Investigation of Secondary Organic Aerosol Formation from Different Sources and Ambient Environments

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INVESTIGATION OF SECONDARY ORGANIC AEROSOL FORMATION FROM DIFFERENT SOURCES AND AMBIENT ENVIRONMENTS

by

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B.S., Pennsylvania State University, 2008
M.S., Pennsylvania State University, 2008

A thesis submitted to the
Faculty of the Graduate School of the
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Investigation of Secondary Organic Aerosol Formation from Different Sources and Ambient Environments
written by Amber Marie Ortega
has been approved for the Department of Atmospheric and Oceanic Sciences

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The final copy of this thesis has been examined by the signatories, and we Find that both the content and the form meet acceptable presentation standards Of scholarly work in the above mentioned discipline.
Ortega, Amber Marie (Ph.D., Atmospheric and Oceanic Sciences)

Investigation of Secondary Organic Aerosol Formation from Different Sources and Ambient Environments

Thesis directed by Associate Professor Jose Luis Jimenez

ABSTRACT

To investigate atmospheric processing of direct urban and biomass burning emissions, I modified and deployed an oxidation flow reactor with submicron aerosol size and chemical composition measurements during FLAME-3, a biomass-burning study at USDA Fire Sciences Laboratory in Missoula, MT, and CalNex, a field study investigating the nexus of air quality and climate change at a receptor site in the LA-Basin at Pasadena, CA. The reactor produces OH concentrations up to 4 orders of magnitude higher than in ambient air, achieving aging by OH reactions in less than 5 minutes that is equivalent to ~2 weeks in the atmosphere. The OH exposure (OH_{exp}) was stepped every 20 min in both field studies. Results show the value of this approach as a tool for in-situ evaluation of changes in OA concentration and composition due to photochemical processing.

In FLAME-3, the average OA enhancement factor was 1.42 ± 0.36 of the initial POA. Reactive VOCs, such as toluene, monoterpenes, and acetaldehyde, decreased with increased OH_{exp}; however, formic acid, acetone, and some unidentified OVOCs increased after significant exposure. Net SOA formation in the photochemical reactor increased with OH_{exp}, typically
peaking around 3 days of equivalent atmospheric photochemical age (OH_{exp} \sim 3.9 \times 10^{11} \text{ molecules cm}^{-3} \text{s}), then leveling off at higher exposures. Unlike other studies, no decrease in OA is observed at high exposure, likely due to lower max OH_{exp} in this study due to very high OH reactivity. The amount of additional OA mass added from aging is positively correlated with initial POA concentration, but not with the total VOC concentration or the concentration of known SOA precursors. The mass of SOA formed often exceeded the mass of the known VOC precursors, indicating the likely importance of primary semivolatile/intermediate volatility species, and possibly of unidentified VOCs as SOA precursors in biomass burning smoke.

Results from CalNex show enhancement of OA and inorganic aerosol from gas-phase precursors. The OA mass enhancement from aging was highest at night and correlated with trimethylbenzene concentrations, indicating the dominance of highly reactive VOC emissions as SOA precursors in the LA Basin. Aging in the reactor mimics atmospheric processing as the elemental composition of ambient and reactor measurements, when plotted in a Van Krevelen diagram, follow similar slopes; additionally, reactor measurements extend over a larger range of oxygen-to-carbon ratios (O/C) compared to that observed in the LA Basin. While reactor aging always increases O/C, often beyond maximum ambient levels, we observe a transition from functionalization to fragmentation at intermediate OH_{exp}, with fragmentation dominating at very high OH_{exp}. Maximum net SOA production is observed between 0.8–4 days of aging and decreases at higher exposures. A traditional SOA model with mostly aromatic precursors underpredicts the amount of SOA formed by an order-of-magnitude, which is consistent with model evaluations for ambient air at many polluted locations.
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CHAPTER I
INTRODUCTION

Atmospheric aerosols, also known as particulate matter (PM) are a collection of liquid droplets or solid particles suspended in air. These aerosols have significant influence on the radiative forcing of climate (Forster, 2007), human health (Pope et al., 2002), regional visibility (Watson, 2002), in addition to the deposition of acids, toxins, and nutrients on ecosystems and crops (Matson et al., 2002). Long-term, historical, and recent investigations have shown elevated levels of particulate matter are responsible for cardiopulmonary and lung cancer mortality, decreased life expectancy, and increased hospitalizations during episodic pollution (Dockery et al., 1993; Pope et al., 1995; Pope et al., 2009). Climate implications of aerosols range in effect from directly interacting with incoming radiation by absorbing or scattering light to cloud processes and reflectivity of clouds in the atmosphere. Aerosol climate uncertainty as well as both long-term and immediate ramifications on human health motivate investigating the formation mechanisms and processes controlling particulate matter in the atmosphere. The impacts on human health and climate depend on the aerosol particle concentration, size distribution, and chemical composition. These impacts vary for different environments with different aerosol size distributions, chemical compositions, and particle concentrations, such as change between environments, e.g. when transitioning from urban to rural locations, or emissions profiles, e.g. industrial production to transportation emissions.

Organic aerosol (OA) represents a significant fraction of fine particle mass (PM$_{1}$, submicron; Kanakidou et al., 2005; Zhang et al., 2007) – 20%-90% (Jimenez et al., 2009). As seen in Fig. 1 from Jimenez et al. (2009), submicron, nonrefractory (vaporizes at or below 600°C),
OA is a major component of submicron aerosol across the mid-latitudes in the Northern Hemisphere, among the most populous regions of the planet. OA is the most diverse and least understood component of submicron aerosols, in part because of a wide variety of biogenic and anthropogenic sources as well as contributions from both direct emission and secondary formation in the atmosphere (Jimenez et al., 2009).

Figure 1. Submicron non-refractory aerosol composition for 30 AMS studies across the Northern Hemisphere (Jimenez et al., 2009) Pie charts show the average mass concentration (μg m⁻³) and composition: sulfate, nitrate, ammonium, chloride, and organic. The OA components were obtained with factor analysis of AMS spectra (Ulbrich et al., 2009). Oxygenated OA (OOA) is typically considered a surrogate for SOA. In some studies only one OOA factor was identified, whereas in other locations two types, semivolatile OOA (SV-OOA, a surrogate for fresher SOA) and low-volatility OOA (LV-OOA, a surrogate for aged OA) were identified. HOA is a surrogate for primary combustion OA, and Other OA includes primary OAs other than HOA that have been identified in several studies, including biomass burning OA (BBOA). Inset: distributions of atomic O:C for the OA components identified at the different sites (Aiken et al., 2008).

OA can be emitted directly to the atmosphere from primary sources OA (POA), such as forest fires and traffic emissions, or formed in the atmosphere through photochemical and aqueous
processing as secondary OA (SOA). SOA can be formed as volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone (O₃) and hydrogen oxides (OH), to form less volatile products that can partition, also known as condensing (partitioning implies that some might remain in the gas phase, while condensing implies that it all goes to the particle – they are not necessarily the same.), into the aerosol phase (Donahue et al., 2006). This oxidation can happen through homogeneous gas-phase oxidation, heterogeneous oxidation by uptake of gas-phase oxidants, and aqueous-phase oxidation (Donahue et al., 2014). Discerning the sources, atmospheric processes, and chemical properties of SOA is necessary to constrain and predict human health and climate influences, as well as expectations of shifting impacts with changing climate and pollution emissions (Hallquist et al., 2009).

Recent studies show SOA levels are underestimated by an order of magnitude when traditional models are applied in polluted regions. The work by Volkamer et al. (2006) compares SOA measured in four field studies with modeled results as a function of photochemical age (Fig. 2). As photochemical age (integrated exposure to oxidative radical hydroxyl, OH) increases, the ratio of measured to modeled results increases. Many possible reasons are proposed to explain underestimated SOA yields, including missing precursors such as primary semivolatile organics or glyoxal, and missing processes such as oligomerization, aqueous chemistry, and multigenerational chemistry (Hallquist et al., 2009, and references therein). Newer, updated, models reduce the errors (measured-to-observed ratio is closer to 1), but even with the measurements collected in the most intensive field experiments (e.g. MILAGRO), it is not possible to be sure whether this agreement occurs for the right reasons (Dzepina et al., 2009; Hodzic et al., 2010). Figure 3, as seen below, is Hodiz et al. (2010)’s update to Volkamer et al. (2006)’s analysis, showing volatility basis set model performance is much closer to observations.
Figure 2. Ratio of measured-to-predicted SOA from the Volkamer et al. (2006) study in Mexico City with other recent studies as a function of photochemical age. NEAQS-2002 refers to the New England Air Quality Study (de Gouw et al., 2005), ACE-Asia to aircraft sampling downwind of China in Spring 2001 (Heald et al., 2005), and TORCH-2003 to sampling at a site several hours downwind of London (Johnson et al., 2006). The photochemical age is calculated here as equivalent time under an OH-radical concentration.

Figure 3. Comparison of observed to predicted SOA ratios as determined in the present study (MILAGRO 2006) and reported in recent studies. MCMA 2003 summarizes results reported by (Volkamer et al., 2006; Dzepina et al., 2009; Tsimpidi et al., 2010); CARBOSOL 2006 refers to (Simpson et al., 2007), TORCH 2003 refers to (Johnson et al., 2006); NEAQS 2003 (de Gouw et al., 2005); ACD-Asia 2001 (Heald et al., 2005). In blue are represented estimates of the traditional SOA approach, while red refers to the volatility basis set.

In order to improve model constraints of SOA formation, more experimental investigations into formation processes and ambient OA evolution are required. Examining SOA formation from oxidation of precursor gases is multifaceted, depending on concentration of volatile organic
compound (VOC) precursors, water vapor content in the atmosphere, temperature, sunlight, and presence of nitrogen oxides (NO\textsubscript{x}; Seinfeld and Pandis, 1998). Environmental smog chambers have long been used to study atmospheric processes, with the ability to perform controlled experiments simulating the atmosphere.

Focused on replicating timescales of atmospheric aging and photochemical reactions leading to SOA formation, typical chambers are large Teflon bags with high volume and long residence times presenting wall loss effects. Typical environmental smog chambers have concentrations of oxidants similar to polluted urban areas, with ozone (O\textsubscript{3}) in the hundreds of ppbv range and OH concentrations between 10\textsuperscript{6} and 10\textsuperscript{7} molecules cm\textsuperscript{-3} (Cocker et al., 2001). Large chamber size is required to effectively simulate timescales of the atmosphere, presenting significant wall effects and affecting the dependability of chamber experiments to reproduce atmospheric processes. Long residence times result in very slow timescales for experiments (e.g. one experiment per day) and large wall loss corrections, hindering the experimental system's ability to respond to rapidly changing precursors. A faster tool with reduced wall losses is critically needed to address SOA formation potential of different sources and airmasses. Progress in this field is hampered by the absence of a field tool to rapidly identify the SOA formation potential of different sources and airmasses.

The concept of potential aerosol mass ("PAM") examines increase in OA mass due to oxidation of precursor gases, in which samples are rapidly oxidized with high concentrations of oxidants forming low volatility compounds resulting in SOA formation (Kang et al., 2007; Kang et al., 2011). Kang et al. (2007) applied this concept to the initial development of small, flow-through chamber with short residence time using ultraviolet (UV) light to produce oxidants. Incoming air is exposed in the reactor to high OH radical concentrations, thus converting aerosol...
precursors (such as SO₂ or SOA VOC precursors) into particles, and then sampled from the reactor with instruments that measure particle characteristics or gas-phase chemicals. Proving a viable tool for experimental laboratory studies, this first-generation PAM reactor had negligible wall effects and short residence time, allowing multiple experiments in a short amount of time. With substantial modifications, the reactor could emerge as a potential field-deployable alternative to traditional environmental chambers by having negligible wall effects and allowing for very rapid experiments (~ a few minutes).

PURPOSE OF THE STUDY

My research goals are to optimize the PAM reactor as the Oxidation Flow Reactor (OFR), applying it to source emission and ambient field studies to answer the following questions:

- Is the reactor an effective tool to study SOA formation? Are the ambient atmospheric aging processes approximately replicated in this reactor?

- How does SOA formation and evolution change with source, airmass, precursors present, aerosol properties (e.g. acidity), and intensity of aging?

- What are the SOA budget contributions from biogenic, anthropogenic, and biomass burning precursors?

The goal of my research is to address the critical research need to identify and quantify SOA formation potential of different sources and airmasses in the real world, by coupling the reactor to the high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, hereafter "AMS");
DeCarlo et al., 2006), and performing ground-based experiments to fully optimize the system for targeting the science questions.

