

JGR Atmospheres

RESEARCH ARTICLE

10.1029/2018JD029674

Key Points:

- Fire size (initial plume size) and background aerosol concentration affects smoke aerosol evaporation, condensation, and coagulation
- Plumes from large fires dilute slowly, undergo rapid coagulation, lose little mass to evaporation, and are unaffected by background aerosol
- Small plumes dilute quickly causing less coagulation and more evaporation, but evaporation slows with increasing background aerosol

Supporting Information:

- Supporting Information S1
- Table S1

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Citation:

Hodshire, A. L., Bian, Q., Ramnarine, E., Lonsdale, C. R., Alvarado, M. J., Kreidenweis, S. M., et al. (2019). 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*, 124, 5589–5611. https://doi.org/ 10.1029/2018JD029674

Received 18 SEP 2018 Accepted 9 APR 2019 Accepted article online 23 APR 2019 Published online 22 MAY 2019

Author Contributions:

Conceptualization: Q. Bian, C. R. Lonsdale, M. J. Alvarado, S. M. Kreidenweis, S. H. Jathar, J. R. Pierce Formal analysis: Q. Bian, E. Ramnarine, C. R. Lonsdale, M. J. Alvarado, S. M. Kreidenweis, S. H. Jathar, J. R. Pierce Funding acquisition: E. Ramnarine, C. R. Lonsdale, M. J. Alvarado Investigation: Q. Bian, E. Ramnarine, C. R. Lonsdale, M. J. Alvarado, S. M. Kreidenweis, S. H. Jathar, J. R. Pierce Methodology: O. Bian, E. Ramnarine, C. R. Lonsdale, M. J. Alvarado, S. M. Kreidenweis, S. H. Jathar, J. R. Pierce (continued)

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More Than Emissions and Chemistry: Fire Size, Dilution, and Background Aerosol Also Greatly Influence Near-Field Biomass Burning Aerosol Aging

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Abstract Biomass burning emits particles (black carbon and primary organic aerosol) and precursor vapors to the atmosphere that chemically and physically age in the atmosphere. This theoretical study explores the relationships between fire size (determining the initial plume width and concentration), dilution rate, and entrainment of background aerosol on particle coagulation, organic aerosol (OA) evaporation, and secondary organic aerosol (SOA) condensation in smoke plumes. We examine the impacts of these processes on aged smoke OA mass, geometric mean diameter (D_g) , peak lognormal modal width $(\sigma_{\rm e})$, particle extinction (E), and cloud condensation nuclei (CCN) concentrations. In our simulations, aging OA mass is controlled by competition between OA evaporation and SOA condensation. Large, slowly diluting plumes evaporate little in our base set of simulations, which may allow for net increases in mass, E, CCN, and Dg from SOA condensation. Smaller, quickly diluting fire plumes lead to faster evaporation, which favors decreases in mass, E, CCN, and D_g . However, the SOA fraction of the smoke OA increases more rapidly in smaller fires due to faster primary organic aerosol evaporation leading to more SOA precursors. Net mass changes for smaller fires depend on background OA concentrations; increasing background aerosol concentrations decrease evaporation rates. Although coagulation does not change mass, it can decrease the number of particles in large/slowly diluting plumes, increasing D_g and E, and decreasing σ_g . While our conclusions are limited by being a theoretical study, we hope they help motivate future smoke-plume analyses to consider the effects of fire size, meteorology, and background OA concentrations.

1. Introduction

Biomass burning smoke is a significant source of primary and secondary atmospheric particles that have impacts on climate (Bond et al., 2013), air quality (e.g., Jaffe & Wigder, 2012; Nie et al., 2015; Xie et al., 2015), and health (e.g., Jassen et al., 2010; Johnston et al., 2012; Naeher et al., 2007; Zhang et al., 2009). Biomass burning emits primary carbonaceous aerosol (both as black carbon and primary organic aerosol; POA; Akagi et al., 2011; Reid, Koppmann, et al., 2005, and references therein), inorganic aerosol, and vapors, where some vapors may serve as aerosol precursors (e.g., Alvarado & Prinn, 2009; Bertrand et al., 2018; Hatch et al., 2017; Jen et al., 2018). Biomass burning particle emissions are dominated by an accumulation mode, with a less-concentrated coarse mode and occasionally a nucleation mode (Reid, Koppmann, et al., 2005). Although the coarse mode is comprised mainly of dust, ash, unburned fuel, and carbon aggregates (Formenti et al., 2003; Gaudichet et al., 1995; Hungershoefer et al., 2008), the accumulation mode is comprised mainly of organic material, with black carbon and inorganic species (such as potassium, chlorine, calcium, and sulfate) making up ~10% each of the remaining fraction, depending on the fuel (Bian et al., 2015; Reid, Koppmann, et al., 2005).

Both the POA and vapors evolve as the initial smoke plume dilutes, entrains background air, and undergoes oxidative aging along with aerosol microphysical processes such as evaporation, condensation, coagulation, and deposition (e.g., Akagi et al., 2012; Alvarado et al., 2015; Hecobian et al., 2011; Sakamoto et al., 2016; Vakkari et al., 2014). Each of these processes help shape the aerosol mass and number size distributions. Understanding the bulk mass evolution of biomass burning aerosols is important from a regulatory and health standpoint and allows for an estimate of their direct radiative effect (DRE) on the Earth's energy balance (Charlson et al., 1992; Heald et al., 2014). Understanding the number size distribution evolution of



Supervision: Q. Bian, M. J. Alvarado, S. H. Jathar, J. R. Pierce Writing – review & editing: Q. Bian, E. Ramnarine, C. R. Lonsdale, M. J. Alvarado, S. M. Kreidenweis, S. H. Jathar, J. R. Pierce

biomass burning aerosols further allows for a more precise understanding of their DRE and provides an estimate of their indirect effect on the Earth's radiative budget through altering cloud properties (e.g., the cloud-albedo aerosol indirect effect [AIE]; Boucher et al., 2013). Further, particle size influences the lung-deposition efficiency and hence may impact health (Hussein et al., 2013; Löndahl et al., 2007, 2009).

The DRE of particles depends, in part, on their relative amounts of scattering and absorption in the atmosphere. The sum of scattering and absorption is given as the particles' extinction (Seinfeld & Pandis, 2006). The mass extinction efficiency is the ratio of the extinction of the particle to the particle's mass; similarly, the mass scattering and absorption efficiencies are the ratios of each particle's scattering and absorption to its mass. Peak mass extinction (or scattering/absorption) efficiencies typically occur for particles between 100 nm and 1 μ m in diameter (D_p). The AIE is determined by cloud condensation nuclei (CCN) properties and concentrations: particles that become CCN can alter cloud reflectivity (albedo) by changing the cloud droplet number concentration (Twomey, 1974). The ability of a particle to act as a CCN depends both on its size and hygroscopicity (Petters & Kreidenweis, 2007); for typical cloud conditions, particles with D_p larger than 40–100 nm can activate into droplets. As biomass burning plumes age, both particle extinction and CCN concentrations are impacted through changes in mass, number, size, and composition.

A large number of field campaigns have analyzed the aging of various normalized biomass burning aerosol properties within the plume. In this study, normalized refers to correcting a property for dilution and background concentrations by subtracting off the background value and then dividing the property by a conserved quantity, usually an effectively inert species, such as CO. Studies focusing on the aging of organic aerosol mass report a range of changes to the net (difference between total secondary organic aerosol [SOA] production and OA evaporation) normalized OA within the plume (Shrivistava et al., 2017): some of these studies reported an OA gain (Alvarado & Prinn, 2009; Cachier et al., 1995; Formenti et al., 2003; Liu et al., 2016; Reid et al., 1998; Vakkari et al., 2014, 2018; Yokelson et al., 2009), some an OA loss (Akagi et al., 2012; Forrister et al., 2015; Hobbs et al., 2003; Jolleys et al., 2012, 2015; May et al., 2015), and others showed no significant change in OA (Brito et al., 2014; Capes et al., 2008; Collier et al., 2016; Cubison et al., 2011; Hecobian et al., 2011; Liu et al., 2016; May et al., 2015; Nance et al., 1993; Sakamoto et al., 2015; Zhou et al., 2017). However, sampling noise due to different sampling times, collection efficiencies, and other issues can also make it ambiguous whether net normalized OA increased in a single fire (e.g., the analysis of Alvarado and Prinn (2009) of the Timbavati fire from Hobbs et al. (2003)). Studies that measured aspects of particle extinction tend to report net normalized increases in total extinction (e.g., Abel et al., 2003; Radke et al., 1995; Reid et al., 1998; Vakkari et al., 2014; Yokelson et al., 2009), although loss in total extinction has been observed past 10 hr of aging (Radke et al., 1995). The majority of studies that have explored CCN aging within plumes have found a normalized increase in CCN with aging (e.g., Eagan et al., 1974; Vakkari et al., 2014) with Vakkari et al. (2014) further reporting no change in CCN for some observed fires. It is as yet unclear if changes in size, total number, or composition are driving observed changes.

