatory decisions based on this analysis. Therefore, further comparisons of O₃ production using multiple models is a key research need.

More work is needed on combining models based on different spatial scales to better simulate the long-range impacts of wildland fire smoke. Regional and global AQ models are needed to examine these impacts and account for the interactions of smoke with anthropogenic pollution, but these models cannot represent the near-source chemistry of smoke plumes as they are still at subgrid scale. Thus, plume-scale models need to be used to develop parameterizations for these subgrid processes (Chap. 4). These parameterizations can be incorporated into regional and global AQ models to correctly represent this near-source chemistry. Some progress has been made (Sakamoto et al. 2016), although more work is needed to develop and test these parameterizations in large-scale models.

Until recently, most plume-scale modeling studies have been limited to single box model studies, which cannot account for the horizontal and vertical variations in concentrations, photolysis rates, and other parameters in smoke plumes. Recent work has tried to address this by representing smoke plumes as 2D Lagrangian “walls” to look at vertical and horizontal gradients within some plumes (Fig. 6.6). For example, the SAM-TOMAS model was used in this fashion to study coagulation of aerosols in smoke plumes (Sakamoto et al. 2015, 2016). A new variant, the SAM-ASP model (Lonsdale et al. 2020), can examine the effects of plume gradients on gas-phase chemistry, aerosol condensation/evaporation, and coagulation within smoke plumes. However, as instrument time response and accuracy have improved, data have become

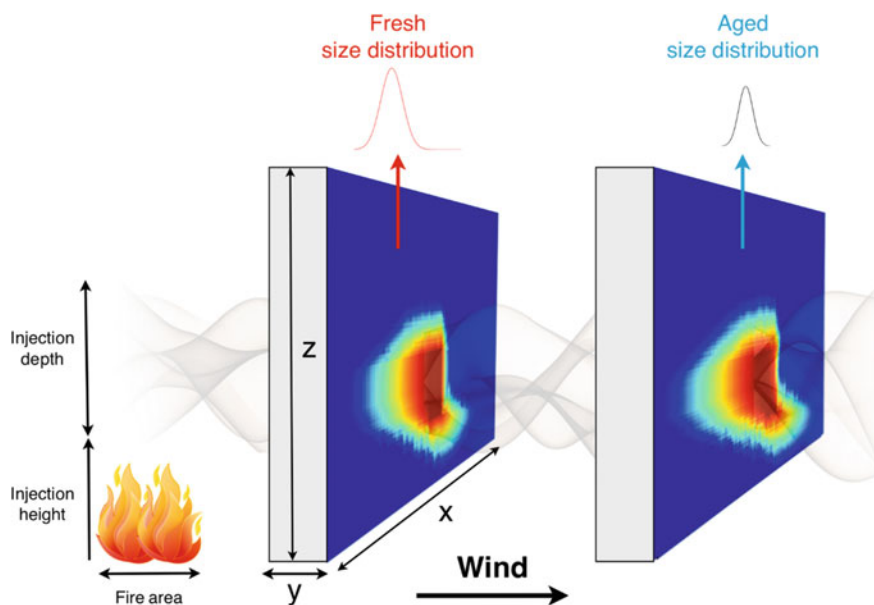


Fig. 6.6 Schematic of a 2D Lagrangian wall SAM-TOMAS simulation [From Sakamoto et al. (2016)]

available to examine these models to allow multiple data points per plume transect (Garofalo et al. 2019). These models require further development and testing to see if they can be used to help parameterize near-source chemistry for regional and global AQ models.

6.4 Vision for Improving Our Understanding of Smoke Chemistry

As wildland fire emissions in the USA are increasing (e.g., McClure and Jaffe 2018; Jaffe et al. 2020) at the same time that most anthropogenic emissions of O_3 and $PM_{2.5}$ precursors are decreasing, due to emission controls (Chan et al. 2018), there is a greater need to understand the chemistry of wildland fire smoke. Here, we discuss opportunities for significant, near-term contributions to the understanding of smoke chemistry (Sect. 6.4.1). We then suggest an approach for addressing and prioritizing research on smoke chemistry knowledge gaps to ensure timely improvement (Sect. 6.4.2).

6.4.1 Near-Term Opportunities

Recent improvements in instrumentation can help identify the organic species emitted by biomass burning (Jen et al. 2019), greatly improving our capability of identifying emitted compounds and understanding their chemistry. Laboratory studies on the OH, O₃, and NO₃ oxidation of newly identified compounds in wildland fire smoke will provide the data needed to improve atmospheric chemical mechanisms for these compounds and predict their influence on O₃ and SOA. Laboratory oxidation studies, including updated instrumentation, are needed for this work.

There is also a near-term opportunity to use existing laboratory and field data to develop simplified, empirical models of smoke PM_{2.5} oxidation and aging to better understand the evolution of organic aerosol within smoke plumes, by accounting for the oxidation, condensation, and evaporation of the organic compounds. These simplified mechanisms could then be incorporated into plume-scale, regional, and global AQ models to better understand and forecast the effects of these chemical changes on the PM_{2.5} impacts of wildland fire smoke.