SCOPE OF THE STUDY

Extensive modifications were implemented to enhance the reactor’s performance in a field setting, such as metal construction to eliminate losses of charged particles, UV lamps inside the chamber to increase transmission of UV light, decreasing overall chamber size for shorter residence time, minimizing wall effects and enhancing plug-flow characteristics.

As part of this project, I designed a computer-controlled system to rapidly scan OH exposures. Quantitative calibrations have been demonstrated in the laboratory and in the field, and have been used to calibrate the system in real time. Combining these efforts, reactor equivalent atmospheric age has been further constrained and applied to all laboratory and field data.

Additionally, I lead and assisted with significant software development of data acquisition systems and computer-controlled voltage output to UV lamps in real-time using Labview, and post-processing analysis tools for the reactor in Igor. This work allowed proliferation of reactor usage and facilitated multiple users in my research group after initial characterization and development.

As a ‘proof-of-concept’ of the OFR-AMS system, I have been the lead/primary experimenter in deployment of the modified reactor in four major field campaigns:

1) International DAURE field campaign contrasting rural and urban environments
   (Winter 2009, Montseny, Spain)
2) An industrial epicenter to study petrochemical and urban emissions
   (SHARP, Spring 2009, Houston, TX)
3) A biomass burning emission study at the USDA Fire Science Research Laboratory (FLAME-3, Fall 2009, Missoula, MT)
4) Research at a receptor site in the Los Angeles Basin
   (CalNex-LA, Summer 2010, Pasadena, CA)

Additionally, I have supported recent reactor deployments at two SOA formation studies looking at biogenic precursors (BEACHON-RoMBAS, Summer 2011, Manitou Forest Observatory, CO; and SOAS, Summer 2013, Talladega National Forest near Brent, Alabama).

THESIS ROADMAP

To limit the length and content of this dissertation, only the results from the FLAME-3 and CalNex deployments of the reactor will be reported in this thesis. As each of these deployments has led to a primary authored manuscript, they have encompassed the bulk of publishable results of my PhD research. Within the dissertation, a chapter will be devoted to each of these experiments as a Biomass Burning Study and Urban Emission Study chapter, concluding with a final summary chapter.

Each experimental chapter will be self-contained including its own abstract, methods, results, conclusion, supplemental information, acknowledgements, and reference sections. Figure and table numbering systems will begin with No. 1 and be independent for each chapter.
REFERENCES


CHAPTER II
BIOMASS BURNING STUDY

Adapted and reformatted from:

Abstract

We report the physical and chemical effects of photochemically aging dilute biomass-burning smoke. A potential aerosol mass “PAM” flow reactor was used with analysis by a high-resolution aerosol mass spectrometer and a proton-transfer reaction ion-trap mass spectrometer during the FLAME-3 campaign. Hydroxyl (OH) radical concentrations in the reactor reached up to ~1000 times average tropospheric levels, producing effective OH exposures equivalent to up to 5 days aging in the atmosphere, and allowing us to extend the investigation of smoke aging beyond the oxidation levels achieved in traditional smog chambers. VOC observations show aromatics and terpenes decrease with aging, while formic acid and other unidentified oxidation products increase. Unidentified gas-phase oxidation products, previously observed in atmospheric and laboratory measurements, were observed here, including evidence of multiple generations of photochemistry. Substantial new organic aerosol (OA) mass (“net SOA”);
secondary OA) was observed from aging biomass-burning smoke, resulting in total OA average of 1.42 ± 0.36 times the initial primary OA (POA) after oxidation. This study confirms that the net SOA to POA ratio of biomass burning smoke is far lower on average than that observed for urban emissions. Although most fuels were very reproducible, significant differences were observed among the biomasses, with some fuels resulting in a doubling of the OA mass, while for others a very small increase or even a decrease was observed. Net SOA formation in the photochemical reactor increased with OH exposure (OH\text{exp}), typically peaking around three days of equivalent atmospheric photochemical age (OH\text{exp} \sim 3.9 \times 10^{11} \text{ molecules cm}^{-3} \text{ s}), then leveling off at higher exposures. The amount of additional OA mass added from aging is positively correlated with initial POA concentration, but not with the total VOC concentration or the concentration of known SOA precursors. The mass of SOA formed often exceeds the mass of the known VOC precursors, indicating the likely importance of primary semivolatile/intermediate volatility species, and possibly of unidentified VOCs as SOA precursors in biomass burning smoke. Chemical transformations continue even after mass concentration stabilizes. Changes in the biomass-burning tracer \text{f}_{50} ranged from substantially decreasing to remaining constant with increased aging. With increased OH\text{exp}, oxidation was always detected (as indicated by \text{f}_{44} and O/C). POA O/C ranged 0.15-0.5, while aged OA O/C reached up to 0.87. The rate of oxidation and maximum O/C achieved differs for each biomass and appear to increase with the initial O/C of the POA.
INTRODUCTION

Atmospheric aerosols, liquid droplets or solid particles suspended in air, have significant influence on the radiative forcing of climate (Forster, 2007), human health (Pope et al., 2002), regional visibility (Watson, 2002), and deposition of acids, toxins, and nutrients on ecosystems and crops (Matson et al., 2002). These impacts depend on the aerosol particle concentration, size distribution, and chemical composition. Organic aerosols (OA) represent a substantial (20–90%) fraction of total submicron aerosol mass (Murphy et al., 2006; Zhang et al., 2007). OA is the most diverse and least understood component of submicron aerosols, in part because of a wide variety of biogenic and anthropogenic sources as well as contributions from both direct emission and secondary formation in the atmosphere (Jimenez et al., 2009). OA is either emitted directly to the atmosphere from such sources as forest fires and transportation as primary organic aerosol (POA), or formed in the atmosphere from photochemical and aqueous reactions as secondary organic aerosol (SOA). Developing a full understanding of the sources, atmospheric processes, and chemical properties of OA is essential to constraining and predicting its impacts on human health and climate, as well as how these impacts may be altered with changing climate and emissions patterns (Hallquist et al., 2009).

Regional ambient aerosol levels can be significantly enhanced by smoke emitted from prescribed burns and wildfires during many seasons and locations (Park et al., 2007; Spracklen et al., 2007). The use of wood as a fuel for heating also increases aerosol levels (Alfarra et al., 2007). Biomass burning can severely influence local and regional air quality and is a major global source of trace gases and aerosols (de Gouw and Jimenez, 2009; McMeeking et al., 2009). Understanding the photochemical evolution of biomass burning OA (BBOA) and volatile organic compound (VOC) emissions when they undergo atmospheric aging is crucial to
obtaining a more complete picture of biomass-burning effects in the atmosphere and developing better estimates of biomass burning impacts in regional and global models.

A number of laboratory experiments and field projects have examined biomass-burning emissions and contributions to overall OA mass. While BBOA is emitted as POA, recent field studies indicate BBOA emissions are semivolatile and can evaporate upon dilution of a smoke plume (Robinson et al., 2007). SOA can also form from biomass-burning VOCs or evaporated POA species. We will refer to the excess mass formed during photochemical aging over the initial POA as “net SOA.” As defined here, net SOA may be positive if SOA formation exceeds POA losses or negative if the opposite is true. Some studies examining photochemical processing of wood smoke indicate production of substantial production of net SOA, which was attributed to mostly gas-phase reactions from semivolatile and intermediate volatility species (S/IVOCs) (Grieshop et al., 2009; Hennigan et al., 2011). Estimates of net SOA from field studies range from a small decrease or no change in mass over the initial POA (Capes et al., 2008; Cubison et al., 2011; Hecobian et al., 2011; Akagi et al., 2012; Jolleys et al., 2012) to net SOA equal to a substantial fraction of the initial POA mass (Yokelson et al., 2009; DeCarlo et al., 2010). OA mass loss from secondary processing (including aging and evolution of an airmass) has been explained by evaporation upon dilution (Robinson et al., 2007), heterogeneous oxidation leading to fragmentation reactions increasing volatility of reaction products (Molina et al., 2004; Lambe et al., 2012), and gas-phase oxidation and fragmentation leading to evaporation of particle-phase semivolatiles that were in equilibrium with the gas-phase species before the latter reacted and fragmented (Donahue et al., 2012).

Quantification of net SOA formation and aging from biomass-burning smoke in the field is thus confounded by substantial variability between studies, which may be due to the different gas
and particle-phase emissions due to variations in fuel type and burning conditions, such as flaming or smoldering (Koppmann et al., 1997), or the environment where the smoke is emitted (Akagi et al., 2012). Laboratory studies of aging of biomass burning can play an important role in elucidating the importance of different factors in smoke aging.

To date, such studies have only been performed with large (~10 m³ or larger) environmental chambers (Grieshop et al., 2009; Hennigan et al., 2011). While large environmental chambers have the advantage of using similar oxidant levels as in the atmosphere, such chambers can typically only be used for one experiment per day and can suffer from wall loses of semivolatiles and particles to walls (Matsunaga and Ziemann, 2010). An experimental technique is needed to characterize the SOA-formation potential of biomass-burning emissions that is capable of rapid operation to allow examining variability of smoke markers, different fuel types, and that responds in real-time to changes in smoke composition during emission.

A “Potential Aerosol Mass” (PAM) flow reactor, developed by Kang et al., (2007; 2011), is a small flow-through reactor that exposes samples to high oxidant levels with a short residence time. Recent work with the PAM reactor has examined SOA yield, oxidation, and chemical changes using single precursors or simple mixtures and has produced results similar to flow-tube and environmental chamber experiments with the same precursors (Kang et al., 2007; Kang et al., 2011; Lambe et al., 2011a; Lambe et al., 2011b). Compared to the Caltech Indoor Chamber Facility (Cocker et al., 2001; Keywood et al., 2004), at similar hydroxyl radical (OH) exposures, SOA from the PAM reactor was more oxidized than chamber SOA; some precursor yields were comparable (e.g. α-pinene), while other (e.g. m-xylene) yields were lower in the reactor than the Caltech chamber (Lambe et al., 2011a). OH oxidation of alkane SOA precursors in the reactor show the effect of functionalization (oxygen addition) and fragmentation (carbon loss) reactions.
in the absence of NOx (Lambe et al., 2012). Also, oxygen-to-carbon (O/C) ratios from reactor oxidation result in a wider range than previously observed in the large chambers, due to higher levels of OH exposure. (Massoli et al., 2010; Lambe et al., 2011b). These studies show that the PAM reactor produces OA with characteristics similar to those of atmospheric OA (Bahreini et al., 2012).

In this study, we photochemically aged smoke from fuels combusted during a biomass-burning study (FLAME-3) at the U.S. Department of Agriculture Fire Sciences Laboratory (FSL) at Missoula, Montana, during September–October 2009. We used a PAM flow reactor and monitored the effect of aging with submicron aerosol and gas-phase composition measurements. We present results from multiple biomasses that show the physical and chemical effects of OA aging and net SOA formation from aging biomass-burning smoke. Our work expands upon the previous literature by using the PAM reactor to study a complex system, biomass-burning smoke, in real-time.

METHODS
FLAME-3 experiment

Experiments with different types of biomass were conducted in the fire chamber at the U.S. Department of Agriculture FSL in a “chamber burn” configuration, in which known quantities of biomass were burned openly to their natural extinction (Yokelson et al., 1996; Christian et al., 2003; McMeeking et al., 2009, as shown in Fig. S1a). Between 0.1–1 kg of fuel was placed on top of a ceramic plate and ignited by heating coils treated with a small amount of ethanol (Hennigan et al., 2011). The smoke from the fire filled the entire ~3000 m³ chamber and was mixed throughout the chamber by large fans. Multiple gas and aerosol measurements indicated
that the smoke was well mixed approximately 15 min after the fire extinguished itself. The initial dilution factor estimated from CO$_2$ concentrations was approximately 500. Smoke was held in the fire chamber for typically 3.5 hours. Slow dilution with ambient air continued during the containment of the smoke because the fire chamber was not completely airtight. Typical ambient outdoor OA concentrations were low (a few µg m$^{-3}$) and did not significantly perturb the chamber OA that was present at much higher concentrations during this slow dilution. The use of the “chamber burn” configuration in the FSL fire chamber prohibited distinguishing between flaming- and smoldering-phases of combustion. Modified combustion efficiency (MCE) and dilution/emission ratios to CO are not presented here due to lack high-quality CO measurements in this study. We also examined the relationship between organic aerosol enhancement and NO$_x$ concentrations, but found no significant correlation. Conditions inside the chamber were stable with average relative humidity of $30.2 \pm 6.5\%$ (mean ± 1σ) ranging from 18.2–42.9% and average temperature of $17.2 \pm 2.6^{°}$C ranging from 11.1–20.3°C.