The net change of organic aerosol (OA) mass in a smoke plume as it dilutes and ages is determined from the balances between initial emissions (which depends upon, e.g., fuel type and burn conditions), SOA production, and evaporation of both POA and SOA (Bian et al., 2017). Biomass burning POA has been observed to undergo evaporation (e.g., Formenti et al., 2003; Huffman et al., 2009; Liousse et al., 1995; May et al., 2013) as semivolatile compounds that are susceptible to evaporation due to dilution can make up a significant fraction, ~20–90% of particle-phase biomass burning POA (Eatough et al., 2003; Grieshop et al., 2009; May et al., 2013; May et al., 2015). The initial plume width (characterized by the fire width) as well as the atmospheric stability (often characterized by stability class; Pasquill, 1961) will determine the dilution and therefore potential OA evaporation rates, with larger fires and more stable atmospheres diluting more slowly and losing less OA through evaporation relative to smaller fires and less stable atmospheres (e.g., Bian et al., 2017). The plume edges will mix more rapidly than the plume core in all cases. Regardless, large smoke plumes will maintain higher particle concentrations (averaged across plume transects at a given distance from the fire) than smaller smoke plumes, all else equal.

The evolution of the total number of particles from biomass burning emissions is controlled by coagulation (Akagi et al., 2012; Capes et al., 2008; Formenti et al., 2003; Radke et al., 1995; Ramnarine et al., 2018; Sakamoto et al., 2016), although deposition plays a minor role early in the plume, and nucleation may



contribute to number in some cases (e.g., Andreae et al., 2001; Hennigan et al., 2012; Hobbs et al., 2003; Vakkari et al., 2018). The rate of coagulation is proportional to the square of the particle number concentration for particles of fixed sizes. Hence, coagulation within plumes will occur the most rapidly within the initial (densest) time period of the plume, and observed net changes in CCN for plumes are likely highly sensitive to the range of the ages of the measurements within the plume (e.g., if the measurements begin after some aging/dilution, coagulation may have already slowed greatly). As well, large fires that dilute more slowly will have more sustained coagulation in plumes than fires with smaller fluxes.

The particle size distribution is impacted by both coagulation and SOA condensation/OA evaporation: coagulation leads to growth of the mean diameter of particles in the plume and a narrowing of the modal width while reducing particle number (Janhäll et al., 2010; Sakamoto et al., 2016). Similarly, SOA condensation/OA evaporation leads to growth/shrinkage of the mean diameter. Changes in the modal width depend on the volatility of the vapors: semivolatile vapors quickly reach equilibrium and condense or evaporate in the quasi-equilibrium limit, which yields diameter growth rates proportional to particle diameter D_p at all sizes (Pierce et al., 2011; Riipinen et al., 2011; Zhang et al., 2012), leading to no changes in lognormal modal width with condensation or evaporation. Conversely, low-volatility vapors condense yielding diameter growth rates independent of particle size in the kinetic regime ($D_p < -50$ nm) but yield diameter growth rates proportional to $1/D_p$ for the continuum regime ($D_p > -1 \mu$ m; Pierce et al., 2011; Riipinen et al., 2011; Zhang et al., 2011; Diameter al., 2011; Zhang et al., 2012), and thus, condensation of low-volatility vapors decreases the lognormal modal width. Thus, understanding the balances between SOA formation, OA evaporation, and coagulation in biomass burning plumes are all essential for understanding net changes in OA mass, number, and size.

As we will argue in this study, the background aerosol concentration that plumes dilute into and entrain in also impacts plume OA mass, number, and size. If smaller fires occur in polluted atmospheres with a high background concentration of OA, evaporation will be reduced as the entraining background aerosol provides organic vapors and mass for organic vapors to partition into (Donahue et al., 2006), assuming that the OA in the background and plume effectively mix with each other, thermodynamically. These background effects can be important for the total size and mass of particles produced, especially in regions that experience high numbers of small fires, such as the Amazon Basin during the dry season (e.g., Martin et al., 2016; Reid et al., 1998), creating high ambient OA concentrations for new smoke plumes to mix into (Baars et al., 2012; Martin et al., 2010; Reid et al., 1998). Only a few studies have reported the explicit ambient background aerosol concentrations in their publications (Cachier et al., 1995; Nance et al., 1993), and as best we can tell, no published field analyses have explicitly accounted for or discussed the potential effect that background aerosol entraining into the diluting plume may have on evaporation rates. We note that for most field studies, data for these background concentrations exist, but for most studies, it has not been explicitly considered in published work.

To our knowledge, no study has systematically investigated how fire size, dilution rates, and background aerosol concentrations are expected to influence biomass burning aerosol aging. In this study, we perform a theoretical analysis of the importance of these factors on total OA mass, number concentration, and particle size through changes to OA evaporation, SOA condensation, and coagulation. Throughout this study, we use "fire size" to mean the area of the fire that is currently burning. The initial plume width is a function of this fire size, and hence, fire size directly impacts the dilution rate of the plume. We use an aerosol microphysics model (described in section 2) to simulate a representative range of plume sizes diluting into different background aerosol concentrations. We do not attempt to simulate any specific previously observed plumes here; instead, we simulate simplified plume test cases that undergo different dilution rates (as represented by different initial plume sizes) into variable background aerosol concentrations in order to carefully characterize the importance of dilution rates and background aerosol concentrations. In these simulations, we hold many known important factors (such as emissions flux; oxidant concentrations; temperature; the amount of UV radiation in the plume, which may be attenuated in thick plumes; and chemical rate constants and yields) fixed in order to isolate the potential impacts of fire size and background OA concentrations; however, we do test the sensitivity of our results to some of these factors. As well, we do not consider black carbon, or the potential formation of tar balls within the plume, although these are likely important features in many smoke plumes (e.g., Forrister et al., 2015; Sedlacek et al., 2018). In this idealized system, we examine the effect of aging on aerosol mass (section 3.1), aerosol size distribution properties (mean diameter and peak lognormal modal width; section 3.2), and aerosol properties that impact



radiative effects (through total extinction cross section and CCN; section 3.3). We discuss limitations of this study in section 3.4. Section 4 discusses real-world fire sizes and background aerosol concentrations and observational studies. Section 5 provides a synthesis of our findings, as well as recommendations for future studies.

2. Methods

2.1. Model Description

We perform simulations of biomass burning aging using the TOMAS (TwO-Moment Aerosol Sectional) microphysics box model (Adams & Seinfeld, 2002; Pierce et al., 2011), coupled to the Volatility Basis Set (VBS; Donahue et al., 2006) as a single-box, expanding, Lagrangian plume model as described in Bian et al. (2017). By assuming a single, Lagrangian box, we do not resolve the effects that dilution may have at the edge (rather than the core) of plumes, which is a limitation of this study that we will discuss more in section 3.4. TOMAS explicitly tracks and conserves number and mass while simulating condensation and coagulation. Condensation and evaporation is calculated through aerosol partitioning theory (Pankow, 1994) using kinetic mass transfer (Pierce et al., 2011). Coagulation is simulated using the (size-dependent) Brownian kernel in Seinfeld and Pandis (2006). We assume that the model simulations occur over time scales short enough that dry deposition is negligible. We do not account for any wet deposition or other aqueous processes (see section 3.4 for a full discussion of the limitations of this study). Our model setup is identical to that of the study of Bian et al. (2017); here we provide a brief overview.

We use 36 logarithmically spaced size sections from 3 nm to 10 μ m. The simulated aerosol species are a nonvolatile inorganic species to represent a generic nonvolatile inorganic species, water, and 15 organic "species" that represent lumped organics with logarithmically spaced effective saturation concentrations (C^*) spanning from 10^{-3} to $10^{11} \,\mu\text{g/m}^3$ within the VBS framework. The inorganic species is assumed to remain inert within the particle throughout each simulation, as our optical and hygroscopicity properties are held fixed (section 2.3). We do not explicitly include black carbon as a separate aerosol species but rather it is implicitly included in the generic inorganic species. All species are assumed to be internally mixed within each size section. We assume a starting organic mass fraction of 0.9, a value roughly representative of many natural fuel types (Bian et al., 2015), with the remaining mass fraction assumed to be the nonvolatile inorganic species. Each simulation is initialized with the initial volatility distribution from Bian et al. (2017), which adapts the findings of May et al. (2013) (for $C^* \leq 10^4 \,\mu g/m^3$) and Hatch et al. (2017) (for $C^* > 10^4 \,\mu \text{g/m}^3$). This merged volatility distribution has significant mass in the $C^* = 10^4 \,\mu \text{g/m}^3$ bin and little mass in the $C^* = 10^5 \,\mu g/m^3$ and $C^* = 10^6 \,\mu g/m^3$ bins, which is likely due to limitations of the two methods. In reality, we expect a more even distribution of volatility across these bins. However, as most of the initial material in the $C^* = 10^4 \,\mu g/m^3$ bin is in the vapor phase (Figures S4 and S5 in the supporting information) for all fire sizes, we do not expect this volatility uncertainty to qualitative impact our results across fire sizes. We assume a fixed temperature of 298 K throughout the entire simulation, both spatially and temporarily, a limitation of this study further discussed in section 3.4.