Recent field campaigns (WE-CAN, FIREX-AQ) have provided new data on the organic species, nitrogen budget, and photolysis rates within wildland fire smoke plumes, including how these parameters vary within the smoke plume (Garofalo et al. 2019). Further analysis of these datasets will clarify the effects of aerosol shading and plume gradients on smoke plume chemistry. These data can be used in box and 2D Lagrangian plume-scale modeling to better understand O₃ and SOA chemistry within these plumes.

Finally, both physical and statistical models of the effects of biomass burning on O₃ have advanced significantly in recent years, but comparisons between these models and observed O₃ have not been conducted. Intercomparisons among statistical, plume-scale, and 3D regional air quality models will help understand the strengths and limitations of each approach and identify priorities for further development of each approach.

6.4.2 Long-Term Priorities for Improving Smoke Chemistry Knowledge

Priorities for smoke chemistry studies should be set according to how much the study will provide near-term, concrete improvements in the information needed to minimize effects of wildfire smoke on human health and other values. We recommend a focus on studies of the impact of wildland fire smoke on exposure to O₃ and PM_{2.5} in rural and urban populations. In addition, as common public health advice during smoke exposure events is to stay indoors and turn on air conditioning and particulate filters, additional study is needed of the indoor chemistry of smoke and how this affects exposure.

6.4.2.1 Exposure of Rural Populations

For rural populations, the key need is for more low-cost and federal equivalent monitors to better assess the near-source chemistry of smoke plumes that are not interacting with significant anthropogenic emissions. Our understanding of the exposure of rural populations is limited by a lack of long-term data on atmospheric chemistry in rural areas, because AQ monitors are primarily near large urban populations. Traditional Federal Reference Method (FRM) and Federal Equivalent Method (FEM) monitoring techniques will likely be too expensive to provide the needed coverage. However, there have been recent advances in low-cost monitoring instruments for air quality, focusing mainly on $PM_{2.5}$, O_3 , NO_x , and CO. These instruments are usually connected to Web portals that provide real-time AQ data, allowing fire managers, AQ managers, and the public to quickly assess the impacts of a given fire. These low-cost sensors require the use of more expensive reference methods for calibration. This could be provided by a small number of FRM/FEM sites, supplemented by mobile laboratories with more detailed instrumentation (Yacovitch et al. 2015) that can be deployed to areas where smoke is present.

Long-term data on wildland smoke concentrations at multiple rural locations can be used to develop improved plume-scale, statistical, and 3D models of smoke chemistry by providing tests of new smoke chemical mechanisms and modeling approaches. These data can also be used in a data assimilation framework to improve smoke chemistry forecasts, ensuring that they are consistent with the latest observations of the smoke plume and chemistry, thus addressing inherent variability in smoke emissions and chemistry.

6.4.2.2 Exposure of Urban Populations

The high levels of anthropogenic emissions of O_3 and $PM_{2.5}$ precursors in urban areas increase the complexity of wildland fire smoke chemistry. Although many urban areas have long-term monitoring of O_3 and $PM_{2.5}$, few have measurements of biomass-burning tracer species (e.g., CO, HCN) that allow easy identification of smoke-influenced days by determining days with concentrations of these species above the normal variation in the urban area. Previous studies looking at the interaction of smoke and urban pollution have used satellite observations of smoke to determine smoke-influenced days (Brey and Fischer 2016), but these observations of smoke throughout the vertical column are not necessarily good proxies for surface-level smoke impacts.

Progress on mitigating the urban impacts of wildland fire smoke will require additional monitoring sites with O_3 , $PM_{2.5}$, and wildland fire tracers. In addition, a “rapid response” observation unit for urban ground measurements, using mobile labs, could be deployed to provide more detailed observations during smoke events. These data would provide more accurate identification of smoke-influenced days and data on how smoke alters urban air quality. They could also be used to train statistical models of air quality on non-smoke-influenced days, which can be used to determine

effective smoke contribution to O_3 and $PM_{2.5}$ on smoke-influenced days. These data would also help refine the treatment of smoke–urban pollution interactions in typical regional air quality models like CMAQ and CAMx. Although plume-scale modeling is unlikely to be directly relevant to studies of urban chemistry, representation of near-source smoke chemistry in these 3D air quality models can be improved, especially downwind interactions with urban areas.

6.4.2.3 Indoor Smoke Chemistry

Although elevated concentrations of ambient $PM_{2.5}$ and O_3 due to fire emissions are well documented, little is known about smoke exposure indoors. This is especially important given that community health warnings during smoke events suggest that residents stay indoors (Chap. 7). The assumption is that indoor air will be significantly cleaner than outdoor air when smoke is present. However, the degree that this assumption is accurate is unclear.

More information is needed to understand indoor smoke concentrations across a range of building types and conditions, how the chemistry and toxicity of wildland fire smoke are altered as it is transported indoors, and the effectiveness of particle filtration for reducing the health impacts of smoke. Building environments are heterogeneous; buildings have wide variability in compound concentrations, temperature, relative humidity, and air exchange (Morrison 2015). Combined with the large number of reactants, products, secondary reactants, and side reactions, each microenvironment has a discrete chemical signature.