FLAME-3 was a targeted investigation of emissions from burning of plant species which are relevant to North American local and regional air quality and often undergo prescribed and wildfire burning (Hennigan et al., 2011). Species used as fuels included chaparral (ceanothus, chamise, and manzanita), pines (lodgepole and ponderosa pine), leafy and desert shrubs (gallberry, turkey oak, and sage), grasses (saw grass, wheat grass, wheat straw, and pocosin), spruces (white and black spruce), and soils (peat and Alaskan duff). In this work, we present data from 16 unique biomasses, used as fuels for 25 different chamber burns, as detailed in Table 1.
Table 1. Experimental results of each fuel from FLAME-3, with maximum (deviation from unity, ER\textsubscript{OA} = 1) sustained five-minute average organic aerosol enhancement ratio (ER\textsubscript{OA}) with associated OH exposure (OH\textsubscript{exp}), maximum unprocessed OA mass concentration, and starting weight of the biomass mass fuel before combustion. In some experiments, the O\textsubscript{3} monitor malfunctioned and thus OH\textsubscript{exp} could not be estimated; however, OH in the reactor was always scanned using the same methodology described. *Number convention used during FLAME-3, \textsuperscript{b}in units of µg m\textsuperscript{-3} (at ambient temperature and pressure), \textsuperscript{c}organic aerosol enhancement ration (ER\textsubscript{OA}= Aged/Unprocessed), \textsuperscript{d}in units of molec. cm\textsuperscript{-3} s.

<table>
<thead>
<tr>
<th>Burn Number\textsuperscript{a}</th>
<th>Fuel</th>
<th>Max Unprocessed\textsuperscript{b}</th>
<th>Max ER\textsubscript{OA}\textsuperscript{c}</th>
<th>OH\textsubscript{exp}\textsuperscript{d}</th>
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PAM flow reactor

To study the effect of photochemical aging on biomass-burning smoke, a “Potential Aerosol Mass” (PAM) flow reactor was used to expose smoke to high levels of OH and O\textsubscript{3} with reduced wall losses and short response time. The reactor is a small (13.1 L) flow-through cylindrical
vessel. The flow rate through the reactor was 4.4 LPM, resulting in an average residence time of approximately 180 s. The reactor is made of conductive aluminum, which eliminates the loss of charged particles due to charge build-up on walls made of insulating material such as glass or Teflon; using a Pyrex reactor in prior experiments led to near complete loss of charged particles. This loss may not be an issue when particles are generated inside of the reactor by nucleation (Lambe et al., 2011b); however, a large fraction of particles emitted from combustion can be charged and would thus be lost to the walls. No correction was made for possible semivolatile losses to walls, as the short residence time and high aerosol surface area of our experiments are expected to limit that problem. Particle mass losses were very small as discussed below.

OH and O3 are produced when UV light from two low-pressure mercury lamps (model no. 82-9304-03, BHK, Inc.) initiates O2, H2O and O3 photochemistry. The 185 nm light photolyzes O2 to produce O3 and H2O to produce OH and HO2, while the 254 nm light photolyzes O3 to produce OH. Subsequent chemistry determines the concentrations of O3, OH, and other chemical species. The lamps were mounted in Teflon sleeves and purged with N2 to control their temperature and avoid lamp exposure to high oxidant concentrations. We use the term “aging” to refer to the combined effect of OH, O3, and light exposure in the flow reactor, although calculations indicate that OH reactions dominate. The intensity of aging was controlled by adjusting the voltage supplied to power the lamps between 50–110 VAC, thus modulating the photon flux and consequently the quasi steady-state oxidant concentrations in the reactor. Typical OH scanning operation is highlighted in Fig. S2, where indicators of changing lamp voltage are marked by calculated photochemical age, see Section 2.5 for details.

While 185 nm UV light photochemically produces both OH and O3, the OH/O3 ratio in the reactor is about 10 times daytime ambient levels. In this study, OH exposure ranged from
1.36×10^{10} to 6.5×10^{11} molec. cm^{-3} s and O_3 exposure from 1.5 ×10^{15} to 3.4×10^{16} molec. cm^{-3} s. Precursor reaction rates with OH are much faster than for O_3 for typical ambient OH and O_3 concentrations, with the exception of some olefinic biogenic VOC (BVOC) that can be comparable, i.e., ranging from ten times faster to slower (Atkinson and Arey, 2003). The UV light could affect some organic species, such as organic peroxides, aldehydes, or aromatics that can be photolyzed by these wavelengths. However, for the estimated maximum photon fluxes in the reactor of 2×10^{13} photons cm^{-2} s^{-1} at 185 nm and 2×10^{14} photons cm^{-2} s^{-1} at 254 nm, photolysis of non-aromatic peroxides and aldehydes should be less than <10% (typically much less, with cross-sections, σ, at 254 nm, ranging 1.6–8×10^{-20} cm^{2}/molec.), while some substituted aromatics (e.g. phenol, σ≈1.5×10^{-17} cm^{2}/molec., benzaldehyde, σ≈1.41×10^{-18} cm^{2}/molec., m-, o-cresol, σ≈1.2–1.6×10^{-17} cm^{2}/molec., respectively, at 254 nm) could photolyze as much as 50-90% during the residence time in the reactor (Trost et al., 1997; Keller-Rudek and Moortgat, last access: 7 March 2013). However, reactions with the OH concentrations produced with these photon fluxes are more than ten times faster than photolysis so that the dominant reaction pathway is with OH.

Instrumentation

Smoke-laden air from the fire chamber was continuously sampled through the flow reactor in an open flow-through configuration via a 14-cm opening (Fig. S1b). Use of any inlet, including passivated SILCO steel, resulted in substantially reduced SOA formation, presumably because of loss of semivolatile to the inlet and front plate of the reactor. For this reason, the reactor was located inside the FSL fire chamber. Reactor output was measured by an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS; hereafter AMS; DeCarlo et
al., 2006), O$_3$ monitor (2B Technologies, Model 205) and for selected burns, a proton-transfer-reaction ion-trap-mass-spectrometer (PIT-MS; Warneke et al., 2005a; Warneke et al., 2005b). A copper bypass line was used to sample unprocessed smoke directly from the fire chamber, as shown in Fig. 1. During measurements, two valves were automatically switched – alternating sampling between the reactor and the bypass line with 1-min time resolution, and with sufficient instrument delays to avoid averaging of data from the previous phase that was still present on the lines after valve switching. This strategy allowed near-continuous measurements of both OA produced by the fire (hereafter, referred to as POA interchangeably with “unprocessed”) and OA aged in the flow reactor.

The AMS measures submicron nonrefractory particles that evaporate in a few seconds or less at 600 °C in a high vacuum. Smoke was transported from the flow reactor to the AMS through a 3 m long insulated-copper inlet. Detailed information on the AMS can be found elsewhere.
AMS measurements were obtained using the “W” mode ion path, which offers higher mass resolution with a trade-off of lower signal-to-noise. Mass resolving power ($\frac{m}{\Delta m}$) was ~ 3400 at mass-to-charge ($m/z$) 200 in W-mode. In this study, concentrations of the fresh smoke emissions were high enough to maintain adequate signal-to-noise ratio in this mode. Data were averaged in one-minute intervals. All data were analyzed using standard AMS software (SQUIRREL v1.50-1.52F and PIKA v1.09-1.11G; Sueper et al., 2007) within Igor Pro 6.21-6.31 (WaveMetrics, Lake Oswego, OR). Although the AMS samples particles 10$^7$ times more efficiently than gases (Canagaratna et al., 2007; Cubison et al., 2011), levels of CO$_2$ were high and variable enough to affect the AMS measurements. The influence of CO$_2$ on the AMS measurements was removed by both a standard particle filter interpolation method and applying a time-series of gas-phase CO$_2$ measurements (Li-Cor Biosciences LI-6262 CO$_2$/H$_2$O analyzer).

A procedure was developed to correctly calculate sulfate and organic concentrations for biomass burning smoke, since the standard AMS unit mass resolution (UMR) “fragmentation table” (Allan et al., 2004) does not work well for very high OA fractions of the total non-refractory aerosols (Fig. S3 and Table S1).

High-resolution mass concentrations were calculated using the HR AMS fragmentation table, detailed in Aiken et al. (2007; 2008). Typical for biomass burning smoke (e.g. DeCarlo et al., 2008), one-quarter of organic mass was above $m/z$ 100, as indicated by a slope of 1.33 in Fig. S4a where UMR organic mass concentration calculated from the full range of $m/z$ is plotted with respect to HR data as calculated up to $m/z$ 100. OA mass concentrations reported in this study are the combined mass of HR data up to $m/z$ 100 and UMR above $m/z$ 100, due to the difficulty of obtaining accurate information from the high-resolution fits at higher $m/z$, from the increasing number of different ions at each $m/z$ and the limited resolution of the mass spectrometer.
The standard method of tracking changes in AMS sensitivity due to degradation of the microchannel plate (MCP) or changes in electron emission, assumes an invariant nitrogen concentration in the sampled air, such that the measured signal at $m/z$ 28, where $\text{N}_2^+$ is the dominant ion, linearly scales with instrument sensitivity. In this study, there was a substantial particle-phase signal at $m/z$ 28 from the ions $\text{CO}^+$, $\text{C}_2\text{H}_4^+$, and $\text{CH}_2\text{N}^+$ (Fig. S5). Using high-resolution analysis techniques (DeCarlo et al., 2006; Sueper et al., 2007), $\text{N}_2^+$ signal was separated from the particle-phase signal at $m/z$ 28, resulting in an $\text{N}_2^+$-only signal. This time series of the fitted $\text{N}_2^+$ ion peak area was used rather than the total integrated signal at $m/z$ 28, as the “airbeam correction” (Allan et al., 2003). Grieshop et al. (2009) attributed all the particle-phase signal at $m/z$ 28 in wood smoke to $\text{CO}^+$ using a quadrupole AMS, but Fig. S5 shows that there can be substantial signals at $\text{C}_2\text{H}_4^+$, and $\text{CH}_2\text{N}^+$ as well. We examined the potential of using other $m/z$ for tracking changes in AMS sensitivity ($m/z$ 40 for $\text{Ar}^+$ and $m/z$ 32 for $\text{O}_2^+$); however, due to high organic loadings in this study, all air $m/z$ had substantial signal from organic ions present.

Quantification of ambient AMS measurements requires application of a collection efficiency (CE) to account for particle bounce at the AMS vaporizer (Canagaratna et al., 2007; Middlebrook et al., 2012). Typical values range from 0.5 to 1. For ambient aerosols, CE can be estimated from aerosol composition (Middlebrook et al., 2012); however, that parameterization does not always apply to laboratory studies, in particular when inorganic signals are very low relative to organic mass such as in this study (Docherty et al., 2013). Since the focus of this study is on relative changes between directly emitted and aged smoke, AMS mass concentrations were calculated with a CE of 1. Two recent biomass-burning studies reported a CE of 1, supported by comparisons with SMPS measurements (Hennigan et al., 2011) and black carbon measurements.
(Heringa et al., 2011). The high levels of OA sampled in some of the burns are not thought to cause significant non-linearity or other detection problems for the AMS, due to the low ion currents measured with the W-mode and the short lifetime of the AMS OA background signal.