Gas-phase functionalization of the organic species within the VBS is simulated assuming that reaction with OH leads to a product vapor four volatility bins lower than the parent molecule. The OH concentration is set to 1.08×10^6 molec/cm³, following Bian et al. (2017), and is held fixed throughout each model run. This OH concentration is lower than what has been reported in studies that have characterized in-plume OH (Akagi et al., 2012; Hobbs et al., 2003; Yokelson et al., 2009), but this may be balanced by our relatively fast OA aging scheme presented below. OH is likely a function of fire size/dilution rates, as these factors can control the amount of light available in-plume as well as the amount of oxidants, and we will leave the exploration of OH and fire size to a future study. We assume that the rate of reactions of OH with organics follows the relationship determined by Jathar et al. (2014) for aromatics: $k_{\text{OH}} = -5.7 \times 10^{-12} \ln(C^*) + 1.14 \times 10^{-10}$. Jathar et al. (2014) also provides a relationship for alkanes: $k_{\text{OH}} = -1.84 \times 10^{-12} \ln(C^*) + 4.27 \times 10^{-10}$. The fit for aromatics with a four volatility bin drop as an upper bound on SOA condensation, following Bian et al. (2017), as this was the chemistry assumption that best fit smog chamber data from the third Fire Lab At Missoula Experiment. The initial OA concentrations in the smog chamber at the third Fire Lab At Missoula Experiment were between ~16 and 86 $\mu g/m^3$. We present our base results using this upper



bound assumption on OA oxidation ("upper bound chemistry"), as this set of assumptions provided the best fits with chamber data in Bian et al. (2017), but we also show in section S5 and Figures S13 and S14 in the supporting information a sensitivity test using the alkane reaction rate with a two-bin volatility bin drop as a lower bound on OA oxidation ("lower bound chemistry"; Bian et al., 2017). The lower bound chemistry simulations could not only be insightful for conditions with reduced reaction rates but can also act as a proxy for conditions with reduced OH concentrations, as may occur for plumes with reduced amounts of light available within the plume. These reaction rates are applied uniformly to all gas-phase organics within the model's VBS (regardless of species type) so as to represent an "average" reaction rate. We further assume that fragmentation is trivial at the time scale of our study (4 hr; Shrivistava et al., 2013) and do not include any fragmentation reactions in the model.

The expansion of our Lagrangian box is simulated with a Gaussian dispersion framework, assuming a uniform pollutant distribution across the expanding volume. The assumption of a uniform pollutant distribution is a limitation of this study that is discussed further in section 2.4. Following Bian et al. (2017), we assume a fixed wind speed in the x direction (the plume's long axis) of 5 m/s. The crosswind width and height of the initial and expanding plume is $4\sigma_v$ and $4\sigma_z$, respectively, but with a maximum plume mixing depth of 2,500 m. We do not explicitly assume that the plume remains within the boundary layer (BL; i.e., this layer with a 2,500-m maximum mixing depth is not necessarily in the BL), but we do not change the temperature and pressure to be representative of free troposphere (FT) conditions. Dispersion may be slower in the FT than the BL, as the FT is generally stable due to lack of significant heating at the bottom of any given layer (Wallace & Hobbs, 2006). We test the sensitivity of our results to moderately stable conditions that may be more representative of dispersion in the free troposphere, as discussed in section 2.2. Pasquill (1961) represent atmospheric stability in the model, and are used to estimate the values of σ_v and σ_z , following Klug (1969). The initial plume width of $4\sigma_v$ is set to be the same as the fire width (square root of the fire area, which is defined here as the area that is currently burning). Thus, in the model, the initial plume concentration is defined by the time spent over the fire and initial values of $4\sigma_v$ and $4\sigma_z$. The dilution rate of the plume is controlled by the initial plume size, the wind speed in the x direction, and the atmospheric stability class within the Gaussian dispersion framework. Figure 1d shows the dilution ratio as a function of time for fire sizes of 100, 1, 10^{-2} , and 10^{-4} km². The model simulates the expanding plume downwind as it ages in a Lagrangian framework. We assume that depositional processes (wet or dry) are minor within the modeled time period (4-8 hr) and do not include them in the model.

2.2. Description of Simulations

Table 1 provides an overview of the simulations performed in this study. The primary sensitivity studies are for seven fires sizes between 10^{-4} and 100 km^2 (0.01 to 10^4 ha; each fire size is separated by an order of magnitude in fire area). Throughout this study, fire size is meant to indicate the area of the fire that is currently burning. Fires between 10^{-4} and 0.1 km² are approximately representative of small prescribed burns (e.g., Huang et al., 2018); the larger fire sizes are representative of the range of large prescribed burns and wildfire sizes (e.g., Giglio et al., 2010). Each simulated plume entrains constant background aerosol concentrations of 0, 5, 20, or 50 μ g/m³ as the plume expands. The background size distribution is assumed to be composed of nonvolatile organics (e.g., well-aged), and once entrained into the plume, these particles undergo coagulation and may take up organic vapors. The background aerosol also provides mass for the plume aerosols and vapors to partition into (Pankow, 1994). These constant background aerosol concentrations of $5-50 \ \mu g/m^3$ can exceed the smoke mass from the fire within the diluting plume, depending upon the initial mass emissions and dilution rate, the consequences of which will be discussed in section 3.1. Real-world background aerosol concentrations vary spatially; hence, our simulated background is idealized. Each initial plume and background size distribution are assumed to be single lognormal modes with lognormal modal number median diameters (D_{g} and $D_{g, bg}$) of 70 and 157 nm (corresponding to lognormal modal mass median diameters of 296 and 365 nm) and lognormal modal widths (σ_g and $\sigma_{g, bg}$) of 2.0 and 1.7, respectively (Table 1). These values were chosen following Carrico et al. (2016) for fresh biomass burning emissions and D'Andrea et al. (2013) for background aerosol, respectively.

In order to determine the individual and combined effects of SOA condensation and coagulation on the smoke size distribution, we run four simulations for each fire size and background combination: (1) chemistry off, coagulation off (ChemOff_CoagOff); (2) chemistry off, coagulation on (ChemOff_CoagOn);





Figure 1. (a–d) Time evolution of total smoke organic aerosol mass concentration enhancement (background organic aerosol subtracted off) in the particle phase for chemistry-on (solid lines) and chemistry-off (dashed lines) simulations for the fire areas of 10^{-4} , 10^{-2} , 1, and 100 km² (colored lines) and background aerosol concentrations (black dotted lines) of (a) 0, (b) 5, and (c) 50 μ g/m⁻³. (d) Time evolution of the dilution ratio for each fire size. Results are for the base simulations (Table 1) from the CoagOn version of each ChemOff/ChemOn case.

(3) chemistry on, coagulation off (ChemOn_CoagOff); and (4) chemistry on, coagulation on (ChemOn_CoagOn). We also run simulations with coagulation on and coagulation off for each background concentration that has no smoke emissions and instead simulates aging of the background as it would be without the presence of the plume over the same time period used for the full (plume plus background) simulations. These simulations are used to determine the number and mass enhancement of the plume above background. Note that since we assume a nonvolatile background without available gas-phase vapors, changes in the background size distribution occur only if coagulation is on.

The base set of primary sensitivity simulations in this work are with the upper bound chemistry scheme (Table 1), a constant mass flux of 5×10^{-6} kg·m⁻²·s⁻¹; neutral atmospheric stability (stability class D); and the mass accommodation coefficient, α , set to 1. As the mass flux and emissions size distribution are held fixed, the particle number emissions per area are also held constant; the total initial number concentrations for each fire size are provided in Table S1. We further run "secondary sensitivity simulations" on a number of parameters (Table 1 and section 2) to provide a more complete framework of the relative importance of fire size, background concentration, SOA condensation, OA evaporation, and coagulation under different potential atmospheric and chemical conditions. Each sensitivity simulation tests one parameter while holding all others at the values of the base cases. We test the following sensitivities: the rate of SOA condensation (using the lower bound chemistry parameterization, discussed above, and a two bin drop in volatility per reaction), α (testing $\alpha = 0.1$ and $\alpha = 0.01$), and the stability class (testing *B*, moderately unstable, and *F*, moderately stable). Reducing the accommodation coefficient can be used to compensate for potential particle-phase diffusion limitations that would occur if the aerosol increased in viscosity (Hodshire et al., 2018). As particlephase diffusion limitations slow or halt the rate at which condensing vapors can diffuse through the particle, the condensing vapors can more easily evaporate. Reducing α accounts for this net reduction in the condensation rate, but it does not account for potential size-dependent diffusion limitations (Zaveri et al., 2017). (We assume liquid particles in our primary cases, which will likely have accommodation coefficients at or close to unity; Julin et al., 2014.) Bateman et al. (2017) found that SOA influenced by biomass burning increased in viscosity over the Amazonian rainforest as compared to purely biogenic SOA, indicating that

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100
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Description Value	$ \begin{array}{c} \text{mulations} \\ \text{Area of fire emissions (km^2)} \\ \text{ation} \\ \text{Background aerosol mass concentration (\mu g/m^3) \\ \text{Whether or not gas-phase chemistry and/or coagulation is on} \\ \text{Molether or not gas-phase chemistry and/or coagulation is on} \\ \end{array} $	simulations ^a In-plume reaction rate constant (cm ³ ·molecule ⁻¹ s ⁻¹) Upper bound chemistry: $-5.7 \times 10^{-12} \ln(C^*) + 1.14 \times 10^{-10}$) bins per reaction with OH Upper bound chemistry: $-1.84 \times 10^{-12} \ln(C^*) + 4.27 \times 10^{-10}$) bins per reaction with OH Upper bound chemistry: 4 (Lower bound chemistry: $-1.84 \times 10^{-12} \ln(C^*) + 4.27 \times 10^{-10}$)	Pasquill stability classes for atmospheric turbulence D (B, F) Accommodation coefficient 1.0 (0.1, 0.01)	Dd How long the simulation is run for (hr) 4 (8)	Dry peak number diameter of emissions and background (nm)70, 157Particle size distribution standard deviation of emissions2.0, 1.7Particle size distribution standard deviation of emissions2.0, 1.7and background5 $^{-2}$ $^{-1}$)5 $\times 10^{-6}$ Fire emission mass flux (kg m ⁻² s ⁻¹)5 $\times 10^{-6}$ Mean boundary layer wind speed (m/s)5 $^{-2}$ Ambient temperature during dilution (K)2.08Maximum depth the plume can mix within (m)2.500In-plume OH concentration (molecules/cm ³)1.08 $\times 10^{6}$	the parameter space of the primary sensitivity simulations (fire size, background aerosol concentration, and chemistry/coagulation), using the constants listed in the final base simulations are composed of the bolded values in the secondary sensitivity simulations. Secondary sensitivity simulations are run using the values in parentheses neitivity simulations.
Parameter	Primary sensitivity simulations Fire size Background concentration Chemistry and coagulation	Secondary sensitivity simulations ^a $k_{\rm OH}$ $k_{\rm OH}$ Decrease in volatility bins per reaction	Stability class α	Simulated aging period	Constants D_g and D_g , b_g σ_g and σ_g , b_g Mass flux Wind speed T Maximum plume mixing depth [OH]	All cases are run within the parameter spac section of the table. The base simulations a within the secondary sensitivity simulation ^a Values in bold are used for the base simu shown in the supporting information.



biomass burning could potentially yield high-viscosity aerosol. As well, some field studies have observed the presence of tar balls, nearly spherical and highly viscous particles (e.g., Adachi & Buseck, 2011; Pósfai et al., 2003, 2004; Sedlacek et al., 2018). Changing the stability class effectively models differing dilution rates, and has an effect similar to changing fire sizes, which is why we treat stability as a secondary sensitivity. The results of the secondary sensitivity tests are briefly discussed in the text, and figures are provided in the supporting information. All cases are run with the constants described in the final section of Table 1.