Wildland smoke $PM_{2.5}$ can enter buildings, where it can be inhaled or deposited on indoor surfaces. Wheeler et al. (2020) showed that roof-cavity dust could be analyzed for smoke compounds to estimate exposure. The rate of smoke infiltration depends on the rate of air exchange and ventilation in the building. Particulate filters (stand-alone or as part of an HVAC system) can reduce indoor $PM_{2.5}$ concentrations, but older buildings without central HVAC can have indoor $PM_{2.5}$ levels like those outside during smoke events (Kirk et al. 2018).

O_3 from wildland fire smoke can react with indoor surfaces to produce additional pollutants that cannot be removed by particulate filters. If oils or other organics are present on these surfaces, the reaction with O_3 can produce SOA and other toxic species such as carbonyls and carboxylic acids. O_3 can also react with terpenes emitted by wood, cleaners, air fresheners, and personal care products (Hodgson et al. 2002), producing similar toxic species. Ozone will also react with tobacco smoke residuals on indoor surfaces and generate volatile products such as cotinine (Petrick et al. 2011). In addition, HONO can be produced indoors from surface reactions of NO_x and will react with tobacco smoke residue on surfaces and produce carcinogenic tobacco-specific nitrosamines (Sleiman et al. 2010). These reactions may also take place within homes where wildland fire smoke residue is present on the walls, ceilings, and floors.

Other toxic species in wildland fire smoke (e.g., aldehydes, isocyanic acid) are also unlikely to be removed by particulate filters. If the observed health effects of

smoke are partially related to these other species, and not just $\text{PM}_{2.5}$ mass, filtering out particles may not fully protect the public from the health impacts of smoke.

In one of the few relevant studies on smoke intrusion into homes, Kirk et al. (2018) examined two homes in the Pacific Northwest during the summer of 2015, a year with high fire occurrence and frequent high $\text{PM}_{2.5}$ days. They found high correlations between indoor (I) and outdoor (O) concentrations, but relatively low I/O ratios of 0.10 to 0.26 for $\text{PM}_{2.5}$. Data from another study show a wider range for the I/O ratio (0.16–0.91) during smoke events for several homes and commercial buildings in the Pacific Northwest during 2018 and 2019 smoke events (D.A. Jaffe, unpublished data). In some cases, homes had indoor $\text{PM}_{2.5}$ concentrations of up to $100 \mu\text{g m}^{-3}$ (I/O ratio of 0.91). Therefore, the assumption that indoor air is “safe” during smoke events is not uniformly correct.

Further work is thus needed to examine the infiltration of wildland fire smoke into different types of buildings, and how the smoke is transformed by reactions inside the building. As a first step, collaboration is needed between smoke chemists and indoor air quality specialists to identify potential studies that can provide initial data on these indoor transformations.

6.5 Emerging Issues

6.5.1 *Higher Particulate Matter, Ozone, and Hazardous Air Pollutants from Fires in Western States*

$\text{PM}_{2.5}$ emissions from wildland fires in 2017 and 2018 were the highest ever observed, at that point in time, at US regulatory monitors (Laing and Jaffe 2019; Jaffe et al. 2020):

- San Francisco, CA: Highest daily $\text{PM}_{2.5}$ ever recorded was $177 \mu\text{g m}^{-3}$ (November 16, 2018).
- Seattle, WA: Highest daily $\text{PM}_{2.5}$ ever recorded was $110 \mu\text{g m}^{-3}$ (August 21, 2018).
- Medford OR: 8 days of $\text{PM}_{2.5}$ over $100 \mu\text{g m}^{-3}$ in 2017, highest daily $\text{PM}_{2.5}$ of $268 \mu\text{g m}^{-3}$ (September 6, 2017).
- Seeley Lake, MT: $\text{PM}_{2.5}$ of $642 \mu\text{g m}^{-3}$, highest ever observed in the USA, (September 6, 2017).

Similar extremes have been observed for O_3 . For example, during the major smoke events of 2017 and 2018, numerous locations experienced O_3 MDA8 values over 100 ppb: 103 ppb at Enumclaw, WA (August 3, 2017), 116 ppb at Carus, OR (August 3, 2017), and 115 ppb at Auburn, CA (August 1, 2018). These extremes occurred due to a large number of concurrent wildfires in the greater Pacific Northwest region and British Columbia (McClure and Jaffe 2018).

6.5.2 How Prescribed Burning Affects Smoke Chemistry

There have been no studies about how ignition methods affect chemistry in the smoke plume, so there is little guidance available for fire managers on the consequences of different methods on local and regional air quality. The effects of fuel conditions (moisture content, nitrogen content, 3D structure) on smoke emissions and chemistry have been studied in a few cases, but not with the goal of providing information to fire managers on how to plan prescribed burning to minimize impacts on human exposure to O_3 , $PM_{2.5}$, and other air toxics.