Elemental analysis was applied to AMS OA measurements to yield ratios of oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) (Aiken et al., 2008). This calculation was performed with HR ion fits up to m/z 100, and implicitly assumes that the elemental composition of larger ions is similar to that of the ions below m/z 100. For the purpose of this study, nitrate, sulfate, ammonium, and chloride are assumed to be from inorganic sources; however, there may be some contribution to these nominally inorganic species from organic compounds (e.g. Farmer et al., 2010). The cation balance analysis, comparing the measured potassium (K+) and ammonium (NH4+) to that predicted when considering sulfate, nitrate, and chloride as fully inorganic ions indicates a deficit of cations (Fig. S4b). We have included K+ (with a relative ionization efficiency of 2.9, Drewnick et al., 2006) in this balance because it is known to be an important cation in biomass-burning smoke (Lee et al., 2010). Na+ was not included due to substantially lower concentrations than K+ in biomass burning smoke (McMeeking et al., 2009) as well as the difficulty of quantifying this ion with the AMS. The most likely explanation for apparent cation deficit observed is inefficient detection by the AMS of K+ or other mineral cations present in the smoke. It could also possibly have a contribution from organonitrates and/or organosulfates present in the smoke particles that would lead to too high estimates of inorganic nitrate or sulfate. However we are not aware of reports of organonitrates or organosulfates in biomass burning aerosols, so that possible explanation remains speculative. Another possible reason for the observed cation deficit would be the presence of H+ if the aerosols are acidic, since H+ cannot be quantified directly by the AMS due to limitations of the time-of-flight mass spectrometer.
VOC Measurement

A custom-built PIT-MS was deployed to quantify VOCs. Proton transfer reaction mass spectrometry (PTR-MS) has become a standard method for quantifying mixing ratios of common VOCs such as oxygenates, aromatics, and alkenes at ambient concentrations (de Gouw and Warneke, 2007). The PIT-MS instrument uses an ion source and drift-tube reactor identical to that of the commercial PTR-MS instrument but is equipped with a three-dimensional ion trap mass spectrometer instead of a quadrupole mass filter (Warneke et al., 2005a; Warneke et al., 2005b), allowing for detection of a full mass spectrum as opposed to a subset of specifically targeted compounds. During FLAME-3, the PIT-MS was used for simultaneous measurements of product ions with \(m/z\) 33–225, trapping times ranging from 0.5–2.0 s depending on VOC concentrations in the fire chamber. A 10 m long 1/8” o.d. Teflon line and a sample flow of 150 sccm were used to sample air from the fire chamber. Calibrations for twelve common VOCs, including toluene, were conducted using a gas standard before and after each burn throughout the experiment. Measurement uncertainty for the calibrated VOCs measured by PIT-MS was estimated to be ± 30% and for the uncalibrated VOCs was estimated to be ~50%. A potential interference in benzene measurements (at \(m/z\) 79) due to water-acetic acid clusters appears to be negligible during FLAME-3 because of low relative humidity during the experiments.

Photochemical age estimation

OH exposure (OH\(_{\text{exp}}\)) is the integral of OH concentration and oxidation time. Typically, offline calibrations of OH exposure can be made by using the decay of SO\(_2\) to reaction with OH
at different UV light intensities, as described in Lambe et al. (2011a). For the conditions in our flow reactor, OH_{exp} can be modeled using measured O_{3}, RH, and flow rate:

\[ OH_{exp} = [OH] \Delta t = \epsilon \frac{[O_{3}]^{\alpha}[H_{2}O]^{\beta}}{flow} \]  

where \( \epsilon = 7.21 \times 10^{-7} \) (with OH_{exp} in units of molec cm^{-3} s, when O_{3} and H_{2}O are in units of molec cm^{-3} and the flow in L/min), \( \alpha = 0.495 \), and \( \beta = 0.70 \), are calibration parameters determined during offline SO_{2} calibration; O_{3} and H_{2}O are in units of molec cm^{-3} and flow is in L min^{-1}. An equivalent “photochemical age” can be calculated by dividing this OH_{exp} by an assumed average atmospheric concentration of OH of 1.5\times10^{6} molecules cm^{-3} (Mao et al., 2009).

However, high concentrations of reactive VOCs can suppress OH by shifting OH to HO_{2}, thus reducing OH_{exp} (in a way not reflected in H_{2}O and O_{3}) so that the calibration equation no longer accurately describes OH_{exp}. In this study, sampling of biomass-burning smoke directly from the fire chamber resulted in very high concentrations of VOCs and POA, greater than 10^{2} ppb VOCs and up to 10^{4} \mu g m^{-3} POA. In order to test for possible OH suppression by this very reactive mixture, OH exposures were calculated from the online decay of toluene and benzene with different OH exposures was examined during burn 55, with white spruce smoke (Fig. 2). Toluene (C_{7}H_{8}) was chosen as a VOC proxy because it has high signal-to-noise, few if any interferences in PIT-MS measurements, minimal wall loss, no expected production, and a reaction rate with OH fast enough that significant toluene is removed but slow enough so that some remains to be measured by the PIT-MS. Benzene (C_{6}H_{6}) was also chosen as a VOC proxy for similar surface loss and production considerations and has an OH reaction rate similar to SO_{2}, which was used in the offline calibrations. During PIT-MS measurements of the reactor output, toluene and benzene decreased because of reactions with OH but also because of dilution of the
smoke. Separating these two concurrent decays required the fire chamber dilution of VOCs to be determined by fitting an exponential decay curve to VOC concentrations drawn directly from the fire chamber (Fig. 2a). Assuming the additional decay was due only to reaction with OH, the concentration of OH can be estimated from Eq. (2).

\[[VOC]_{\text{out}} = [VOC]_0 e^{-(k[OH] \Delta t)}\] (2)

Where \([VOC]_0\) is the mixing ratio of the VOC (toluene or benzene) entering the reactor, and \([VOC]_{\text{out}}\) is the mixing ratio exiting the reactor. For toluene, \(k_{OH} = 5.63 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\), and benzene \(k_{OH} = 1.22 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) s\(^{-1}\) (Atkinson and Arey, 2003). \(\Delta t\) is the residence time in the flow reactor (180 s). The results of calculating the OH concentration in the reactor for burn 55 are shown in Fig. 2b. With one lamp at 75% of its max voltage, \(OH_{\text{exp}}\) is estimated at 1.5×10\(^{11}\) and 8.5×10\(^{10}\) molecules cm\(^{-3}\) s using benzene and toluene, respectively. With one lamp at 100%, \(OH_{\text{exp}}\) is estimated at 5.6×10\(^{11}\) and 2.5×10\(^{11}\) molecules cm\(^{-3}\) s using benzene and toluene, respectively.

![Fig. 2. VOC observations in the reactor at two different UV lamp settings used to calibrate \(OH_{\text{exp}}\). Percentage of light reported is one lamp at 75 or 100% of maximum supplied voltage. (a) Data from burn 55, white spruce, showing fire chamber measurements of toluene and benzene made by PIT-MS (gray points). A fit of the dilution of the fire chamber concentrations is shown as a solid gray line. Flow reactor measurements of toluene and benzene are colored brown and yellow, respectively. Fits of the VOC concentrations after the flow reactor were used to calculate OH concentrations. (b) \(OH_{\text{exp}}\) in the reactor calculated from PIT-MS benzene and toluene measurements.](image-url)
The OH$_{exp}$ calibration equation (Eq. 1) was adjusted to account for OH suppression by comparing the OH$_{exp}$ calculated by offline SO$_2$ calibration and OH$_{exp}$ from real-time VOC decays (Fig. S6). The difference between these OH estimation methods using online benzene and toluene measurements was combined to obtain an average suppression factor of 3.7 ± 0.28 (average ± 1σ), that is, OH was an average of 3.7 times lower than calculated using the offline SO$_2$ calibration. This factor was applied to Eq. 1 and used for all experiments where OH$_{exp}$ is presented. Taking OH suppression into account, OH$_{exp}$ in this study ranged from 1.36×10$^{10}$ – 6.5×10$^{11}$ molec. cm$^{-3}$ s, equivalent to 0.1 – 5.0 days of photochemical aging. Due to the high OH reactivity of our samples (estimated to be 15500 s$^{-1}$), this range of OH exposures is lower than in other experiments using a similar flow reactor configuration because of the high VOC levels.

RESULTS

Observations

Following each biomass fuel’s ignition, aerosol and VOC concentrations increased rapidly during the first 10 min as smoke mixed throughout the chamber. Peak concentrations were observed within 15 min from fire ignition. Maximum concentrations were followed by a slow decay over a few hours because of FSL fire chamber dilution with ambient air of much lower aerosol concentrations. Over the course of a typical 3.5-hour measurement period, unprocessed smoke drawn from the fire chamber slowly diluted on average by a factor of 4.5 ± 2.2 (mean from all experiments ± 1σ) as measured from peak OA at the start of the burn.
VOC observations

Comparing VOC concentrations from the flow reactor in the absence of photochemical aging \((\text{OH}_{\text{exp}} = 0)\) and air drawn directly from the fire chamber through tubing that bypassed the reactor showed no significant mass spectral differences when scaled for ongoing fire chamber dilution. Hence, the flow reactor itself does not appear to affect either the concentration or the composition of the VOC mixture measured with the PIT-MS. VOC abundances evolved during burn experiments as the sample air was exposed to different degrees of OH exposure. Figure 3 shows the evolution of some key VOCs for wire grass (Burn 56). The total measured VOCs decrease over the sample period due to dilution. As OH exposure increased, xylenes, monoterpenes, toluene, and benzene decreased, while formic acid increased. Acetaldehyde initially increased at lowest OH exposure and then decreased with higher exposure, suggesting that it may be an initial oxidation product before additional photochemistry degraded it. Formic acid was present in the raw smoke and was greatly enhanced by aging. Several unidentified compounds (e.g., \(m/z\) 157, not shown in Fig. 3 for simplicity) follow the temporal trend of formic acid, indicating that they evolved from photochemical production. Similar production of formic acid and unidentified compounds (such as \(m/z\) 157) have been observed with PTR-MS in chamber oxidation of terpenes (Lee et al., 2006).
Fig. 3. Time series for select VOCs and oxidants measured after the reactor during burn 55, white spruce. The time series begins with lights off in the reactor, then transitions to increasing O$_3$ concentration (blue, bottom panel) and OH exposures (purple, bottom panel) in steps. The reactor was sampled with lights off (gray), then at OH$_{exp}$ = $5.2 \times 10^{10}$ molec. cm$^{-3}$ s ($\sim$ 0.4 days aging, white), OH$_{exp}$ = $1.6 \times 10^{11}$ molec. cm$^{-3}$ s ($\sim$ 1.25 days aging, light yellow), and OH$_{exp}$ = $2.6 \times 10^{11}$ molec. cm$^{-3}$ s ($\sim$ 2 days aging, bright yellow). Diamond markers indicate where the mass spectra presented in Fig. 4 were taken.

PIT-MS mass spectra (Fig. 4) for the same burn as Fig. 3 illustrate the effect of photochemical aging on VOC composition. During a similar study, Warneke et al. (2011) was able to identify less than 40% of the total PIT-MS signal in most burn experiments. Besides the
trends already illustrated in Fig. 3, the full mass spectrum allows for examination of whether unidentified VOC masses increase or decrease with aging (Fig. 4c). The majority of the \(m/z\) detected decrease with aging as seen in Fig. 4c; however, about two dozen VOCs are enhanced by aging such as \(m/z\) 157, 167 and 171.

Fig. 4. PIT-MS mass spectra showing the changes in VOC composition with photochemical age, i.e., OH exposure. (a) Mass spectrum after the flow reactor with \(\text{OH}_{\text{exp}} = 0\) (unprocessed). (b) Mass spectrum after the flow reactor with \(\text{OH}_{\text{exp}} = 2.6 \times 10^{11}\) molec. cm\(^{-3}\) s (~ 2 days aging). (c) Percentage enhancement of VOCs in the flow reactor between unprocessed and aged. The data are from the same experiment shown in Fig. 3 (mass spectra taken at times indicated by black diamonds on the x axis Fig. 3, which shows associated OH exposures). Each spectrum is the average of 50 PIT-MS trapping cycles of 2 s. The same VOCs shown in Fig. 3 are highlighted here (with the addition of sesquiterpenes).
Aerosol observations

The continuous time series of AMS measurements show a sawtooth pattern (Fig. S2), reflecting the switching from sampling aged and unprocessed smoke. Once separated, the time series of OA in Fig. 5a shows aged and unprocessed smoke for two fuels, turkey oak (burn 45) and ponderosa pine (burn 40). For turkey oak smoke, the resultant OA mass after aging is higher than POA. In contrast, for ponderosa pine smoke, after aging, total aged OA is lower than POA. Two AMS chemical markers are shown in Fig. 5. The signal at m/z 44, which is dominated by both CO$_2^+$ and C$_2$H$_4$O$^+$ (see Fig. S7 for details), is a marker of oxidized species and can come from the original POA, SOA, or heterogeneous oxidation of POA. The signal at m/z 60, which is dominated in this study by C$_2$H$_4$O$_2^+$, a fragment from levoglucosan and similar POA species, is often used as a tracer for primary biomass burning emissions (Lee et al., 2010; Cubison et al., 2011; Ng et al., 2011b). m/z 60 can also have a contribution at C$_2$H$_4$O$_2^+$ from SOA due to species such as organic acids.

Fig. 5. Time series of OA data for turkey oak (burn 45) and ponderosa pine (burn 40) smokes. (a) OA mass concentration, (b) oxidation marker (m/z 44) and primary biomass-burning marker (m/z 60), (c) O$_3$ and OH exposure. The gray boxes denote a period when the UV lights in the flow reactor are turned off.
Tracers \textit{m/z} 44 and \textit{m/z} 60 show similar temporal trends as OA, with peak values at the start of burns and a decrease due to dilution. The oxidation tracer \textit{m/z} 44 is enhanced by photochemical aging more in turkey oak smoke than in ponderosa pine smoke (Fig. 5b) and increased with intensified aging (Fig. 5c), due to the increase of the CO$_2^+$ ion. The POA tracer \textit{m/z} 60 is substantially depleted after aging for ponderosa pine and decreases slightly with aging, but does not change significantly for turkey oak smoke, possibly due to canceling effects from increased organic acids produced from aging or to slow diffusion in the POA that may protect levoglucosan and similar species from oxidation. The two burns presented in Fig. 5 illustrate a diverse chemical evolution upon the aging of biomass-burning smoke. The observed trends are repeatable for a given biomass, and encompass the variability of smoke aging observed over the entire campaign.