For brevity, we only show results for fire sizes of 10^{-2} , 1, and 100 km^2 with background concentrations of 0, 5, and 50 µg/m³ for each base case and sensitivity simulation as these capture the main features of these dimensions; we also include the fire size of 10^{-4} in our mass discussion. Results for all fires sizes and background are included in Figures S1, S3, S6, S7, S10, and S12 in the supporting information for the base cases. We analyze all simulations after 4 hr of aging but also provide results for the base simulations after 8 hr of aging in the supporting information. We chose 4 hr as our analysis time as dilution is generally slow past this time, and the assumption of a constant OH concentration is less valid over longer time periods.

Two-moment sectional models can artificially distort the size distribution through size-bin emptying, and thus to remove numerical artifacts, the simulated distributions were smoothed. Section S1.1 in the supporting information provides further details on the smoothing technique used (Stevens et al., 1996).

2.3. Calculations of Smoke Size Distribution, CCN, and Extinction

We determine each simulation's contribution of smoke toward total OA mass, total extinction cross section (E), and CCN. We find the in-plume enhancement of each metric (OA mass, E, and CCN) by subtracting the matching metric from the background aerosol size distribution (that is, the background OA mass, E, and CCN) of an otherwise identical simulation that has no smoke emissions, as described in section 2.2 (We match both the background concentration used and whether coagulation is on or off in our background correction.) Each enhancement (ΔOA mass, ΔE , and ΔCCN) is normalized by the enhancement of CO above its background (ΔCO) to allow us to determine if these metrics have increased or decreased relative to their values at emission. Emissions factors of CO vary from study to study but are generally on the order of 10 times greater than that of PM_{2.5} emissions (e.g., Akagi et al., 2011; Burling et al., 2011), and so for this study we assume that CO emissions are 10 times that of particle mass emissions. Correcting the distributions for the background and normalizing the time-evolving simulations by ΔCO can be referred to as the normalized excess mixing ratio (e.g., Akagi et al., 2012), a common metric in field campaigns, in which the in-plume concentrations of species X are background-corrected (ΔX) and normalized by the inert background-corrected tracer ΔY that has been measured at the same time and location. We note that the exact values of $\Delta OA/\Delta CO$, $\Delta E/\Delta CO$, and $\Delta CCN/\Delta CO$ will vary with the values of mass, number, and CO emissions under different real plumes, as well as the values used for particle hygroscopicity and refractive index (as described below). However, we are not attempting to simulate any specific observed plumes and argue that the specific values of these metrics are less important than their relative changes between different fire sizes/dilution rates and background aerosol concentrations. We hypothesize that the qualitative conclusions of this work will hold across studies. The total initial and final OA mass from smoke is found by summing the mass (explicitly tracked in TOMAS) across all bins. We calculate the peak diameter (D_{g}) and lognormal modal width (σ_{σ}) of the smoke plume using the methods of Whitby et al. (1991); further details are given in section S2 in the supporting information.

 $\Delta E / \Delta CO$ is calculated through

$$\frac{\Delta E}{\Delta CO} = \frac{\sum \Delta N_i \cdot Q_{ext} \cdot A_i}{\Delta CO} \tag{1}$$

where *i* indicates the size bin, ΔN_i is the total number of background-corrected particles in the plume per bin, $Q_{\text{ext},i}$ is the extinction efficiency in each bin, and A_i is the cross-sectional area of the particles per bin, assuming spherical particles. $Q_{\text{ext},i}$ is calculated through the Python module bhmie_herbert_kaiser_ july2012.py (https://code.google.com/archive/p/scatterlib/downloads). The module finds $Q_{\text{ext},i}$ through Mie scattering theory, using the code published in Bohren and Huffman (1983). We assumed a wavelength of 500 nm and a refractive index of 1.5–0.08*i* (Mack et al., 2010) for the particles regardless of OA and inorganic aerosol content. We also ignore potential changes to the refractive index that would occur if black carbon or brown carbon was present in the particles, since we do not include black carbon or brown carbon



as a modeled aerosol species. Our rationale for using a fixed refractive index is to isolate how the changes in the aerosol size and number affect extinction. The particle extinction is also a function of potentially evolving particle morphology and refractive index in the plume during aging (Pei et al., 2018), but we do not attempt to address these changes here with justification given in the next paragraph.

 Δ CCN/ Δ CO at 0.2% supersaturation was calculated using the kappa formulation of Petters and Kreidenweis (2007), assuming a hygroscopicity parameter, κ , of 0.2 for both the smoke aerosol and the background aerosol. Aging biomass burning aerosol have been observed to rapidly converge to a κ value of 0.2 \pm 0.1 (Engelhart et al., 2012). Similar to extinction, we do not attempt to address aging of κ within the plume and hold this value fixed for all simulations, and thus, changes in CCN are effectively functions of the change in number concentration and size for this study. We note that both optical and hygroscopic properties are anticipated to change through aging. However, the changes in the refractive index and κ with aging are inconsistent between aging cases, with some cases showing increases and some studies showing decreases with age in each of these parameters (e.g., Adler et al., 2011; Engelhart et al., 2012; Haywood & Boucher, 2000). As the direction of change with aging is likely fuel and burn-conditions dependent, we limit this study to determining the impacts of size distribution changes through aging.

In order to determine the relative contributions of SOA and POA to the aging size smoke OA, we make a simple estimate of the mass fraction of SOA to the total mass as follows:

SOA mass fraction(t) =
$$\frac{(\text{OA-ChemOn}_{\text{total mass}}(t) - \text{OA-ChemOff}_{\text{total mass}}(t)}{\text{OA-ChemOn}_{\text{total mass}}(t)}$$
(2)

where OA_ChemOn_{total_mass}(*t*) and OA_ChemOff_{total_mass}(*t*) are the total mass concentrations of the ChemOn_CoagOn and ChemOff_CoagOn cases, respectively, at time *t* for a given fire size and background aerosol concentration (coagulation does not impact mass and therefore we do not look at the CoagOff cases). And then the POA mass fraction is simply (POA mass fraction) = 1 - (SOA mass fraction). A limitation of the approach is that SOA condensation in the ChemOn simulations reduces the amount of POA evaporation relative to the ChemOff simulations; however, equation (2) allows us to qualitatively show under which conditions we expect the SOA fraction (or the amount of oxygenation of the OA) to increase more or less rapidly.

A discussion of the limitations of our methods in this study is presented in section 3.4.

3. Results

3.1. Smoke Mass Aging Depends on Fire Size, Dilution, Evaporation, and Condensation

In a diluting plume, the total OA mass will depend on how much OA evaporates versus how much SOA is formed through condensation, at least for our modeled system. The total mass is mostly unaffected by coagulation, as coagulation conserves mass (although not number and hence affects the size distribution and may change the condensation sink time scale). Figure 1 provides the time-evolving absolute smoke mass enhancement (that is, the excess OA from smoke above the background aerosol concentration), ΔOA (in μ g/m³), and the time-evolving dilution ratio for fire sizes of 10⁻⁴, 10⁻², 1, and 100 km² and constant background aerosol concentrations of 0, 5, and 50 μ g/m³ for the base simulations from the CoagOn version of each ChemOff/ChemOn case. (Figure S1 provides the same information for all modeled fire sizes and background concentrations. Figure S2 provides the time-evolving ΔCO for fire sizes of 10^{-4} , 10^{-2} , 1, and 100 km².) When the background aerosol concentration is $0 \,\mu g/m^3$, ChemOn cases lose less mass with a mass increase of up to ~140% between ChemOn and ChemOff than the ChemOff cases due to SOA condensation. However, SOA condensation is minor (around a 1% increase compared to ChemOff) for the smallest fire size with no background due to very low OA concentrations inside the plume to facilitate partitioning. As the background aerosol concentration increases, evaporation of the plume aerosol is slowed due to increased aerosol mass from the background aerosol concentration being entrained in. As vapors can partition into this background aerosol, this extra mass from the background facilitates increased partitioning of the plume aerosol to the particle phase (Donahue et al., 2006, 2009), and SOA condensation increases by over 200% compared to the $0 \,\mu g/m^3$ background case for the 10^{-2} - and 10^{-4} -km² fire sizes. Conversely, the evaporation and condensation rates for the 1- and 100-km² fire sizes are unaffected by the background aerosol concentrations, as their mass enhancements remain above or near the background concentration throughout the





Figure 2. (a) The in-plume normalized organic aerosol mass enhancement $(\Delta OA/\Delta CO)$ initially and after 4 hr of aging for the ChemOff and ChemOn base cases (Table 1). Warm colors indicate an increase in $\Delta OA/\Delta CO$ after 4 hr of aging, and cool colors represent a decrease. The *y* axis represents fire size/dilution rate; the *x* axis represents the background aerosol concentration. (b) Qualitative summary of the impacts of fire size (*y* axis) and background aerosol concentration (*x* axis) on $\Delta OA/\Delta CO$.

dilution period shown (8 hr). OA for the smaller fires quickly decreases to at or below the variability in background aerosol concentrations (Figures 1 b and 1c), making these plumes difficult to follow downwind in observational studies and also making the accuracy of the excess values measured in the plume marginal.