Different ignition methods and fuel conditions can lead to variations in smoke emissions and plume dynamics, including the initial plume size, injection height, and plume chemistry (Chap. 4). For example, a more concentrated plume will have lower photolysis rates within and below the core of the plume, potentially delaying the photolysis of radical sources like HONO and HCHO, delaying the loss of NO_x , and delaying or reducing the formation of O_3 and the oxidation of the NMOCs. A more concentrated plume will also have more of the semivolatile and intermediate-volatility organic compounds (S/IVOCs) present in the particle phase, potentially altering downwind chemistry. A higher plume injection height will also alter the chemistry taking place within the smoke plume. Higher altitudes tend to have colder temperatures, which favors the formation of PAN and condensation of organic vapors into $PM_{2.5}$. Smoke at higher altitudes is also more likely to be transported long distances in the troposphere before being transported back to the surface where it can affect O_3 and $PM_{2.5}$ downwind of the fire source.

However, plume-scale LES models like SAM-TOMAS and SAM-ASP could be used to investigate how focused field studies could clarify how different prescribed burn ignition methods and fuel conditions affect downwind air quality impacts. The chemistry of smoke plumes could be sampled downwind using small aircraft and/or surface mobile laboratories to characterize the formation of O_3 and $PM_{2.5}$. These studies can then be used to revise plume-scale models to better account for the effects of ignition methods and provide guidance to fire manager efforts to minimize the formation of O_3 and $PM_{2.5}$.

6.5.3 Clarifying Specific Health Effects

Little work has been done to examine how the aging of wildland fire smoke $PM_{2.5}$ affects human health (Chap. 7). Toxicological studies could help to determine if aged smoke has similar impacts as fresh smoke, building on the work of Gilmour et al. (2015). However, epidemiological studies are likely to be difficult to perform. As aged smoke tends to be more dilute than fresh smoke, the public may take fewer precautions to reduce exposure to aged smoke than they do for concentrated fresh smoke, confounding the analysis of the relative health effects.

There is also a need to distinguish between the health effects due to multiple air toxics within smoke (e.g., carbonyls, isocyanic acid, aromatics) versus $PM_{2.5}$. Even if $PM_{2.5}$ is not a major concern, the remaining air toxics may represent substantial health impacts. However, measurements of these additional air toxics in wildland fire smoke are rare outside of dedicated field campaigns, so estimating exposure to these species is difficult.

6.6 Links with Other Components of the Smoke Assessment

Many of the challenges in other components of understanding smoke (Chaps. 2, 3, 4, 5 and 7) have links to understanding wildland fire smoke chemistry. We note a few of these links below.

6.6.1 Fire Behavior and Plume Dynamics

As noted above, injection height and initial plume concentrations of different pollutants are critical to understanding the subsequent chemistry of the smoke plume. Injection height affects the temperature where the initial plume chemistry is occurring and affects the dilution rate of smoke, both of which alter the chemical formation of O_3 and evolution of $PM_{2.5}$ within the smoke plume. In addition, the size of the plume will have significant effects on the dilution and chemistry taking place within the smoke plume. Thus, a better understanding of fire behavior and near-source plume dynamics is critical for better predictions of the effects of wildland fires on local and regional O_3 and $PM_{2.5}$.

6.6.2 Fuel Characterization

The size, chemical composition, and 3D structure of fuels can directly affect the chemical composition of emissions, and thus downwind chemistry. For example, because O_3 formation in smoke plumes is generally NO_x -limited (Jaffe and Wigger 2012), understanding the emissions of NO_x from wildland fires is critical to understanding smoke plume chemistry. Emissions of NO_x from wildland fires are in turn a function of the combustion efficiency (itself a function of fuel size, structure, and moisture content) and fuel nitrogen content, which can vary from 0.2 to 4.0% between fuel types and can vary between seasons for a single ecosystem (Mebust and Cohen 2013). Different combustion efficiencies and fuel composition can also lead to changes in emissions of organic $PM_{2.5}$ and other air toxics (Jen et al. 2019). An

assessment of the typical nitrogen content of wildland fuels would benefit studies of smoke chemistry by reducing uncertainty about the initial NO_x emissions and chemistry.

6.6.3 *Smoke Emissions*

Understanding the chemical transformations of smoke requires understanding the speciated emission of trace gases and aerosols within smoke and how these mixtures of species depend on fuel type, fuel structure, fuel moisture, and fire behavior (e.g., rate of spread). This requires more than an estimate of the total PM emissions from a fire. Information is needed on emissions of individual gases, including air toxics such as formaldehyde and HNCN, as well as information on the organic and inorganic species within PM (e.g., volatility, hygroscopicity, and chemical reactivity). Detailed measurements are needed to understand the chemical composition of fresh smoke, extending it to subsequent chemical reactions as the smoke moves downwind.

6.6.4 *Effects on People, Health, Transportation, and Commerce*

Understanding the impacts of smoke on health requires an understanding of the chemical transformations taking place within smoke, as not all people exposed to wildfire smoke are exposed to the same mixture of compounds. Fresh and aged smoke differ chemically, and these differences may alter impacts on human health. For example, understanding the chemistry of smoke plumes is important for understanding the impact of smoke on O_3 exposure. Fresh smoke is usually depleted in O_3 , whereas aged smoke can be enhanced in O_3 and thus have increased health effects. Understanding how smoke chemistry increases or decreases the amount of OA and $\text{PM}_{2.5}$ present in smoke also is needed to accurately estimate health impacts. In addition, individual air toxics within smoke have different chemical lifetimes and may increase downwind (e.g., formaldehyde), so understanding rates of change of individual air toxics will provide a better picture of which components of smoke are responsible for health impacts.