To examine potential particle losses to the walls of the reactor and tubing in the absence of aging, the reactor UV lights were turned off for fifteen minutes after at least 30 minutes had passed from fuel ignition. During this “dark” period, OH exposure is negligible and only a ~1% difference in aerosol mass was observed between air that had flowed through the reactor vs. the bypass tubing, indicating minimal particle mass losses in the reactor and associated tubing.

Organic aerosol enhancement

One of the key results of this experiment is the net effect of aging on OA mass. The ratio of OA mass after aging to the OA mass before aging is defined as the net OA enhancement ratio ($\text{ERR}_\text{OA} = \text{Aged/Unprocessed smoke}$). Since the two unprocessed 1 min data points before and after each 1 min aged point are used, there is no need to further correct for the slow ongoing dilution in the chamber. $\text{ERR}_\text{OA} = 1$ indicates no difference between the OA mass from aged vs.
unprocessed smoke, while ER\textsubscript{OA} >1 (or <1) indicates mass increased (or decreased) during aging. An increase of mass can be due to SOA formation as semi-volatile or non-volatile gas-phase oxidation products partition to the aerosol, and/or the heterogeneous oxidation of the primary or secondary OA because the addition of oxygen can lead to increased particle mass even if no new carbon condenses from the gas phase. A decrease in mass can be due to heterogeneous chemistry followed by evaporation of some of the products or to gas-phase reaction of semivolatiles that leads to evaporation of particle-phase species in equilibrium with them. Our measurements cannot by themselves distinguish among these processes.

Table 1 shows ER\textsubscript{OA}, calculated as the maximum deviation from unity (ER\textsubscript{OA} =1) due to aging and sustained over a five-minute average during each burn experiment, with associated OH\textsubscript{exp} reported. ER\textsubscript{OA} varies strongly with OH\textsubscript{exp} and fuel type (Fig. 6). These four biomass fuels are good examples to illustrate the diversity of results observed for all fuels. As OH\textsubscript{exp} increases, most fuels showed maximum absolute value ER\textsubscript{OA} (max. deviation from 1) around 3–4 days of aging, then leveled off even with increasing OH\textsubscript{exp}. However, chemical transformations continued after ER\textsubscript{OA} had reached a maximum deviation from unity, as discussed in more detail in Section 3.4. Of these four fuels, only ponderosa pine smoke showed a reduction in total OA, indicating that heterogeneous oxidation and/or evaporation of semivolatiles after aging overwhelmed any SOA formation. Sage smoke showed the highest ER\textsubscript{OA} and it is not clear whether a plateau is reached within the range of OH\textsubscript{exp} achieved. This result stands in contrast to biomass-burning measurements of gas-phase emission ratios of different fuels which show that sage smoke is similar to the smoke from other biofuels (Warneke et al., 2011). In burn 49 (sage), the organic fraction is only 70% of the unprocessed total aerosol measured, the lowest observed. It might be expected that ER\textsubscript{OA} would decrease with continuing OH\textsubscript{exp} as observed in previous
laboratory studies (e.g. Lambe et al., 2012), but the maximum $\text{OH}_{\text{exp}}$ was limited in FLAME-3 by the large VOC concentrations to values below the observed turnover point for the OA mass, which was in the range of $5 \times 10^{11} - 1 \times 10^{12}$ molec. cm$^{-3}$ s.

Fig. 6. OA enhancement ratio as a function of photochemical age and OH exposure for four fuels (ponderosa pine, burn 40; wire grass, burn 42; turkey oak, burn 45; and sage, burn 49). The range of OH exposure examined in smog chambers at Caltech (Chhabra et al., 2011) and Carnegie Mellon’s mobile laboratory (Hennigan et al., 2011) are shown for reference.

An overview of campaign-wide maximum ER$_{\text{OA}}$ observations shows that ER$_{\text{OA}}$ was highly dependent on fuel type, as shown in Fig. 7a which illustrates the maximum ER$_{\text{OA}}$ (over a 5-min average) for all fuels, with standard error for fuels repeated in multiple burn experiments.
Most ER\textsubscript{OA} were reproducible within <10\% for repeated burns of the same biomass, although a few showed more variability. The observed variability is thought to be due to variability in the burning process dynamics, which was observed visually for some fuels. This may include the fraction of the combustion time (fraction of the fuel burned) in flaming and smoldering fire phases. The burn-to-burn variability we observed was also recorded using other aging methods (Hennigan et al., 2011) at this same study, as well as in other laboratory and field biomass burning studies (Grieshop et al., 2009; McMeeking et al., 2009; Cubison et al., 2011; Akagi et al., 2012). Aging of smoke from most fuels resulted in a net OA increase. Negligible increase or a net decrease was observed for only two fuel types: ponderosa and lodgepole pine. Figure 7b shows the statistical distribution of maximum ER\textsubscript{OA} for all burns, with an average ER\textsubscript{OA} of 1.42 ± 0.36 (mean ± 1σ).
During FLAME-3, Carnegie Mellon University (CMU) deployed a mobile 7 m³ Teflon chamber in which a combination of natural sunlight, UV blacklights, and injected nitrous acid (HONO) were the source of OH. The smoke was transferred to the chamber through a 12 m transfer line heated to 40°C and was diluted a factor of ~25 (Hennigan et al., 2011). ER_{OA} for the CMU chamber ranged from 0.7 to 2.9, with a project average enhancement of 1.7 ± 0.7 (mean ± 1σ). While the flow reactor sampled 25 burns during FLAME-3, CMU’s chamber sampled 18. It was limited to one experiment per day because of much slower aging at lower OH exposures and required downtime for at least 12 hours of clean air flushing for bag cleaning between
experiments. The distributions of maximum ER$_{OA}$ for all burns aged in the CMU chamber are consistent with those from the flow reactor (Fig. 7c). Both aging methods observe, on average, substantial net OA enhancement from aging with a wide distribution. While CMU’s data has a higher mean ER$_{OA}$, the median of both methods is more similar: 1.39 for the flow reactor and 1.47 for CMU’s smog chamber. Smoke from ponderosa pine burning resulted in a decrease in OA mass from both aging methods (Hennigan et al., 2011).

A possible cause for the differences between our results and CMU’s are the much higher levels of dilution employed in the CMU experiment. Additional dilution decreases the gas-phase concentration of some semivolatile organics, causing net evaporation from the POA and thus reduction in OA mass (Robinson et al., 2007). During FLAME-3, smoke POA concentrations spanned two orders of magnitude. In Fig. 8a, the relationship between absolute OA mass enhancement due to aging and initial POA is shown for both our flow reactor and the CMU chamber, demonstrating that to first order the absolute mass enhancement due to aging scales with POA, but with a less than proportional increase at high POA values. Figure 8b shows ER$_{OA}$ vs. initial POA for both the flow reactor and chamber. Both aging methods show a downward trend in ER$_{OA}$ with increasing POA (with less scatter for the flow reactor data) which is qualitatively consistent with our hypothesis. Fuels whose combustion produces higher POA result in less net SOA formation when normalized to the initial POA mass. Although VOC data are only available for a few burns, the absolute or relative enhancement of OA does not correlate with the sum of the detected VOCs or with individual known precursors such as aromatics or isoprene. In addition, the total amount of SOA formed exceeds the total mass of known SOA precursors (aromatics, isoprene, monoterpenes). Both facts suggest either VOCs measured but not identified by the PIT-MS, and/or that semivolatile and intermediate volatility species not
measured by the PIT-MS contribute to a major fraction of the SOA formed from biomass-burning smoke. The inverse correlation of $\text{ER}_{\text{OA}}$ with POA suggests that semivolatile and intermediate volatility species are more likely to be the dominant precursors, as more of those species will be in the gas-phase at lower POA concentrations, due to gas/particle equilibrium. $\text{ER}_{\text{OA}}$ does not appear to correlate with other burn parameters such as black carbon, NOx, or CO emissions.

Fig. 8. OA enhancement as a function of unprocessed OA for all fuels, with CMU’s mobile air-quality laboratory smog chamber (red), as reported in Hennigan et al. (2011), and flow reactor (blue). (a) OA mass enhancement (aged minus unprocessed) vs. POA (unprocessed). To plot data with logarithmic y axis, fuels whose aged smoke resulted in net mass loss are shown as the negative log of the absolute value of the difference between aged and unprocessed smoke, and plotted on a separate y axis. (b) OA enhancement ratio (i.e., relative enhancement) vs. unprocessed (POA).
Effect of aging on chemical composition

Aerosol mass spectral evolution with age

To investigate chemical transformations due to smoke aging, aged vs. unprocessed AMS mass spectra are compared for two fuels, one with high ER\textsubscript{OA} and one with low ER\textsubscript{OA} (Fig. 9). Unprocessed spectra (Fig. 9a) show characteristics typical of biomass-burning POA spectra in the AMS, including strong signals at m/z 60 and 73 from levoglucosan and related species (Aiken et al., 2009; Lee et al., 2010). The net effect of aging on aerosol composition is calculated by subtracting the unprocessed mass spectra from those of the aged smoke (aged in Fig. 9b, difference in Fig 9c). Aged smoke from turkey oak has an ER\textsubscript{OA}>1 (Figs. 6), and a few m/z decreased significantly with aging. The spectrum of the difference signal is very similar to that of fresh oxidized OA (OOA) observed in ambient air and some laboratory experiments, with similar characteristics independent of the initial POA or SOA precursor source (e.g., Jimenez et al. 2009, and references therein). Ponderosa pine has an ER\textsubscript{OA}<1 (Fig. 6) and most m/z, including almost all m/z > 50, decrease from aging, likely because of heterogeneous oxidation of the initial POA and/or evaporation of POA semivolatiles after dilution or oxidation of the gas-phase species in equilibrium with them. A few m/z increase with aging, in particular m/z 28 and 44, showing that the oxidized POA and/or SOA in this sample also evolves similarly to OOA observed elsewhere. These observations are typical of other fuels not shown, where m/z 28 and 44 always increase and spectrum-wide production or consumption tend to follow overall ER\textsubscript{OA}. 
Fig. 9. Effect of photochemical processing on mass spectra of two fuels: turkey oak, burn 45, and ponderosa pine, burn 40. All data were collected 15–25 min after the start of fuel combustion and averaged over 10 min of sampling with moderate OH exposure. (a) Average mass spectrum of unprocessed smoke, (b) average mass spectrum of aged smoke, and (c) difference (1OA) between aged and unprocessed smoke. All plots are colored by ion type.

The mass spectra of the ER$_{OA}$ for these two fuels, shown in Fig. S8, exhibit similar picket-fence spacing. To summarize, we see that oxidation does not favor odd/even m/z but does have a cycle of ~14 m/z. These features are more distinct for ponderosa pine smoke where mass is lost. One interpretation of the ER$_{OA}$ mass spectral shape could be that if aging oxidizes POA without condensing new OA mass, POA should lose mass fairly equally across m/z (on a relative scale), in this case Fig. S8b would be a near flat line of sticks < 1. However, if simultaneously adding new OA mass, with a similar spectrum to that in Fig. S8a, the combined effect could produce the ER spectrum shown in Fig. S8b, and indeed the spectrum appears very consistent with this hypothesis. This would suggest for fuels with ER$_{OA}$< 1, aging may fragment/evaporate POA and simultaneously add new OA mass (through condensation or heterogeneous addition of oxygenated functional groups) of similar signature to other burns where ER$_{OA}$ is > 1.
Examining chemical transformations from aging shows increased signal at m/z 28 and 44 (Fig. 9c and Fig. S8). High-resolution data shows these signals are dominated by increases in CO\(^+\) (enhanced CO\(^+\) ion at m/z 28 in Figs. S5, S7) and CO\(_2\)\(^+\) ions (Fig. S7), with small contributions from C\(_2\)H\(_4\)\(^+\) and C\(_2\)H\(_4\)O\(^+\), respectively. Note that at m/z 44, unprocessed smoke can have a higher contribution from C\(_2\)H\(_4\)O\(^+\) than CO\(_2\)\(^+\), as seen for Ponderosa Pine in Fig. S7 these two ions have comparable signals after aging.