The top panel of Figure 2 provides ΔOA normalized by $\Delta CO (\Delta OA / \Delta CO)$ for the base simulations at the time of emission and after 4 hr of aging, again showing only the CoagOn version of each ChemOff/ChemOn case (Figure S3 provides the same information for all modeled fire sizes and background concentrations and includes the CoagOff cases). We note that the y axis for Figures 2-5 is fire size, as fire size is a simple proxy for dilution rate in this study. However, the y axis increases from slow to fast dilution rates, represented by large to small fires. Under the assumptions of the base simulations, $\Delta OA/\Delta CO$ decreases when chemistry is off (ChemOff) between 10 and 60% due to OA evaporation for all fire sizes and background aerosol concentrations modeled. When chemistry is on (ChemOn), organic vapors in our simulations shift to lower volatilities through gas-phase reactions with OH and may partition to the condensed phase. Figures S4 and S5 in the supporting information provide initial and final volatility distributions after 4 hr for both ChemOn and ChemOff, showing how dilution alone (ChemOff) and chemistry (ChemOn) change the aging volatility distributions.

For ChemOn cases, $\Delta OA/\Delta CO$ always increases by 15–20% for the 1- and 100-km² fires, regardless of background aerosol concentration. For the 10^{-2} - and 10^{-4} -km² fire sizes, evaporation exceeds condensation for the $0-\mu g/m^3$ background aerosol concentration and $\Delta OA/\Delta CO$ decreases by up to 60%. Condensation instead exceeds evaporation when the background aerosol concentration reaches 5–50 $\mu g/m^3$ (Figures 2 and S2), indicating that normalized ΔOA in small fires can still undergo net (overall change when accounting for all processes) increases up to 40% under nonzero background aerosol loadings, even when ΔOA is less than the background aerosol concentration (Figure 1). OA concentrations in summertime forested regions are often on the order of 5 $\mu g/m^3$ (Jimenez et al., 2009), and although there are likely some instances in which smoke plumes in, for example, boreal remote regions would be diluting into truly pristine (between 0.1 and 1 $\mu g/m^3$) backgrounds, we expect results from

such cases to scale between the 0- and 5- μ g/m³ cases. For the cases shown in Figure 2, the maximum OA gain after 4 hr is only ~40% above the initial plume, a modest increase consistent with some studies that do report a net increase in OA at the time of measurement (e.g., Reid et al., 1998). We reiterate that the exact values of Δ OA/ Δ CO here depend on our assumed emissions ration between OA and CO, and many factors vary between real fires/plumes that we are not testing here.

We note that for our simplified system of only changing fire size and background aerosol (all else fixed) that $\Delta OA/\Delta CO$ is predicted to increase over the first 4 hr for the 1- through 100-km² fire sizes, regardless of background concentration, but that some studies have reported net losses or no net change for larger fires (e.g., Collier et al., 2016; Forrister et al., 2015). This discrepancy could be related to potential light attenuation within the plume (Hobbs et al., 2003), leading to reduced oxidant concentrations and chemistry rates, as well as differences in POA volatility and precursor vapors. As well, some studies show no net change or slight decreases in normalized OA for intermediate fire sizes (e.g., Akagi et al., 2012; Liu et al., 2016). There are regions within our parameter space of our sensitivity studies in which intermediate plumes do not increase in normalized OA mass (Figures S15 and S17 in the supporting information). Further, some field experiments have seen factors of 2–3 in mass enhancements (Vakkari et al., 2014, 2018; Yokelson et al., 2009), higher than observed in this study, and this discrepancy could be related to differences in particle and





Figure 3. The relative fractions of SOA and POA to total Δ OA (just the OA enhancement above background) initially and after 4 hr of aging. The *y* axis represents fire size/dilution rate; the *x* axis represents the background aerosol concentration. The simulation with the smallest fire (10^{-2} km^2) and $0 \,\mu\text{g/m}^3$ background concentration is far out of equilibrium partitioning (due to a low condensation sink), which is why the SOA fraction is lower for this case than expected.

precursor-vapor emissions, in-plume oxidant concentrations (Yokelson et al., 2009), or other factors not explored in this study. The differences in our model results here and previously observed measurements should be investigated in a future study in order to attempt to discern what other factors are strongly controlling net OA mass, especially in larger fires.

Regarding the time evolution of OA, many cases with increases in $\Delta OA/\Delta CO$ do not show a net gain in $\Delta OA/\Delta CO$ (above the initial value) until after 2–3 hr of aging (Figure S6), indicating that field studies that measure plumes only within the first 1–2 hr after emission may observe and conclude that the fire undergoes a net OA loss rather than gain. Further, sets of observations in which the earliest measurement is taken 1–2 hr after emissions may be biased high in their estimate of net production from subsequent measurements. We note that Figure S6, which shows $\Delta OA/\Delta CO$ as a function of time for 8 hr of aging, could be interpreted to imply that OA mass will continually be added to the diluting plume over time. In the real atmosphere, as the plume continues to dilute and age further, many processes will likely slow, halt, or reverse further OA production, such as diurnal cycles in oxidants, OA loss to fragmentation (e.g., Kroll et al., 2009), and depositional processes (e.g., Knote et al., 2015).

The bottom panel in Figure 2 qualitatively summarizes the key message for the impact of fire size and background aerosol concentration on aging of smoke OA. For our specific modeled system, $\Delta OA/\Delta CO$ is anticipated

to increase for large fires due to greater SOA condensation rates than evaporation rates. For smaller fires, $\Delta OA/\Delta CO$ is anticipated to decrease when the background aerosol concentration is low (evaporation exceeds condensation) but will instead increase when the background aerosol concentration is high enough to slow evaporation rates enough that condensation exceeds evaporation.

Atmospheric or chemical conditions that favor decreasing condensation or increasing evaporation all lead to slower OA formation, causing relative decreases in $\Delta OA/\Delta CO$ from the base cases (Figure 2). Table 1 and section 2.2 describe the sensitivity cases performed in this study: decreasing the accommodation coefficient, rate of chemical reactions and number of volatility bins dropped per reaction (lower bound chemistry), and simulating a moderately unstable atmosphere all lead to relative decreases in $\Delta OA/\Delta CO$. As discussed in section 2.1, the lower bound chemistry simulation can provide insight to conditions with reduced OH concentrations (e.g., a thick plume from a large fire with little actinic flux). If plumes from large fires do indeed have lower UV and oxidant levels, our sensitivity simulations indicate that there may be less net OA mass produced than if oxidants were held fixed (Figure S17). Simulating a moderately stable atmosphere and running the base simulation for 8 hr instead favor increased net condensation and lead to increases in $\Delta OA/\Delta CO$. Section S5 and Figures S13–S24 in the supporting information provide further discussion on the impact of the sensitivity simulations on $\Delta OA/\Delta CO$ as well as normalized smoke extinction, CCN, modal width, and lognormal number median diameter.

Figures 2, S3, and S6 show that the mass results for fire sizes 10^{-2} , 10^{-3} , and 10^{-4} km² are very similar. Thus, for the remainder of the main analyses, we will only discuss fires between 10^{-2} and 100 km², and note that our results for the 10^{-2} -km² fire are likely applicable to fires smaller than 10^{-2} km².

Figure 3 shows an important point related to Figure 2: even though the $\Delta OA/\Delta CO$ is lower after 4 hr for smaller fires than larger fires, when chemistry is on, the relative contribution of SOA (versus POA) is higher for smaller fires in all but the cleanest background. Figure 3 provides the mass fractions of smoke POA and smoke SOA to total ΔOA (calculations described in section 2.3) for fire sizes 10^{-2} , 1, and 100 km² and constant background aerosol concentrations of 0, 5, and 50 µg/m⁻³. The SOA mass fraction for the largest fire modeled is ~25% SOA after 4 hr, and this ratio increases as fire size decreases to up to ~40–50% SOA. As shown earlier by Bian et al. (2017), the low fractional contribution of SOA for large fires is because little POA evaporates from these fires, which (1) keeps the POA contribution high and (2) limits the SOA precursors to just IVOCs and VOCs as the SVOCs remain as POA in the particle phase. For smaller fires, SVOCs





(a) D_g and σ_g : quantitative

Background aerosol concentration

Figure 4. (a) Smoke (background corrected) lognormal median diameter of the lognormal mode (D_g ; x axis) and lognormal modal width (σ_g ; y axis) initially and after 4 hr of aging for the base cases (Table 1). The color bar is $\Delta OA/\Delta CO$ initially and after 4 hr of aging for the base cases (same color bar as Figure 2a). (b) Qualitative summary of the impacts of fire size (y axis) and background aerosol concentration (x axis) on aged biomass burning D_g . Although not shown, σ_g has approximately the opposite behavior as that of D_g , although changes in σ_g depend also on the volatility of condensing/evaporating vapors.

evaporate from the POA and act as SOA precursors that can undergo chemical aging and recondense, which (1) reduces the POA contribution and (2) increases the SOA contribution. An exception to this SOA-fraction trend occurs in Figure 3 for the smallest fire with no OA background, where the SOA fraction is lower than expected. This exception is due to the low condensation sink in this small-fire/no-background case, so that even though low-volatility vapors are being created in the gas phase, they take hours to find a particle to condense on. If given enough time to approach equilibrium, this small-fire/no-background case would similarly show an SOA fraction around 0.4-0.5. Additionally, increasing the background OA contribution decreases the SOA fraction for similar reasons: high background OA prevents POA from evaporating, which increases the POA contribution and limits the amount of SOA precursor vapors. Hence, our results show that for our system, OA should become oxidized (e.g., as measured by Aerosol Mass Spectrometer measurements) more quickly in plumes of small fires and/or under lower background concentrations (when all else is equal). Under conditions where OA concentrations remain high, we expect OA to become oxidized more slowly.