6.7 Conclusions

6.7.1 Key Research Needs and Priorities

Initial smoke emissions are transformed through chemical processes at time scales from a few minutes to days and at spatial scales from meters to thousands of kilometers. These transformations alter the effects of smoke on human health and climate. Critical reviews, laboratory campaigns, field studies, and model development efforts in the last decade have improved our knowledge of the organic species in wildland fire smoke and their subsequent chemistry. However, current knowledge is insufficient to explain the wide variability in smoke chemistry from different wildland fires. Key scientific challenges in smoke chemistry include: (1) understanding O₃ formation in isolated and mixed smoke plumes, as well as when smoke mixes with urban emissions, (2) understanding SOA formation in smoke plumes and the aging of OA in smoke plumes, and (3) developing improved statistical and physical models of smoke chemistry.

Several emerging issues in smoke chemistry also merit research attention including the role of increasing PM, O₃, and hazardous air pollutants from fires in Western states, how different prescribed burn approaches can affect the chemistry of the smoke, and how the indoor environment alters the chemistry of wildland fire smoke.

Critical research needs include:

- Better information on the spatial and temporal distributions of the primary (directly emitted) and secondary (formed by chemistry after emission) pollutants formed from wildland fire smoke,
- Better forecast models to inform prescribed burning decisions,
- Information on how different prescribed burning methods affect the subsequent chemistry of the smoke.

Near-term opportunities for improving our understanding of smoke chemistry include:

- Examining the chemistry of newly identified smoke species,
- Developing empirical models of smoke fine particulate matter (PM_{2.5}) aging,
- Investigating the impact of plume gradients,
- Performing physical and statistical model intercomparisons.

Long-term priorities include increasing the data available on the effects of wildland fire smoke on O₃ and SOA in rural and urban areas, and examining how wildland fire smoke affects indoor AQ. More research is needed to understand how chemical properties affect the toxicity of smoke as it is chemically transformed in the atmosphere. This would inform how the complexity of chemistry may be simplified in models to predict the chemical properties most relevant to informing decisions on public health.

Additional data on smoke chemistry from laboratory and field studies are needed to:

- Improve forecast and impact models and close the nitrogen budget,
- Determine the chemistry of recently identified organic compounds, and
- Examine how aerosol shading and other effects result in horizontal and vertical gradients in the smoke plume chemistry.

Model development is needed to:

- Improve the chemical mechanisms within air quality models to represent smoke species,
- Develop parameterizations of the near-source chemistry of fires for inclusion in regional and global models, and
- In form development of statistical models of the impact of fires on air quality.

6.7.2 Opportunities for Shared Stewardship to Improve Smoke Science and Management

There are several opportunities for federal agencies, states, tribes, and the research community to collaboratively to address the research priorities above. First, coordination among the US Forest Service, USEPA, USDOD, and other scientific agencies could facilitate laboratory studies of the oxidation of newly identified organic compounds in wildland fire smoke. This would improve atmospheric chemical mechanisms for these compounds and predict their impacts on O₃ and SOA. These studies will require coordinating large numbers of investigators and instruments, including significant data analysis and modeling work after laboratory studies are completed. In addition, fully mining the WE-CAN and FIREX-AQ datasets to improve air quality models would be facilitated by a coordinated approach among agencies.

Increasing the amount of monitoring data on smoke-related O₃ and PM_{2.5} would also be easier with coordination between agencies and other interested parties. This will require expertise in wildland fire, air quality, and local conditions to develop the best monitoring plan for each region. In addition, improving smoke forecast and air quality models would benefit from coordination among federal agencies, including the US Forest Service, USEPA, and NOAA.

References

- Ahern AT, Goldberger L, Jahl L et al (2018) Production of N₂O₅ and ClNO₂ through nocturnal processing of biomass-burning aerosol. *Environ Sci Technol* 52:550–555
- Ahern AT, Robinson ES, Tkacik DS et al (2019) Production of secondary organic aerosol during aging of biomass burning smoke from fresh fuels and its relationship to VOC precursors. *J Geophys Res Atmos* 124:3583–3606