Changes of AMS fractional tracer ion contributions \(f_i\) with aging

The fractional contribution of a specific m/z to total OA mass \(f_i\) provides information on the OA chemical transformations with aging. Previous studies have used \(f_{44}\) (m/z 44/OA) as a tracer of SOA and aging, \(f_{43}\) (m/z 43/OA) as a tracer of POA and fresh SOA, and \(f_{60}\) (m/z 60/OA) as a tracer of biomass burning POA (Ng et al., 2010; Cubison et al., 2011). To characterize the aging of biomass-burning smoke, Cubison et al. (2011) proposed the use of the scatterplot \(f_{44}\) vs. \(f_{60}\), which facilitated comparison of ground, aircraft, and laboratory observations. Results from Cubison et al. (2011) showed that very aged smoke can retain an elevated \(f_{60}\) signature above background levels.

The evolution of \(f_{44}\) with aging for smoke from four fuels is shown in Fig. 10a. As expected, \(f_{44}\) always increases with OH\(_{\text{exp}}\), though to a lesser degree in experiments with fuels having an ER\(_{\text{OA}}\) < 1 (in part due to the decrease of ions other than CO\(_2\)\(^+\), Fig. S7). To compare aged smoke with atmospheric measurements of OA, typical ranges of \(f_{44}\) for semivolatile oxidized organic aerosol (SV-OOA) and low-volatility oxidized organic aerosol (LV-OOA) (Jimenez et al., 2009; Ng et al., 2010) are shown on the right in Fig. 10a. The fresh smoke from turkey oak and wire grass, fall at the lower end of the SV-OOA range of ambient measurements.
and approach the higher at maximum aging. In contrast, fresh sage smoke falls well within the
SV-OOA range and reached the LV-OOA range after 1.5 days of aging. For all experiments, the
rate at which $f_{44}$ changed as the OA oxidized differs for each fuel and this rate appears to
increase with initial $f_{44}$ of POA. We speculate the observations in Fig. 10a are due to greater
fractional partitioning of SVOCs to the particles at higher OA concentrations. Since the
oxidation kinetics of SVOCs are substantially slower in the particle phase compared to the gas-
phase (e.g. May et al., 2012), such partitioning would result in less gas-phase oxidation and thus
less of an increase in $f_{44}$ for the fuels with higher initial POA concentrations.

A similar approach can be used to investigate the decay of $f_{60}$ (Fig. 10b). Smoke from
wire grass and turkey oak (both with ER_{OA}>1) show decreasing $f_{60}$ with increasing aging; in
contrast, smoke from sage and ponderosa pine show a constant $f_{60}$ with age. Across all
experiments, $f_{60}$ always remained elevated above background ambient biomass-burning free
levels (~0.3%±0.06%; DeCarlo et al., 2008; Aiken et al., 2009; Cubison et al., 2011). Plots of $f_{60}$
vs. POA for unprocessed smoke (Fig S9b) showed an increase in $f_{60}$ at the lower POA
concentrations, followed by a stabilization and then a small decrease at the highest
concentrations.
While aging always increased $f_{44}$, it does so at very different rates for different smokes. The relationship between $f_{44}$ and $f_{60}$ is shown in Fig. 10c. $f_{60}$ decreased for the majority of fuels, which can be due to gain of new SOA mass with low $f_{60}$, and/or to reaction or volatilization of levoglucosan and similar POA species. In a few burns (where ER$_{OA}$ < 1) $f_{60}$ remained unchanged despite aging by OH, indicating that m/z 60 was reduced by aging proportionally to the rest of the OA. Regardless of decay or not, $f_{60}$ remains elevated above background levels (in the absence of biomass burning) for all fuels (Fig. 10c). As the CO$_2^+$ ion is the main oxidation reaction product at m/z 44, the relation between $f_{CO2^+}$ and $f_{60}$ (Fig. S9c) is very similar to that of $f_{44}$ and $f_{60}$, though the rise is $f_{CO2^+}$ is sharper with increased aging.
These results are consistent with those observed in the field by Cubison et al. (2011), forming and filling a triangle of $f_{44}$ vs. $f_{60}$ space for aging of biomass-burning smoke. POA measured in this study have $f_{60}$ values consistent with ambient fire plumes (Cubison et al., 2011), while $f_{60}$ values from traditional chamber-smoke aging experiments (Hennigan et al., 2011) are much lower than ambient measurements in smoke plumes. Huffman et al. (2009) showed using a thermal denuder that $m/z$ 60 had consistently higher volatility than the bulk OA for smoke from burning multiple biomasses, which is consistent with our data vs. POA concentration discussed above. Thus, the difference in $f_{60}$ between the different aging methods is due to high dilution of fresh smoke into a chamber that may result in higher fractional evaporation of the species producing $m/z$ 60.

A different triangle plot, of $f_{44}$ vs. $f_{43}$ has been used to study aging of OOA and other OA types, where OOA ambient observations across many field studies, described by Ng et al. (2010), lie within lines forming a triangle. Multiple field and laboratory studies observed that during early stages of aging, $f_{43}$ increases (Ng et al., 2011a). In contrast, for ongoing aging, $f_{44}$ increases as $f_{43}$ decreases. High-resolution AMS measurements from previous studies have shown that this shift is due to increased CO$_2$+ with aging, which results in increased $f_{44}$, while further oxidation of molecules that produce C$_3$H$_7^+$ and C$_2$H$_3$O$^+$ in the AMS at $m/z$ 43 reduces these signals with aging (Aiken et al., 2008; DeCarlo et al., 2010). Figure 11a shows $f_{44}$ plotted vs. $f_{43}$, from the aging of smoke from four biomasses. POA from fuels are located towards the lower-left corner, consistent with ambient observations of primary BBOA, and exemplified by average factors determined from Positive Matrix Factorization of multiple studies from Ng et al. (2011b). With increased OH$_{exp}$, all fuels, at first, show a trajectory upward and to the right, moving into the window of atmospheric SV-OOA. With increasing aging, the trajectory begins to turn as $f_{44}$
begins to increase and $f_{43}$ remains constant or decreases. This change is true for all burns in which ER$_{OA} > 1$. $f_{43}$ continually increases with aging for ponderosa pine smoke (and other fuels with ER$_{OA} < 1$). These patterns are very consistent with those reported for other photooxidation flowtubes and chamber studies presented in Ng et al. (2010) for oxidation of hydrocarbon-like OA (HOA), POA, and biogenic precursors.

The presence of high initial POA concentrations in these experiments complicates the comparison against the OOA-only evolution discussed by Ng et al. (2010). To examine the evolution of $f_{44}$ and $f_{43}$ due to SOA formation only, the $f_{44}$ of only the added mass ($\Delta f_{44}$) is plotted with respect to the $f_{43}$ of only the added mass ($\Delta f_{43}$) in Fig. 11b. $\Delta f_i$ is calculated by Eq. 3,

$$\Delta f_X = \frac{\Delta C_X}{\Delta C_{OA}} = \frac{C_X(\text{PAM}) - C_X(\text{Unprocessed})}{C_{OA}(\text{PAM}) - C_{OA}(\text{Unprocessed})}$$  \hspace{1cm} (3)
where $C_x$ is the concentration at $m/z \, X$ and $C_{OA}$ is the organic mass from either aged or unprocessed smoke. This parameterization assumes the POA remains unchanged and it is only meaningful for fuels with $ER_{OA} > 1$. Using this metric, relatively high $f_{44}$ in the added SOA is observed, starting near typical ambient SV-OOA and then surpassing ambient LV-OOA levels (Fig. 11b). This trend is seen in other laboratory applications of the flow reactor, where aging rapidly increases $f_{44}$ beyond the right boundary of the triangle of ambient observations (Lambe et al., 2011b). Thus, the qualitative chemical evolution of biomass burning OA and SOA with aging is similar to that observed for OA and SOA from other sources, consistent with previous studies (e.g. Jimenez et al., 2009).

Effect of aging on elemental composition

The high-resolution capability of the AMS allows quantification of OA elemental composition. For all experiments, the campaign average POA O/C was $0.30 \pm 0.07$ and spanned the range of 0.15-0.5, while OA after aging (SOA and OPOA) had a campaign average O/C of $0.43 \pm 0.14$, with a maximum of 0.87.

Fig. 12a shows O/C as a function of OH$_{exp}$ for four fuels. Lambe et al. (2012) used this type of plot to assess the correlation of O/C with OH$_{exp}$ for reactor-generated SOA from alkane precursors (gray shaded area). All burns present in Fig. 12a are in or near that range and evolve similarly as for alkane precursor SOA, except for sage where initial O/C is higher and increases faster with OH$_{exp}$ (similar to $f_{44}$ in in Fig. 10). The differences between the O/C at zero OH$_{exp}$ for these four cases show the varying degree of oxidation of fresh smoke POA, and the corresponding increases of O/C increase with oxidation suggests that the degree of oxidation of initial POA affects the rate of increase and maximum O/C from aging.
Elemental ratios provide insight into oxidation mechanisms because different types of functionalization and fragmentation result in different relative evolutions in H/C and O/C ratios (Van Krevelen, 1950). Figure 12b shows the evolution of OA as H/C vs. O/C with aging from the same four burns. As OH$_{\text{exp}}$ increases, O/C increases and H/C decreases, but at a slower rate than O/C increases. Slopes corresponding to different functionalization pathways are shown in Fig. 12b, for reference. Each fuel has a unique slope, suggesting different oxidation functionalization for each fuel, as highlighted for these six fuels in Fig. S10a. Ponderosa pine, burn 40, has a slope of 0.02 ± 0.03, suggesting alcohol/peroxide functionalization (although the range was small for that burn), while the other fuels have a slope close to -0.5. Together, the range of elemental ratios from all fuels, as seen in Fig. S10b, have a trajectory that falls between the slopes-lines of -1 and -0.5, consistent with the addition of both acid and alcohol functional
groups without fragmentation or the addition of acid groups with carbon-carbon bond breakage. Aged smoke from this study falls within the window of ambient measurements (Ng et al., 2011a).

The relationship between O/C and $f_{44}$ can be useful since many AMS instruments can only produce unit-resolution data, as well as for quick-look analysis of high-resolution data during data acquisition. Examining the relationship of O/C and $f_{44}$ (Fig. 13), aged and unprocessed smoke from different fuels follow relatively similar slopes, with the exception of Ponderosa Pine. Using ambient ground and aircraft AMS measurements near Mexico City, Aiken et al. (2008) reported an O/C vs. $f_{44}$ slope of 3.82, while the slope of all burns in this study is 3.83. Although the lines are nearly parallel, there is a vertical offset for smoke data that results in higher O/C for the same $f_{44}$ compared to the ambient data. Additionally, BBOA-only data from Aiken et al. (2008)’s field measurements are plotted in Fig. 13, and show a similar offset as the data from this study. Thus, it seems for both biomass-burning POA and SOA, $f_{44}$ is a reasonable surrogate for O/C if high-resolution data is not available, but the difference in the offsets should be kept in mind.
Fig. 13. Aged and unprocessed smoke O/C as a function of $f_{44}$ for all burns with four fuels highlighted (ponderosa pine, burn 40; wire grass, burn 42; turkey oak, burn 45; and sage, burn 49). Each highlighted burn, as well as all data, is fitted with a linear ODR fit. Aiken et al. (2008)’s fit of O/C vs. $f_{44}$ for ambient Mexico City measurements is plotted with BBOA-only data from that study highlighted for reference.

Using maximum O/C after aging from each burn experiment and the corresponding O/C of POA (unprocessed) during each burn experiment, Fig. 14a shows that maximum O/C after aging is strongly correlated with O/C of unprocessed OA. Fig. 14b shows the O/C of the net mass added (under the assumption that POA remains constant). The ratio of net change in oxygen to the net change in carbon from aging, i.e. the O/C of the added SOA (equivalent to Eq. 3), is correlated with POA O/C showing that for each additional unit of initial O/C, the maximum O/C of the added SOA increased by 3.27 units. Since the intercept is near zero, the max O/C of
the added SOA is approximately 3.27 times the O/C of the unprocessed POA. The O/C of the added SOA are within the range of 0.4–1.0, reaching levels of very oxidized aerosol (produced by condensing highly oxidized SVOC and/or adding oxygen to POA). Note, calculation of net O/C mass added assumes unchanged POA and thus results in an upper limit for the O/C of the added SOA, where ER_{OA} < 1 fuels are not plotted (since it would not be meaningful). Colored by ER_{OA}, both plots in Fig. 14 show fuels with highest POA O/C have the highest O/C added from aging. These results indicate the degree of oxidation of initial POA strongly affects maximum O/C from aging.