3.2. Smoke Aerosol Size Distribution Aging

The plume lognormal modal number mean diameter, D_{g} , and lognormal modal width, σ_g , also evolve as the plume dilutes and undergoes coagulation, OA evaporation, and SOA condensation. The top panel of Figure 4 shows the initial and final (after 4 hr of aging) plume D_g and σ_g values for the base simulations fire sizes of 10^{-2} , 1, and 100 km² and constant background aerosol concentrations of 0, 5, and 50 μ g/m³, colored by $\Delta OA/\Delta CO$. (The color bars in Figures 2 and 4 are the same.) Figure S7 in the supporting information provides the same information for all modeled fire sizes down to 10^{-2} km² and all background concentrations. Figures S8 and S9 in the supporting information also provide the final number and volume size distributions for a subset of fire sizes and background concentrations for the base cases. OA evaporation and SOA condensation are still important processes for controlling D_g , σ_g , and the smoke OA mass (section 3); however, for the size distribution, coagulation also is an important process for controlling D_g and σ_g in plumes that do not undergo rapid dilution (the larger fires in Figure 3a).

OA evaporation results in smaller particles, shifting D_g to smaller values. Without coagulation and chemistry (ChemOff_CoagOff), evaporation does not change σ_g for the largest fire sizes but slightly broadens the distribution (increasing σ_g) for the smaller fire sizes. Conversely, SOA condensation grows particles, shifting D_g to larger values, and narrowing the size distribution, decreasing σ_g , as evident in the ChemOn cases. The impact of evaporation and condensation on σ_g is dependent on both the

volatilities of the evaporating/condensing vapors as well as the sizes of the growing particles (e.g., Pierce et al., 2011; Riipinen et al., 2011; Zhang et al., 2012); section S4 of the supporting information provides a detailed discussion of evaporation, condensational growth, and the roles of volatility and size on changes to the lognormal width.

Coagulation also shifts D_g to larger values (through coagulational growth) and narrows the size distribution, decreasing σ_g , by removing smaller particles (Sakamoto et al., 2016). Figure 4 shows that for CoagOn cases, this coagulational increase in D_g is most evident in larger (1 km² and greater) fire sizes, with increases up to a D_g of 200 nm from coagulation alone. As discussed in section 1, coagulation rates are proportional to the square of the number concentration, and thus, the coagulation-caused increase in D_g amplifies with





Figure 5. (a) The normalized extinction efficiency ($\Delta E/\Delta CO$) initially and after 4 hr of aging for the primary cases (Table 1). (b) The normalized CCN ($\Delta CCN/\Delta CO$) from smoke aerosol at 0.2% supersaturation initially and after 4 hr of aging, for the base cases (Table 1). Warm colors in (a) and (b) indicate an increase in the normalized values while cool colors represent a decrease. (c and d) Qualitative summaries of the impacts of fire size (*y* axis) and background aerosol concentration (*x* axis) on aged biomass burning (c) $\Delta E/\Delta CO$ and (d) $\Delta CCN/\Delta CO$. Although we predicted that the net change in normalized CCN to be an increase for all fire sizes and background concentrations for the primary cases presented in Figure 5, we expect that normalized CCN will decrease under sufficient OA evaporation/low SOA condensation rates (sections S4 and S5 and Figures S12–S23).

increasing fire sizes that take longer to dilute as well as for fires with higher emission fluxes leading to higher initial concentrations (Sakamoto et al., 2016). Additionally, decreasing dilution rates through a more-stable atmosphere for a given smoke emission flux and size will also amplify the coagulational effect on D_g (section S5 and Figures S20 and S22). For the largest fire size (100 km²), coagulation alone (ChemOff_CoagOn) increases D_g more than SOA condensation alone (ChemOn_CoagOff); for the remaining fire sizes, SOA condensation increases D_g more than coagulation.

The bottom panel of Figure 4 provides a qualitative summary of the anticipated impact of fire size and background aerosol concentrations on aging smoke D_g . For the system we have modeled, background aerosol concentration impacts D_g similar to OA mass; in general, an increasing background allows for a greater increase in D_g (more SOA condensation and less OA evaporation). However, the effect of background aerosol on D_g is slight for all but the smallest simulated fires, and coagulation plays an important role in increasing D_g , especially for the largest fires simulated. The qualitative summary of aging smoke σ_g (not shown) is essentially the opposite of D_g . For σ_g , coagulation and SOA condensation generally decrease σ_g for large- and medium-sized fires and small fires with high background concentrations. Like D_g , if OA evaporation is the dominant process over SOA condensation and coagulation (small fires with low background concentrations), σ_g also decreases. Background aerosol has little effect on σ_g except for the smallest fire sizes in which σ_g slightly increases with increasing background concentration, due to more vapors being allowed to condense (see the discussion in section S4).

3.3. Radiative Properties: Extinction and CCN Evolution

3.3.1. Extinction Cross Section as a Proxy for the Direct Radiative Effect

The extinction cross-section enhancement, ΔE , normalized by ΔCO ($\Delta E/\Delta CO$) is used to quantify the changes in extinction as our simulated plumes age (ignoring potential composition/morphology changes). $\Delta E/\Delta CO$ further allows for an estimate of the changes in the DRE. Figure 5a shows the initial and final



 $\Delta E/\Delta CO$ for fire sizes of 10⁻², 1, and 100 km² and constant background aerosol concentrations of 0, 5, and 50 µg/m³. (Figure S10 in the supporting information provides the same information for all modeled fire sizes down to 10⁻² km² and all background concentrations.) For the assumptions of our study of spherical particles with a refractive index of 1.5–0.08*i* at a wavelength of 500 nm, the peak extinction efficiency is at a particle diameter of ~500 nm (Figure S11 in the supporting information).

The aged $\Delta E/\Delta CO$ values corroborate the expectation that as plume OA mass increases through SOA condensation and particle size increases through SOA condensation and/or coagulation, $\Delta E/\Delta CO$ will increase, as D_g increases toward the peak of mass extinction efficiency. SOA condensation (OA evaporation) is the strongest driver of increases (decreases) in $\Delta E/\Delta CO$. However, it can be seen that for fires 1 km² and larger, coagulation increases $\Delta E/\Delta CO$ compared to cases without coagulation by up to 40%, due to the shifting of particle mass to larger diameters. Similar to mass, increasing background concentrations for fires with rapid dilution rates decreases loss of OA to evaporation, allowing for a greater increase in total extinction cross section than similar cases with cleaner background concentrations.

Figure 5c shows the qualitative summary of the anticipated impact of fire size and background aerosol concentration on aging smoke extinction: for our specific system modeled here, SOA condensation, coagulation, and increasing background concentrations all contribute to greater values of extinction, with an expected increase in the DRE, with the largest fire sizes producing the highest values of extinction. Similar to mass, OA evaporation decreases smoke extinction, and this process is expected to dominate for small fires in clean conditions.

3.3.2. CCN as a Proxy for the Aerosol Indirect Effect

The AIE depends on the number concentration of particles large enough to act as CCN. Figure 5b shows the enhancement of CCN (Δ CCN) from smoke aerosol normalized by Δ CO (Δ CCN/ Δ CO) for the base cases (Table 1) after 4 hr of aging for the same fire sizes and background concentrations as Figure 5a. (Figure S12 in the supporting information provides the same information for all modeled fire sizes down to 10^{-2} km² and all background concentrations.) These results are for a supersaturation of 0.2% (a supersaturation typical of stratiform clouds) and the assumption that both the plume and the background particles have a hygroscopicity parameter of $\kappa = 0.2$; these metrics correspond to a critical activation diameter of 121 nm, with 25% of the total initial particles in each plume able to act as a CCN.

When dilution and evaporation are the only processes occurring (ChemOff CoagOff), $\Delta CCN/\Delta CO$ after 4 hr of aging is reduced for all fire sizes as the particles shrink, leaving fewer particles above the activation diameter (121 nm). The impact of coagulation alone (ChemOff_CoagOn) on the 100-km² fire sizes is to decrease $\Delta CCN/\Delta CO$ further, as coagulation acts to reduce particle number, including CCN-sized particles (this CCN reduction by coagulation exceeds CCN production from coagulation due to the increase in the mode diameter [Figure 4]). As previously discussed, coagulation rates are proportional to the square of the number concentration N, and thus, coagulation rapidly decreases N for large fires where number concentrations are sustained through high initial concentrations (air spends a longer time over larger fires leading to larger concentrations in our simulations) and slow dilution rates. However, as is the case for total plume mass, mean diameter, modal width, and total extinction, once the fire is small enough $(~1 \text{ km}^2)$ for coagulation rates to be trivial, coagulation has little impact on the aged $\Delta CCN/\Delta CO$ concentrations, although for the smaller fire sizes, ChemOff CoagOn cases sometimes slightly increase $\Delta CCN/\Delta CO$ compared to ChemOff_CoagOff cases due to coagulational growth influencing CCN more than coagulational losses (Figures 4 and 5). We note that there are likely conditions in which coagulation is still important for smaller fires. For instance, Akagi et al. (2012) observed that coagulation was likely important within a smoke plume from a fire that was $\sim 1 \text{ km}^2$ for increasing net normalized scattering. However, the wind speeds in that study were much slower than the wind speeds used in this study (0.5-2.2 compared to 5 m/s), which would lead to an increased initial concentration and slower dilution rate.