- Akagi SK, Yokelson RJ, Wiedinmyer C et al (2011) Emission factors for open and domestic biomass burning for use in atmospheric models. *Atmos Chem Phys* 11:4039
- Akagi SK, Craven JS, Taylor JW et al (2012) Evolution of trace gases and particles emitted by a chaparral fire in California. *Atmos Chem Phys* 12:1397–1421
- Akagi SK, Yokelson RJ, Burling IR et al (2013) Measurements of reactive trace gases and variable O₃ formation rates in some South Carolina biomass burning plumes. *Atmos Chem Phys* 13:1141–1165
- Alvarado MJ, Logan JA, Mao J et al (2010) Nitrogen oxides and PAN in plumes from boreal fires during ARCTAS-B and their impact on ozone: an integrated analysis of aircraft and satellite observations. *Atmos Chem Phys* 10:9739–9760
- Alvarado MJ, Lonsdale CR, Yokelson RJ et al (2015) Investigating the links between ozone and organic aerosol chemistry in a biomass burning plume from a prescribed fire in California chaparral. *Atmos Chem Phys* 15:6667–6688
- Baker KR, Woody MC, Tonnesen GS et al (2016) Contribution of regional-scale fire events to ozone and PM_{2.5} air quality estimated by photochemical modeling approaches. *Atmos Environ* 140:539–554
- Baker K (2015) Simulating fire event impacts on regional O₃ and PM_{2.5} and looking forward toward evaluation. Paper presented at the 14 Annual CMAAS Conference, UNC-Chapel Hill, 5–7 Oct 2015
- Baylon P, Jaffe DA, Wigder NL et al (2015) Ozone enhancement in western US wildfire plumes at the Mt. Bachelor Observatory: the role of NO_x. *Atmos Environ* 109:297–304
- Baylon P, Jaffe DA, Hall SR et al (2018) Impact of biomass burning plumes on photolysis rates and ozone formation at the mount bachelor observatory. *J Geophys Res Atmos* 123:2272–2284
- Bian Q, Jathar SH, Kodros JK et al (2017) Secondary organic aerosol formation in biomass-burning plumes: theoretical analysis of lab studies and ambient plumes. *Atmos Chem Phys* 17:5459–5475
- Brey SJ, Fischer EV (2016) Smoke in the city: How often and where does smoke impact summertime ozone in the United States? *Environ Sci Technol* 50:1288–1294
- Brown T, Clements C, Larkin N et al (2014) Validating the next generation of wildland fire and smoke models for operational and research use—A national plan (Final report, Project 13-S-01–01. U.S. Joint Fire Science Program, Boise. https://www.firescience.gov/projects/13-S-01-01/project/13-S-01-01_final_report.pdf. 22 June 2020
- Burling IR, Yokelson RJ, Akagi SK et al (2011) Airborne and ground-based measurements of the trace gases and particles emitted by prescribed fires in the United States. *Atmos Chem Phys* 11:12197–12216
- Buysse CE, Kaulfus A, Nair U, Jaffe DA (2019) Relationships between particulate matter, ozone, and nitrogen oxides during urban smoke events in the Western US. *Environ Sci Technol* 53:12519–12528
- Chan EA, Gantt B, McDow S (2018) The reduction of summer sulfate and switch from summertime to wintertime PM_{2.5} concentration maxima in the United States. *Atmos Environ* 175:25–32
- Coggon MM, Lim CY, Koss AR et al (2019) 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* 19:14875–14899
- Cubison MJ, Ortega AM, Hayes PL et al (2011) Effects of aging on organic aerosol from open biomass burning smoke in aircraft and laboratory studies. *Atmos Chem Phys* 11:12049–12064
- DeBell LJ, Talbot RW, Dibb JE et al (2004) A major regional air pollution event in the north-eastern United States caused by extensive forest fires in Quebec, Canada. *J Geophys Res Atmos* 109:D19305
- Decker ZC, Zarzana KJ, Coggon M et al (2019) Nighttime chemical transformation in biomass burning plumes: a box model analysis initialized with aircraft observations. *Environ Sci Technol* 53:2529–2538
- Donahue NM, Robinson AL, Stanier CO, Pandi SN (2006) Coupled partitioning, dilution, and chemical aging of semivolatile organics. *Environ Sci Technol* 40:2635–2643