Fig. 14. Changes in O/C from aging fresh smoke. (a) Maximum O/C from aging as a function of unprocessed smoke O/C. (b) The ratio of change in oxygen (aged-unprocessed) to the change in carbon (aged-unprocessed) as a function of unprocessed O/C, for fuels where this ratio is positive (ER_{OA} > 1). Both plots are colored by organic aerosol enhancement ratio (ER_{OA}).
SUMMARY AND CONCLUSIONS

Several experimental innovations were demonstrated in this study, which is the first real-time flow reactor aging experiment of a complex mixture, such as smoke, with real-time scanning of OH, an open-flow-through configuration, multiplexing AMS and PIT-MS allowing for concurrent measurements of unprocessed and aged smoke. Fast photochemistry, short residence time, and controllable OH concentrations allowed for multiple burn experiments per day and scanning a large range of OH$_{\text{exp}}$ during each experiment thus allowing for investigation of OA enhancement and chemical evolution as a function of age for a range of biomass types. VOC mass spectral evolution results showed aromatics and terpenes decrease with increasing OH$_{\text{exp}}$, while formic acid and other unidentified compounds increase. Although VOC total signal decreased with OH$_{\text{exp}}$, some gas-phase oxidation products increased with aging. Further exploration of gas-phase SOA precursors and products from this study and future experiments is important for identifying these compounds and understanding mechanisms governing photochemical processing.

Aging of smoke in the reactor resulted in a wide range of OA mass enhancement, 0.6–2.3, spanning from net OA mass loss to substantial SOA production. On average, considerable SOA was produced from smoke aging, with an average enhancement factor of 1.42 ± 0.36. The variability in OA enhancement observed in this study is consistent with the literature from both field and laboratory studies of biomass-burning aging. OA mass losses are plausibly from heterogeneous oxidation and volatilization (Molina et al., 2004) or oxidation of gas-phase semivolatiles leading to fragmentation and evaporation of particle-phase species that were in equilibrium with the aerosol phase (Donahue et al., 2012; Lambe et al., 2012). The results indicate that fuels with higher POA emissions result in less relative OA enhancement from
photochemical aging. This study confirms that the net SOA to POA ratio of biomass burning emissions is far lower than that observed for urban emissions (DeCarlo et al., 2010; Hayes et al., In Press., 2013). This is thought to be due to the much higher organic ratio of urban emissions (Heald et al., 2008). Note that the ratio of net SOA to CO (often used to monitor the evolution of SOA in the field) is similar between both sources and can often be higher for biomass burning emissions (Cubison et al., 2011; Jolleys et al., 2012).

As $\text{OH}_{\text{exp}}$ was increased, most fuels showed maximum ER$_{\text{OA}}$ (deviation from 1) around three days of photochemical age ($\text{OH}_{\text{exp}} \sim 3.9 \times 10^{11}$ molecules cm$^{-3}$ s$^{-1}$), then leveling off and remaining constant even with increasing $\text{OH}_{\text{exp}}$. Since the VOCs measured with the PIT-MS do not correlate with the enhancement of OA, the formation of net SOA suggests the importance of primary intermediate volatility and semivolatile gases as SOA precursors. Calculations suggest that while heterogeneous processes can be important in conditions where gas-phase oxidation cannot occur, that gas-phase oxidation will be more effective most of the time (Donahue et al., 2012).

Independent of net OA mass increase or decrease, some consistent chemical transformations were observed from aging in every burn experiment. $m/z$ 28 and 44 are always enhanced ($\text{CO}^+$ and $\text{CO}_2^+$ increase), even in fuels that undergo a net mass decrease from aging (ER$_{\text{OA}} < 1$). The rate at which $f_{44}$ changes (as the smoke from each of the fuels is oxidized) differs for each fuel and this rate appears to increase with initial $f_{44}$ of POA. $f_{60}$ either remains constant or significantly decreases with increased $\text{OH}_{\text{exp}}$ (always remaining elevated above 0.3%, background ambient biomass-burning-free levels).

For all experiments, POA O/C spanned 0.15-0.5, with aged OA O/C ratios enhanced up to 0.87, and the O/C of added mass (when there was net enhancement) ranged from 0.4-1.0. The
relationship of O/C with OH_{exp} for most aged smoke show similar increasing slope to alkane precursor SOA (Lambe et al., 2012). ER_{OA} and maximum O/C from aging correlates with degree of oxidation of POA; therefore, POA characteristics, both intrinsic, i.e. chemical composition, and extrinsic, i.e. correlation with POA concentration, appear to be important predictors of SOA formation from biomass-burning smoke. As OH_{exp} increases, H/C vs. O/C showed different slopes for different fuels, suggesting slightly different functionalization for each biomass. The net SOA added in this study falls within the ambient OOA window of Van Krevelen space (Ng et al., 2011a).

This study shows photochemical aging of smoke from biomass burning can account for a significant enhancement of initial emitted OA mass. These secondary processes, which include functionalization and fragmentation reactions, need to be included in climate and air quality models to improve our constraints on aerosol in climate, global OA budgets, as well as support air quality policy, forecasting, and mitigation in regions susceptible to wildfires or controlled burning.
SUPPLEMENTAL INFORMATION

Table S1. Standard AMS fragmentation table for unit mass resolution (UMR) analysis and updated table for calculating sulfate and organic mass fragments for biomass burning smoke measurements with high organic fraction of total aerosol mass.

**Standard Frag Table for Unit Mass Resolution AMS Analysis**

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_organic</th>
<th>frag_sulphate</th>
<th>frag_SO3</th>
<th>frag_H2SO4</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>0.5*frag_organic[62]</td>
<td>frag_SO3[48], frag_H2SO4[48]</td>
<td>48,-frag_organic[48], -frag_sulphate[48], 5.93<em>frag_H2SO4[81], 5.93</em>frag_H2SO4[98]</td>
<td></td>
</tr>
<tr>
<td>64</td>
<td>0.5<em>frag_organic[50], 0.5</em>frag_organic[78]</td>
<td>frag_SO3[64], frag_H2SO4[64]</td>
<td>64,-frag_organic[64], frag_H2SO4[64], 5.90<em>frag_H2SO4[81], 5.90</em>frag_H2SO4[98]</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>0.75*frag_organic[94]</td>
<td>frag_SO3[80], frag_H2SO4[80]</td>
<td>0.25<em>80,-0.25</em>frag_organic[80], 0.75<em>80,-0.75</em>frag_organic[80]</td>
<td></td>
</tr>
<tr>
<td>81</td>
<td>0.5<em>frag_organic[67], 0.5</em>frag_organic[95]</td>
<td>frag_H2SO4[81]</td>
<td>81,-frag_organic[81]</td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>0.5<em>frag_organic[84], 0.5</em>frag_organic[112]</td>
<td>frag_H2SO4[98]</td>
<td>98,-frag_organic[98]</td>
<td></td>
</tr>
</tbody>
</table>

**Updated Frag Table for Unit Mass Resolution AMS Analysis**

<table>
<thead>
<tr>
<th>m/z</th>
<th>frag_organic_BB</th>
<th>frag_sulphate_BB</th>
</tr>
</thead>
<tbody>
<tr>
<td>48</td>
<td>0.032<em>0.5</em>frag_organic_BB[17], 0.012<em>0.5</em>frag_organic_BB[49]</td>
<td>48,-frag_organic_BB[48]</td>
</tr>
<tr>
<td>64</td>
<td>64,-frag_sulphate_BB[64]</td>
<td>1.14*frag_sulphate_BB[48]</td>
</tr>
<tr>
<td>80</td>
<td>80,-frag_sulphate_BB[80]</td>
<td>0.32*frag_sulphate_BB[48]</td>
</tr>
<tr>
<td>81</td>
<td>81,-frag_sulphate_BB[81]</td>
<td>0.23*frag_sulphate_BB[48]</td>
</tr>
<tr>
<td>98</td>
<td>98,-frag_sulphate_BB[98]</td>
<td>0.124*frag_sulphate_BB[48]</td>
</tr>
</tbody>
</table>

Fig. S1. Photo of (a) Fire Sciences Laboratory’s (FSL) fire chamber in open/chamber burn configuration for burn 58, saw grass, taken by Dan Bon, (b) PAM reactor in open-flow-through configuration with both lamps on, taken by Amber Ortega.
Fig. S2. Sawtooth pattern from switching OA measurements (light lines) between aged (dashed lines) and unprocessed (solid lines) sampling for organic aerosol and aerosol markers: oxidation ($m/z$ 44, pink lines) and primary biomass burning ($m/z$ 60, brown lines) for two burns, turkey oak (burn 45) and ponderosa pine (burn 40). Tags indicate typical operations, such as changes in OH, filters, and sampling.

Discussion of Figure S3

The standard AMS fragmentation table is the foundation for calculating OA mass in ambient AMS measurements (Allan et al., 2004). Unlike typical ambient observations, OA dominated the total aerosol mass spectra (campaign averaged, OA was 93% of total aerosol). Hence, the standard fragmentation table needed to be adjusted to account for high organic-mass loadings (see Fig. S3). In this modification, sulfate was treated as interference on the organic peaks, as opposed to organic as an interference on the sulfate peaks, as in the default treatment of the “ambient” fragmentation table. To accomplish this, $m/z$ 48 was used as the basis for estimating the sulfate contribution. As seen in Fig. S3, the ratio of dominant ions at $m/z$ 48, $C_4^+$ and $SO^+$, were plotted as a function of OA mass to show that this ratio asymptotes to a constant value with increasing OA mass. See Table S1 for the modified fragmentation table.
Fig. S3. A procedure developed to correctly calculate sulfate and organic concentrations for biomass burning smoke. The top left plot is the ratio of C$_4$ to SO$^+$ at m/z 48 vs. unprocessed OA mass, colored by SO$^+$ ion signal for three fuels (ponderosa pine, burn 40; lodgepole pine burn 50; and turkey oak, burn 45). The rest of the plots compare standard fragmentation table calculations of sulfate to the updated biomass burning specific UMR fragmentations table (see Table S1) for burn 42, wire grass. The top right plot is a time series of sulfate from standard (labeled “Std Frag SQ”) and updated (labeled “BB Frag SQ”) calculations for UMR (red) and high-resolution (black) data. The bottom left plot is the mass spectra of sulfate from standard (labeled “Std Frag SQ”) and updated (labeled “BB Frag SQ”) calculations, and the bottom right plot is the sulfate mass spectra comparison of UMR (labeled “SQ”) and high-resolution (labeled “PK”) data for the standard (labeled “Std Frag SQ”) and updated (labeled “BB Frag SQ”).
Fig. S4. (a) Comparison of organic mass time series for all data from all burns of unit mass resolution to high-resolution analysis (as calculated up to m/z 100). (b) Cation balance with high-resolution data, measured to predicted cations K$^+$ and NH$_4^+$ based on neutral inorganic ion stoichiometry.

Fig. S5. Average difference (open-closed) high-resolution spectrum at m/z 28 averaged from 08:46:00–08:57:00 on 9/22/2009 during burn 42, wire grass for (a) aged and (b) unprocessed smoke. Note that the contribution of CO$^+$ from CO(g) is negligible due to the strong discrimination against gases (by $10^7$) by the AMS inlet.
Fig. S6. OH\textsubscript{exp} as calculated from offline SO\textsubscript{2} calibrations versus OH\textsubscript{exp} calculated from real-time VOC decays with all data in light circles and stable data in dark circles for benzene (red) and toluene (blue).

Fig. S7. Evolution of aerosol ions at m/z 28 and m/z 44 from high-resolution analysis for two biomass fuels, turkey oak (burn 45) and ponderosa pine (burn 40), normalized to peak CO\textsuperscript{+} and CO\textsubscript{2}\textsuperscript{+} concentration in each burn. The sawtooth pattern is the result of switching between aged and the unprocessed smoke sample.
Fig. S8. The mass spectra ratio, ER\textsubscript{OA}, of aged to unprocessed smoke of two fuels: turkey oak, burn 45, and ponderosa pine, burn 40, where an increase in ion signal is shown in green (ER\textsubscript{OA} > 1) and decrease in ion signal (ER\textsubscript{OA} < 1) is shown in red.