SOA condensation in the ChemOn (relative to the ChemOff cases) greatly increases the $\Delta CCN/\Delta CO$ through particle growth for all cases except for the smallest fire with no background aerosol, with $\Delta CCN/\Delta CO$ increases of up to 70% for the ChemOn_CoagOff cases. However, when both chemistry and coagulation are on, coagulation decreases $\Delta CCN/\Delta CO$ (as compared to ChemOn_CoagOff) by up to ~40% for the 100-km² fire size simulations due to the relatively high coagulation rates. Indeed, after 8 hr of



aging, $\Delta CCN/\Delta CO$ has decreased below the initial $\Delta CCN/\Delta CO$ values for the 100-km² fire size simulations (Figure S23 in the supporting information). Similarly, our sensitivity simulations show that conditions that lead to relatively lower SOA condensation (e.g., the lower bound chemistry case; Figures S17 and S18) leads to a net decrease in $\Delta CCN/\Delta CO$ after 4 hr of aging due to the high coagulation rates not being sufficiently compensated by particle growth. Conversely, for the smaller fires, in the highest background cases, ChemOn_CoagOn cases increase CCN concentrations beyond ChemOn_CoagOff cases, as coagulation is able to grow enough particles to past the activation diameter (121 nm) (although coagulation will slightly decrease particle number).

Figure 5d gives the qualitative summary of the anticipated impact of fire size and background aerosol concentration on aging smoke CCN. For the system we have modeled in this study, coagulation decreases CCN for the largest fires. When the fire size is small enough that coagulation rates are slow and SOA condensation/OA evaporation are the dominant modeled processes, CCN follows the same patterns as smoke extinction, OA mass, and mode diameter. Although we predicted that the net change in normalized CCN to be an increase for most fire sizes and background concentrations for the primary cases presented in Figure 5b, normalized CCN will decrease with aging under sufficient conditions that lead to decreases in the lognormal modal width or mean diameter, caused by significant OA evaporation and/or low SOA condensation rates (see sections S4 and S5 for further discussion). Again, we note that the precise values of both CCN and extinction may change under variable mass, number, and CO emissions, but we hypothesize that the qualitative conclusions will remain similar.

3.4. Study Limitations

In this study, our objective is to isolate the impact of fire size, dilution, and background OA concentrations on coagulation and OA partitioning. There are many important processes that we are not simulating, and many important factors vary between fires/plumes that we leave fixed in this study.

We note that our simulations do not provide context for how the aerosol size distribution may change under aqueous processing for plumes that interact with clouds or elevated relative humidities as they age, so our results here illustrate factors that may be important during clear-sky conditions. We also do not account for particle-phase or heterogeneous chemistry that could occur within the plume. Accretion reactions in the particle phase of organic molecules have been observed in laboratory studies to create lower volatility products (e.g., Barsanti & Pankow, 2004; Kalberer et al., 2004; Wang et al., 2010), which would decrease the rate at which OA can evaporate, potentially leading to a greater than predicted increase in net (difference between total SOA condensation and OA evaporation) OA. Gelencsér et al. (2000) demonstrated that phenolic acids from biomass burning readily undergo polymerization under reaction with OH. Further, it is hypothesized that tar balls may be formed through oligomerization (Adachi & Buseck, 2011; Pósfai et al., 2004). Conversely, heterogeneous reactions of OA with OH can result in fragmentation products that can evaporate from the particle if the volatility is sufficiently increased, contributing to aerosol aging (e.g., Hodshire et al., 2018; Hu et al., 2016; Kroll et al., 2009) and potentially leading to a greater loss in net OA than predicted in this study. Although we ran tests varying the accommodation coefficient as a proxy for phase state, we did not explicitly address potential size-dependent changes in phase state (Zaveri et al., 2017). We do not explicitly include black carbon or brown carbon as an aerosol-phase species, although black carbon and brown carbon have been observed within smoke plumes and can alter smoke aerosol optical properties (e.g., Forrister et al., 2015). We hold the organic to inorganic/black carbon emission flux constant throughout the study, although the actual ratio will depend both on fuel type and burn conditions (e.g., Akagi et al., 2012; Bian et al., 2015; Zhang et al., 2015).

We assume that each plume is homogeneous in their dilution across their widths (orthogonal to the direction of plume transport) as well as homogeneous concentrations of OH, whereas real plumes always display varying degrees of heterogeneity within the plume. This heterogeneity could arise both from imperfect mixing as well as potential light attenuation within the plume (Hobbs et al., 2003), particularly within larger plumes, that could reduce oxidant concentrations and thus in-plume chemistry. We also do not explicitly explore variable injection heights in our analyses. While we do test the sensitivity of our results to different stability classes (we expect dispersion to generally follow stable conditions in the free troposphere), we do not change any of the temperature and pressure assumptions to be representative of FT conditions. As well, we do not address changes to oxidation rates related to variable OH concentrations; reported in-plume OH



concentrations estimates range between 5×10^6 and $> 10^7$ molec/cm³, but we are only aware of a few studies have made these estimates (Akagi et al., 2012; Hobbs et al., 2003; Yokelson et al., 2009). We test two chemistry assumptions based on the results of Bian et al. (2017), applying the reaction rates to all species uniformly within each VBS bin as a representative average reaction rate. However, real-world species of similar volatility will undergo variable reaction rates and this is not accounted for. As well, we have not accounted for the possibility that the in-plume average reaction rate may be even faster or slower than that of our chemistry two assumptions. We hold the emission flux and size distribution constant for all the simulations, even though in reality the mass and number flux will change between different fuels and even within the same fire over time. We also hold the hygroscopicity and refractive index of the particles constant throughout the simulation time period, as the changes (including the sign of the changes) in these parameters during aging are likely burn- and fuel-dependent (e.g., Adler et al., 2011; Haywood et al., 2003; Reid, Eck, et al., 2005, and references therein). We assume that each plume has the same volatility distribution (regardless of size), that the temperature is held constant throughout the entire plume and entire simulation time period, and that the plumes entrain in constant nonvolatile background aerosol concentrations (representative of, e.g., aged organics) with no additional background gas-phase compounds. In reality, the plume's initial volatility distribution is likely to change based on the fuel burned (e.g., Hatch et al., 2017), which can impact SOA formation due to the variable mix of available SOA precursors. The background will likely contain both additional gas-phase compounds and semivolatile particles that would further alter the partitioning of smoke compounds between the particle and gas phases, and this will further increase the sensitivity of the plume evolution to background concentrations beyond what we predict here. As well, the plume can entrain in further species such as NO_x and O_3 that may impact the aging plume's chemistry. Finally, we only assume a temperature of 298 K in this study. Plumes in the free troposphere may be at much colder temperatures, which will impact the organic partitioning in the plumes and will impact the results (e.g., Donahue et al., 2006; Huffman et al., 2009). Each of these processes will be left to future studies.

4. Fire Size, Background Aerosol Concentrations, and Observational Studies

Our test cases indicate that fire size is anticipated to play an important role in determining the climate impacts from smoke plumes through its impact on plume dilution rates. Figure 6 is an estimate for the distribution of fire sizes (both for wildland and prescribed fires) for the United States in 2014 from the National Emissions Inventory (U.S. EPA NEI, 2014). Figure 6a is the histogram of fire sizes, reported in km² blackened per day (not the area of the fire burning at any instant, but the closest proxy that we could find), showing that in the United States, the majority of fires by number are smaller than 1 km^2 per day, the size range at which we find that the interacting background aerosol concentration begins to impact the evaporation rates of the plume aerosol size distributions. Figure 6b shows the total PM_{2.5} emissions for each bin in kg. While the annual estimated emissions from fires within the 0.1-, 1-, 10-, and 100-km² fire sizes have a similar magnitude of $PM_{2.5}$ emissions, this study shows that the aging of smoke $PM_{2.5}$ could differ between these fire sizes, all other important factors (e.g., emissions flux, oxidant concentrations, chemistry rates/vields) set equal. Although it is likely that the exact fire-size distribution will vary within different geographical regions as well as from year to year, (small) agricultural and prescribed fires are among the dominant sources of biomass burning for many tropical and midlatitude regions (e.g., Giglio et al., 2010; Reid et al., 1998; van der Werf et al., 2010). We note that it is likely that the histogram in Figure 6a underestimated the number of small fires: the burned area detection methods used to construct the database may not detect some of the small fires (e.g., Larkin et al., 2014), as even active fire detection misses many small fires (e.g., Nowell et al., 2018). Also, the total $PM_{2,5}$ emissions estimated in Figure 6b may underestimate the importance of larger fires, as larger fires have been observed to have higher emissions factors than smaller fires (e.g., Liu et al., 2016) but the NEI estimate assumes that emission factors do not depend explicitly on fire size (Anderson et al., 2004; Raffuse et al., 2012).