- Dreessen J, Sullivan J, Delgado R (2016) Observations and impacts of transported Canadian wildfire smoke on ozone and aerosol air quality in the Maryland region on June 9–12, 2015. *J Air Waste Manag Assoc* 66:842–862
- Finewax Z, de Gouw JA, Ziemann PJ (2018) Identification and quantification of 4-nitrocatechol formed from OH and NO₃ radical-initiated reactions of catechol in air in the presence of NO_x: implications for secondary organic aerosol formation from biomass burning. *Environ Sci Technol* 52:1981–1989
- Garofalo LA, Pothier MA, Levin EJ et al (2019) Emission and evolution of submicron organic aerosol in smoke from wildfires in the western United States. *ACS Earth Space Chem* 3:1237–1247
- Gilmour MI, Kim YH, Hays MD (2015) Comparative chemistry and toxicity of diesel and biomass combustion emissions. *Anal Bioanal Chem* 407:5869–5875
- Gong X, Kaulfus A, Nair U, Jaffe DA (2017) Quantifying O₃ impacts in urban areas due to wildfires using a generalized additive model. *Environ Sci Technol* 51:13216–13223
- Hatch LE, Yokelson RJ, Stockwell CE et al (2017) Multi-instrument comparison and compilation of non-methane organic gas emissions from biomass burning and implications for smoke-derived secondary organic aerosol precursors. *Atmos Chem Phys* 17:1471–1489
- Hobbs PV, Sinha P, Yokelson RJ et al (2003) Evolution of gases and particles from a savanna fire in South Africa. *J Geophys Res Atmos* 108:8485
- Hodgson AT, Beal D, McIlvaine JER (2002) Sources of formaldehyde, other aldehydes and terpenes in a new manufactured house. *Indoor Air* 12:235–242
- Hodshire AL, Bian Q, Ramnarine E et al (2019a) More than emissions and chemistry: Fire size, dilution, and background aerosol also greatly influence near-field biomass burning aerosol aging. *J Geophys Res Atmos* 124:5589–5611
- Hodshire AL, Akherati A, Alvarado MJ et al (2019b) Aging effects on biomass burning aerosol mass and composition: a critical review of field and laboratory studies. *Environ Sci Technol* 17:10007–10022
- Jaffe DA, Wigder NL (2012) Ozone production from wildfires: a critical review. *Atmos Environ* 51:1–10
- Jaffe D, Bertschi I, Jaeglé L et al (2004) Long-range transport of Siberian biomass burning emissions and impact on surface ozone in western North America. *Geophys Res Lett* 31:L16106
- Jaffe DA, Wigder N, Downey N et al (2013) Impact of wildfires on ozone exceptional events in the western US. *Environ Sci Technol* 47:11065–11072
- Jaffe DA, O'Neill SM, Larkin NK et al (2020) Wildfire and prescribed burning impacts on air quality in the United States. *J Air Waste Manag Assoc* 70:583–615
- Jen CN, Hatch LE, Selimovic V et al (2019) Speciated and total emission factors of particulate organics from burning western US wildland fuels and their dependence on combustion efficiency. *Atmos Chem Phys* 19:1013–1026
- Kim YH, King C, Krantz Q et al (2019) The role of fuel type and combustion phase on the toxicity of biomass smoke following inhalation exposure in mice. *Arch Toxicol* 93:1501–1513
- Kim YH, Warren SH, Krantz QT et al (2018) Mutagenicity and lung toxicity of smoldering vs. flaming emissions from various biomass fuels: Implications for health effects from wildland fires. *Environ Health Perspect* 126:017011
- Kirk WM, Fuchs M, Huangfu Y et al (2018) Indoor air quality and wildfire smoke impacts in the Pacific Northwest. *Sci Technol Built Environ* 24:149–159
- Koplitz SN, Nolte CG, Pouliot GA et al (2018) Influence of uncertainties in burned area estimates on modeled wildland fire PM_{2.5} and ozone pollution in the contiguous US. *Atmos Environ* 191:328–339
- Koss AR, Sekimoto K, Gilman JB et al (2018) 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* 18:3299–3319

- Kroll JH, Smith JD, Che DL et al (2009) Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol. *Phys Chem Chem Phys* 11:8005–8014
- Laing JR, Jaffe D (2019) Wildfires are causing extreme PM concentrations in the Western United States. *EM Magazine* (June). Air and Waste Management Association, Pittsburgh. <http://pubs.awma.org/flip/EM-June-2019/jaffe.pdf>. 22 June 2020
- Lindaas J, Farmer DK, Pollack IB et al (2017) Changes in ozone and precursors during two aged wildfire smoke events in the Colorado Front Range in summer 2015. *Atmos Chem Phys* 17:10691–10707
- Lonsdale CR, Alvarado MJ, Hodshire AL et al (2020) Simulating forest fire plume dispersion, chemistry, and aerosol formation using SAM-ASP version 1.0. *Geoscientific Model Dev Discuss* 13:4579–4593
- Lonsdale CR, Brodowski CM, Alvarado MJ (2017) Improving the modeling of wildfire impacts on ozone and particulate matter for Texas air quality *planning* (Final report, Project 16–024, August). Texas Air Quality Research Program, Austin. http://aqrp.ceer.utexas.edu/viewprojects/FY16-17.cfm?Prop_Num=17-024. 22 June 2020
- Mauzerall DL, Logan JA, Jacob DJ et al (1998) Photochemistry in biomass burning plumes and implications for tropospheric ozone over the tropical South Atlantic. *J Geophys Res Atmos* 103:8401–8423
- May AA, Levin EJ, Hennigan CJ et al (2013) Gas-particle partitioning of primary organic aerosol emissions: 3. Biomass burning. *J Geophys Res Atmos* 118:11327–11338
- McClure CD, Jaffe DA (2018) US particulate matter air quality improves except in wildfire-prone areas. *Proc National Acad Sci USA* 115:7901–7906
- McDonald-Buller E, Kimura Y, Wiedinmyer C et al (2015) Targeted improvements in the fire inventory form NCAR (FINN) model for Texas air quality planning (Final report, Project 14–011, December). Texas Air Quality Research Program, Austin. http://aqrp.ceer.utexas.edu/projectinfo/FY14_15%5C14-011%5C14-011%20Final%20Report.pdf. 22 June 2020
- McKeen SA, Wotawa G, Parrish DD et al (2002) Ozone production from Canadian wildfires during June and July of 1995. *J Geophys Res Atmos* 107:4192
- Mebust AK, Cohen RC (2013) Observations of a seasonal cycle in NO_x emissions from fires in African woody savannas. *Geophys Res Lett* 40:1451–1455
- Morrison G (2015) Recent advances in indoor chemistry. *Curr Sustain/renew Energy Rep* 2:33–40
- Murphy BN, Donahue NM, Robinson AL, Pandis SN (2014) A naming convention for atmospheric organic aerosol. *Atmos Chem Phys* 14:5825–5839
- Pankow JF (1994) An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos Environ* 28:189–193
- Petrick LM, Sleiman M, Dubowski Y et al (2011) Tobacco smoke aging in the presence of ozone: a room-sized chamber study. *Atmos Environ* 45:959–965
- Real E, Law KS, Weinzierl B et al (2007) Processes influencing ozone levels in Alaskan forest fire plumes during long-range transport over the North Atlantic. *J Geophys Res Atmos* 112:D10S41
- Sakamoto KM, Allan JD, Coe H et al (2015) Aged boreal biomass-burning aerosol size distributions from BORTAS 2011. *Atmos Chem Phys* 15:1633
- Sakamoto KM, Laing JR, Stevens R et al (2016) The evolution of biomass-burning aerosol size distributions due to coagulation: dependence on fire and meteorological details and parameterization. *Atmos Chem Phys* 16:7709–7724
- Sekimoto K, Koss AR, Gilman JB et al (2018) High- and low-temperature pyrolysis profiles describe volatile organic compound emissions from western US wildfire fuels. *Atmos Chem Phys* 18:9263–9281
- Shiraiwa M, Berkemeier T, Schilling-Fahnestock KA et al (2014) Molecular corridors and kinetic regimes in the multiphase chemical evolution of secondary organic aerosol. *Atmos Chem Phys* 14:8323–8341
- Shrivastava M, Easter RC, Liu X et al (2015) Global transformation and fate of SOA: Implications of low-volatility SOA and gas-phase fragmentation reactions. *J Geophys Res Atmos* 120:4169–4195