Regarding background concentrations, isolated smoke plumes will generally evolve in a clean background (generally similar to the $5-\mu g/m^3$ case tested here; Jimenez et al., 2009). However, regions with many small concurrent fires can create a high background aerosol concentration (Baars et al., 2012; Martin et al., 2010; Reid et al., 1998), which can then influence the aging and evaporation rates of individual plumes. For





Figure 6. (a) Annual data for the number of recorded fires with different fire sizes in km^2 blackened per day (that is, the total area in km^2 burned per day) for the United States for 2014, from the National Emissions Inventory (U.S. EPA NEI, 2014). (b) Total annual PM_{2.5} emissions in kg from each fire size for 2014 from the same data set.

example, within the Amazon Basin during the dry season, daily average background aerosol concentrations can reach between 50 and 600 μ g/m³ (Martin et al., 2010; Reid et al., 1998). Midlatitude regions with many nearby wild or prescribed fires may also have elevated background OA concentrations (Brey et al., 2018).

A number of field campaigns have taken place over the last few decades with the explicit purpose of characterizing plume aging. Table S2 (section S6) in the supporting information provides an overview of our attempt at a complete set of published biomass burning field studies that focus on plume aging. Table S2 provides the available details of fire size and type, approximate age of the measurement, atmospheric conditions, background concentration, and the normalized OA, extinction, and CCN that were provided in publications. Many of the published studies do not provide fire size and/or emissions rates. Similarly, few published studies report direct background aerosol concentrations or in-plume aerosol concentra-



Figure 7. Conceptual overview of the roles of fire size and background concentration on net normalized changes to aged smoke OA and number concentrations. Shown are the anticipated net normalized changes to OA mass, extinction, and CCN for large versus small fires in high versus low background concentrations.

tions, even though some studies are of fires small enough that the background concentration may be able to influence the OA concentrations (e.g., Akagi et al., 2012; Cachier et al., 1995; Liu et al., 2016; Yokelson et al., 2009). For field observations, dilution rates can be directly obtained from the change of CO concentrations (or another inert tracer) with time rather than relying on the fire-size/Gaussian-plume method that we used here, but we find that regardless, the absolute OA concentration and absolute background OA concentrations should be important to understand the evolution of particle properties within the diluting plume. Further, direct comparisons of $\Delta OA/\Delta CO$ between campaigns can miss the key differences between the systems (fire, atmospheric, and background conditions) and may incorrectly attribute differences in observed $\Delta OA/\Delta CO$ evolution solely to differences in chemistry or emissions (even if these factors are also very important). Due to each of the published field analyses having a missing piece or pieces of information (e.g., fire size, background aerosol concentration, wind speed), and each measured fire having different emission fluxes, oxidant levels, etc., the interpretation of the published field analyses through the lens of the present study is a challenging endeavor for future work. Many of these data parameters currently missing from published field analyses described in section 4 may be available in the campaign data repositories, and we highlight key needs for the modeling community in section 5.



5. Synthesis, Recommendations, and Conclusions

In this study, we have investigated the potential importance of fire size/dilution rate and background aerosol concentrations on OA evaporation, SOA production from condensation of vapors, and coagulation, which in turn impact normalized aged smoke OA mass, median diameter and modal width, total extinction cross section, and CCN. There are a number of important limitations of our study, as detailed in section 3.4; many of these limitations stem from our simplification of the smoke-plume system to isolate potential fire-size and background effects. This study did not attempt to simulate any specific plumes that have been observed. Discrepancies between our results here and observational studies (section 3.1) indicate that our current modeling framework still requires further improvements in future studies. For example, some studies have seen much higher mass enhancements than any of the cases modeled here, indicated potentially a missing major OA source for those specific systems (Vakkari et al., 2014, 2018; Yokelson et al., 2009). We fix many aerosol/plume properties that are likely to vary across real plumes. These include the initial volatility distribution and plume size distribution parameters, temperature, emissions flux, oxidant concentrations, available light within the plume for photooxidation, chemical rate constants and yields, aerosol hygroscopicity, refractive indices, and the explicit impacts of varying injection heights. Further, we assume that our plume expands as a homogeneously mixed box, whereas real plumes have concentration gradients in vertical and cross-wind transects, which would impact our results.

Within our test framework we have shown that fire size and a nonvolatile background aerosol concentration can impact aged mass, extinction, and CCN, even with accounting for these other factors, indicating that fire size and background aerosol are important factors that should be included in future analyses. Figure 7 provides a qualitative summary of the importance of fire size and background concentration on OA, extinction, and the CCN for the general system modeled in this study. Total extinction cross section was used as a proxy for the DRE, as to first order, the DRE will scale with extinction, ignoring refractive index changes and changes to the phase function (Chylek & Wong, 1995). CCN was used as a proxy for the AIE, as to first order, the AIE will scale sublinearly with CCN (Twomey, 1977). Although both large and small fires lose mass through dilution-driven evaporation, the rate of SOA condensation versus the rate of OA evaporation will determine if the net normalized change in smoke OA mass is an increase or a decrease.

Large, slowly diluting fires with slow rates of evaporation can undergo sufficient SOA condensation relative to POA evaporation to yield a net increase in smoke OA, provided the fire produces sufficient precursor vapors. The aerosol concentration within these large plumes greatly exceeds that of most background aerosol concentrations, and evaporation rates will not be significantly impacted by background aerosol concentrations, leading to very similar net smoke OA changes under variable background aerosol concentrations. However, as evaporation rates are so low in large fires, the majority of the total aged OA will remain as POA (rather than SOA). However, if chemistry is slowed due to, for example, reduced available UV radiation within the plume, then production of SOA will also be slowed, leading to relatively less SOA formation.

Conversely, small, rapidly diluting fires will undergo much faster rates of POA evaporation that may exceed that rate of SOA condensation (at least initially). The smoke contribution to OA concentrations within these small plumes can quickly dilute to concentrations near or below the background contributions to OA concentrations, and thus, more-polluted background conditions reduce evaporation more than cleaner conditions, leading to greater net smoke OA mass changes during aging. Due to rapid evaporation rates that provide a relatively higher concentration of vapors that could oxidize and recondense, a higher fraction of the total aged OA mass will be SOA (rather than POA) for small fires over large fires. The inclusion of back-ground aerosol is anticipated to be particularly important for regions that experience intense fire seasons that may provide large ambient background concentrations into which fresh plumes are mixed. To our knowledge, however, the background aerosol concentration has not been explicitly considered in previous analyses of field data.

As extinction generally scales with mass, it will also tend to increase/decrease with increasing/decreasing OA, following a similar pattern with changing background aerosol and fire size. Extinction undergoes some additional shifts dependent upon particle size as discussed in section 3.1.1. CCN instead scales with number and particle size. Within large fires that undergo significant SOA condensation and little OA evaporation, CCN will increase if a sufficient number of particles can grow past the critical activation diameter. However, particle coagulation rates can also be significant within large fires, and thus, whether CCN



increases or decreases with plume aging depends on the relative strengths of SOA condensation and coagulation. Small fires undergo less coagulation on these time scales, and thus, if OA mass increases, CCN concentrations will increase due to particle growth to larger sizes. If the modal width decreases or evaporation is large (decreasing the mode diameter), CCN concentrations will decrease, and thus, the tendency of aged CCN will depend strongly upon the relative OA evaporation/SOA condensation rates.

In order for the modeling community to better verify the conclusions presented here as well as improve upon the limitations of this study, we recommend that future publications on analyses of field studies should characterize and report as many of the following conditions as possible: fire size, emissions rate/flux, background aerosol concentrations, and relevant meteorological conditions (e.g.,. wind speeds, temperature, the amount of UV radiation in the plume, stability class, boundary layer height, plume injection height) that help control dilution, mixing, and chemical rates in future studies of PM_{2.5} and OA biomass burning plumes. We also encourage a wider sampling of fire sizes when possible, but we acknowledge the challenge of tracking highly diluted plumes, especially for cases when the absolute excess OA concentration in the plume is less than the variability in the background OA concentration. Finally, size-distribution measurements of aging plumes also across a wide sampling will assist in better constraining the radiative impacts from smoke, as both the direct and indirect effects have particle size and number dependencies. These data will allow for more comprehensive comparisons between measured plumes and allow the hypotheses presented in this paper to be tested.

This study has shown that fire size and the background aerosol concentration may impact aged mass, extinction, and CCN. As a next step, our conclusions and simplifications must be tested in plume models, including models that can better-resolve in-plume gradients (e.g., Liu et al., 2016), against well-characterized observed plumes of different sizes and background aerosol concentrations. The validation of this work and related studies against field data can then allow for future work on creating plume-processing parameterizations to be used in regional and global atmospheric models that do not explicitly spatially resolve plumes.

Acknowledgments

The authors declare they have no financial or other conflicts of interest. The version of TOMAS used for this study is available at http://dx.doi.org/ 10.25675/10217/194164. This research was supported by the U.S. National Oceanic and Atmospheric Administration, an Office of Science, Office of Atmospheric Chemistry, Carbon Cycle, and Climate Program, under the cooperative agreement awards NA17OAR430001. NA17OAR4310002, and NA17OAR4310003: the U.S. National Science Foundation, Atmospheric Chemistry program, under grants AGS-1559607 and AGS-1558966; and the Joint Fire Science Program (JFSP) under project 14-1-03-26. We are grateful to Steven Brey, Bonne Ford, Benjamin Brown-Steiner, and Jose-Luis Jimenez for the useful discussions. We also appreciate the comments of three anonymous reviewers in helping us improve this manuscript.

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