- Sleiman M, Gundel LA, Pankow JF et al (2010) Formation of carcinogens indoors by surface-mediated reactions of nicotine with nitrous acid, leading to potential thirdhand smoke hazards. *Proc Nat Acad Sci USA* 107:6576–8651
- Stein AF, Rolph GD, Draxler RR et al (2009) Verification of the NOAA smoke forecasting system: model sensitivity to the injection height. *Weather Forecast* 24:379–394
- Teakles AD, So R, Ainslie B et al (2017) Impacts of the July 2012 Siberian fire plume on air quality in the Pacific Northwest. *Atmos Chem Phys* 17:2593
- Tkacik DS, Robinson ES, Ahern A et al (2017) A dual-chamber method for quantifying the effects of atmospheric perturbations on secondary organic aerosol formation from biomass burning emissions. *J Geophys Res Atmos* 122:6043–6058
- U.S. Environmental Protection Agency (USEPA) (2016) Final guidance on the preparation of exceptional events demonstrations for wildfire events that may influence ozone concentrations. U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park. https://www.epa.gov/sites/production/files/2018-10/documents/exceptional_events_guidance_9-16-16_final.pdf. 22 June 2020
- Vakkari V, Kerminen VM, Beukes JP et al (2014) Rapid changes in biomass burning aerosols by atmospheric oxidation. *Geophys Res Lett* 41:2644–2651
- Vakkari V, Beukes JP, Dal Maso M et al (2018) Major secondary aerosol formation in southern African open biomass burning plumes. *Nat Geosci* 11:580–583
- Val Martin M, Honrath RE, Owen RC et al (2006) Significant enhancements of nitrogen oxides, black carbon, and ozone in the North Atlantic lower free troposphere resulting from North American boreal wildfires. *J Geophys Res Atmos* 111:D23S60
- Wheeler AJ, Jones PJ, Reisen F et al (2020) Roof cavity dust as an exposure proxy for extreme air pollution events. *Chemosphere* 244:125537
- Wolfe GM, Marvin MR, Roberts SJ et al (2016) The framework for 0-D atmospheric modeling (FOAM) v3. 1. *Geoscientific Model Dev* 9:3309–3319
- Yacovitch TI, Herndon SC, Pétron G et al (2015) Mobile laboratory observations of methane emissions in the Barnett Shale region. *Environ Sci Technol* 49:7889–7895
- Ye C, Zhang N, Gao H, Zhou X (2017) Photolysis of particulate nitrate as a source of HONO and NO_x. *Environ Sci Technol* 51:6849–6856
- Yokelson RJ, Crounse JD, DeCarlo PF et al (2009) Emissions from biomass burning in the Yucatan. *Atmos Chem Phys* 9:5785–5812
- Yu S, Bhave PV, Dennis RL, Mathur R (2017) Seasonal and regional variations of primary and secondary organic aerosol over the continental United States: Semi-empirical estimates and model evaluation. *Environ Sci Technol* 41:4690–4697
- Zaveri RA, Easter RC, Shilling JE, Seinfeld JH (2014) Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: representing effects of volatility, phase state, and particle-phase reaction. *Atmos Chem Phys* 14:5153–5181
- Zhang L, Jacob DJ, Yue X et al (2014) Sources contributing to background surface ozone in the US Intermountain West. *Atmos Chem Phys* 14:5295–5309
- Zhou S, Collier S, Jaffe DA et al (2017) Regional influence of wildfires on aerosol chemistry in the western US and insights into atmospheric aging of biomass burning organic aerosol. *Atmos Chem Phys* 17:2477–2493

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