Fig. S9. Fractional contribution of oxidation and biomass burning tracers vs. POA concentration. (a) \(f_{44}\) vs. POA for unprocessed smoke from all burn experiments. (b) \(f_{60}\) vs. POA for unprocessed smoke from all burn experiments. (c) Aging effects on \(f_{\text{CO}_2^+}\) and biomass-burning marker, \(f_{60}\), for four select fuels (ponderosa pine, burn 40; wire grass, burn 42; turkey oak, burn 45; and sage, burn 49). Dotted lines are from ambient biomass burning measurements from Cubison et al. (2011).
Fig. S10. Van Krevelen diagram, showing hydrogen-to-carbon (H/C) ratio vs. oxygen-to-carbon ratio (O/C). (a) Six fuels (ponderosa pine, burn 40; pocosin, burn 41; wire grass, burn 42; turkey oak, burn 45; sage, burn 49; and lodgepole pine, burn 61), with associated slopes from a linear orthogonal distance regression fit. (b) All fuels, with associated slopes from a linear orthogonal distance regression fit reported in legend (lines not shown for simplicity), slopes from Heald et al. (2010; solid lines), ambient measurements of OOA data first presented in Ng et al. (2010) and transformed into Van Krevelen space in Ng et al. (2011)’s work (dashed lines) with shaded region (gray area) denoting ±10% uncertainty.

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REFERENCES


CHAPTER III

URBAN EMISSION STUDY

Real-time Measurements of Secondary Organic Aerosol Formation and Aging from Ambient Air in an Oxidation Flow Reactor in the Los Angeles Area

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\textsuperscript{^}now retired

Abstract

Field studies in polluted areas over the last decade have observed large formation of secondary organic aerosol (SOA) that is often poorly captured by models. The study of SOA formation using ambient data is often confounded by the effects of advection, vertical mixing, emissions, and variable degrees of photochemical aging. An Oxidation Flow Reactor (OFR) was deployed to study SOA formation in real-time during the CalNex campaign in Pasadena, CA, in 2010. A high-resolution aerosol mass spectrometer (AMS) and a scanning mobility particle sizer (SMPS) alternated sampling ambient and reactor-aged air. The reactor produced OH
concentrations up to 4 orders of magnitude higher than in ambient air, achieving equivalent atmospheric aging from hours up to several weeks in 3 minutes of processing. OH radical concentration was continuously stepped, obtaining measurements of real-time SOA formation and oxidation at multiple equivalent ages from 0.8 days–6.4 weeks of age. Enhancement of OA from aging showed a maximum net SOA production between 0.8–6 days of aging with net OA mass loss beyond 2 weeks. Reactor SOA mass peaked at night, in the absence of ambient photochemistry and correlated with trimethylbenzene concentrations. Reactor SOA formation was inversely correlated with ambient SOA and O₅, which along with the short-lived VOC correlation, indicates the importance of relatively reactive (τOH ~0.3 day) SOA precursors in the LA-Basin. Evolution of the elemental composition in the reactor was similar to trends observed in the atmosphere (O:C vs. H:C slope ~ -0.65). Oxidation state of carbon (OSc) in reactor SOA increased steeply with age and remained elevated (OSc ~2) at the highest photochemical ages probed. The ratio of OA in the reactor output to excess CO (ΔCO, ambient CO above regional background) vs. photochemical age is similar to previous studies at low to moderate ages and also extends to higher ages where OA loss dominates. The mass added at low-to-intermediate ages is due primarily to condensation of oxidized species, not heterogeneous oxidation. The OA decrease at high photochemical ages is dominated by heterogeneous oxidation followed by fragmentation/evaporation. A comparison of urban SOA formation in this study with a similar study of vehicle SOA in a tunnel supports the dominance of vehicle emissions in urban SOA. Pre-2007 SOA models underpredict SOA formation by an order of magnitude, while a more recent model performs better but overpredicts at higher ages. These results demonstrate the value of the reactor as a tool for in situ evaluation of the SOA formation potential and OA evolution from ambient air.
INTRODUCTION

Atmospheric aerosols are the most uncertain aspect of the climate radiative forcing (Myhre et al., 2013), and have negative impacts on human health (Pope et al., 2002) and visibility (Watson, 2002). Organic aerosol (OA) represents a large fraction of fine particle mass (Murphy et al., 2006; Zhang et al., 2007) and is the least-characterized component of submicron aerosol due to its complexity and wide variety of emission sources and atmospheric processes (Jimenez et al., 2009). OA can be emitted directly into the atmosphere from primary OA sources (POA), such as traffic or biomass burning, or formed through atmospheric processing as secondary OA (SOA). SOA can be formed when volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone and hydroxyl radicals (O3 and OH), to form less-volatile products that can partition into the aerosol phase (Pankow, 1994; Donahue et al., 2006), as well as through heterogeneous and multiphase processes (Ervens et al., 2011). An improved understanding of the sources, atmospheric processes, and chemical properties of SOA is necessary to constrain and predict current impacts on human health and climate as well as shifting impacts with changing climate and emissions (Hallquist et al., 2009).

SOA concentrations are typically underestimated by over an order of magnitude when pre-2007 models are applied in urban regions (Volkamer et al., 2006; de Gouw and Jimenez, 2009; Hodzic et al., 2010; Morino et al., 2014; Hayes et al., 2015). These “traditional” models treated SOA formation as partitioning of semivolatile products from gas-phase oxidation of VOCs, using aerosol yields and saturation concentrations from older environmental chamber studies. More recently updated models have incorporated (higher) SOA yields from VOCs from more recent chamber studies. Some studies have used artificially higher yields based on “aging” of the VOC products, although these are unconstrained by chamber studies (e.g. Tsimpidi et al., 2010), or
increased yields to account for losses of semivolatile gases to chamber walls (Zhang et al., 2014; Hayes et al., 2015). Donahue et al. (2006) developed the volatility basis set (VBS) formalism for modeling OA partitioning, in which organic species are distributed into volatility bins, which has been adopted by many SOA modeling schemes. Semi-volatile and intermediate volatility compounds (S/IVOCs) have been identified as additional precursors that were not considered in traditional models (Robinson et al., 2007). These updated approaches have been applied to several urban datasets leading to better closure between measured and modeled bulk OA, but have resulted in other problems such as several-fold overpredictions of SOA at long aging times (Dzepina et al., 2011; Hayes et al., 2015; Zhang et al., 2015) or SOA that is much too volatile compared to observations (Dzepina et al., 2011). These models remain under-constrained, and it is unclear whether the updated models increase predicted SOA formation for the right reasons. Targeted field studies in urban areas, with sufficient constraints and with novel approaches for focused investigation of SOA formation, are essential for continued model testing and improvement.

In order to characterize the SOA formation potential of urban emissions, an experimental technique is needed that is capable of rapid operation to allow examination of the variable potential of changing air masses. The “Potential Aerosol Mass” (PAM) oxidation flow reactor (OFR), was developed by Kang et al., (2007; 2011), and used in many laboratory experiments and recent field studies. It is a small flow reactor that exposes air samples to high oxidant levels (100-10,000 times atmospheric concentrations) with short residence time (<5 min). Recent work with the reactor has examined SOA yield, oxidation, and physicochemical changes using single precursors or simple mixtures in laboratory experiments, producing results similar to environmental chamber experiments (Massoli et al., 2010; Kang et al., 2011; Lambe et al., 2011a;
Lambe et al., 2011b; Bruns et al., 2015). SOA yields in the reactor are comparable or somewhat lower than for similar OH exposures in large environmental chambers, which has been suggested to be due to the short residence time of the reactor not being sufficient to allow complete condensation of semivolatiles (Lambe et al., 2015) or increased wall losses of gas-phase species due to the higher surface area to volume ratios of the reactor (Bruns et al., 2015). OH oxidation of alkane SOA precursors in the reactor show the effect of functionalization (oxygen addition) and fragmentation (carbon loss) reactions (Lambe et al., 2012). Recent reactor application to aging of biomass burning smoke showed that total OA after reactor oxidation was on average 1.42±0.36 times the initial primary OA (POA) with similar aging of biomass burning tracers to that observed in aircraft measurements (Cubison et al., 2011; Ortega et al., 2013). Aging measurements of vehicular exhaust using the reactor in a highway tunnel in Pittsburgh, PA indicated peak SOA production after 2.5 days of atmospheric equivalent photochemical aging (at OH = 3×10^6 molec cm^{-3}) and concluded the chemical evolution of the OA inside the reactor appears to be similar to that observed in the atmosphere (Tkacik et al., 2014). Other studies also show that the reactor produces SOA with characteristics similar to that formed in the atmosphere for crude oil evaporation (Bahreini et al., 2012a; Li et al., 2013). The radical chemistry in the reactor has been recently characterized (Li et al., 2015; Peng et al., 2015). Thus, the reactor is a useful tool for elucidating SOA formation processes under field conditions where utilizing large-scale environmental chambers is not practical and/or if a higher degree of aging is targeted.

Due to meteorological conditions (e.g. diurnal fluctuations in land-sea breeze patterns with weak synoptic forcing) and topography (e.g. the surrounding coastal mountain ranges) ventilation of air in the LA-Basin can be limited, historically resulting in high pollution levels. Several field campaigns have investigated SOA in the LA-Basin, including the 2005 Study of
Organic Aerosol at Riverside (SOAR; Docherty et al., 2011) and the 2009 Pasadena Aerosol Characterization Observatory (PACO; Hersey et al., 2011). These studies identified SOA as a major fraction of total OA in the LA Basin in the summer, consistent with findings in previous urban field campaigns (Volkamer et al., 2006; de Gouw and Jimenez, 2009). This situation is in contrast to previous studies in this region which reported that primary OA was higher than SOA, other than during severe photochemical smog episodes; however, these estimates were likely affected by apportionment biases or the greatly underestimated SOA production of traditional models (Docherty et al., 2008).

The 2010 California Research at the Nexus of Air Quality and Climate Change (CalNex) was a multiplatform large-scale field study, which utilized ground sites at Bakersfield and Pasadena, California, NOAA WP-3D and Twin Otter aircraft, and the research ship R/V Atlantis (Ryerson et al., 2013). In this study, we measured submicron aerosol size and composition alternately for ambient air and for ambient air that had been aged in an oxidation flow reactor by systematically changing the OH exposure. This work is compared to the previous literature but extends beyond it with the new information provided by the in situ aging studies. By combining results from the ambient aerosol and aged ambient aerosol measurements, we provide a stronger test of current SOA models.

EXPERIMENTAL METHODS

CalNex Field Campaign

The work in this study will focus on measurements from the Pasadena ground site during CalNex. The Pasadena site was located on the California Institute of Technology (Caltech) campus in Pasadena, CA (34.1406 N, 118.1225 W, 236 m above mean sea level); the location,
airmass transport, and key measurements have been described in detail previously (Washenfelder et al., 2011; Hayes et al., 2013). The measurement period for our reactor study is 29 May–10 June 2010, hereafter referred to as the “sampling period.” Meteorological conditions, including prevailing winds, boundary layer height, temperature, and relative humidity information are summarized by Washenfelder et al. (2011) and Hayes et al. (2013). An overview of the 2010 CalNex field campaign (Ryerson et al., 2013) and aerosol observations at the Pasadena Supersite (Hayes et al., 2013) can be found in previous publications. A gas-chromatography mass spectrometer (GC-MS) from NOAA was located at the same field site (Hayes et al., 2013; Warneke et al., 2013) and used for VOC measurements reported in this study. The NOAA WP-3D research aircraft sampled in situ meteorological, trace gas, and aerosol conditions aloft during CalNex (Bahreini et al., 2012b; Ryerson et al., 2013). Non-refractory submicron aerosol composition measurements aboard the NOAA WP-3D were made using an Aerodyne compact time-of-flight aerosol mass spectrometer (C-ToF-AMS, Drewnick et al., 2005). Details of operation, analysis, and quantification can be found in Bahreini et al. (2012b).

Oxidation Flow Reactor

To study SOA formation and OA aging in-situ, we deployed a Potential Aerosol Mass (PAM) oxidation flow reactor (Kang et al., 2007; Kang et al., 2011) at the Pasadena ground site. Fig. 1a shows a diagram of the operational setup. The reactor and ambient sample lines were located adjacent to one another, on the roof of the instrument trailer at 7.2 meters above ground (Fig. 1b). Ambient air was continuously sampled in an open flow-through configuration via a 14-cm diameter opening with coarse-grid mesh screen coated with an inert silicon coating (Sulfinert by SilcoTek, Bellefonte, PA). The mesh was designed to block debris and insects, as well as
break up large eddies while allowing VOCs and oxidized gases to be sampled efficiently. This

![Diagram of oxidation flow reactor](image)

Fig. 1. (a) Schematic of the oxidation flow reactor (OFR) coupled to an Aerodyne high-resolution time-of-flight aerosol mass spectrometer (AMS), scanning-mobility particle sizer (SMPS), and ozone (O$_3$) monitor. An ambient sampling line allowed for direct sampling of ambient air. Computer-controlled switching valves allowed for sampling in alternation from the reactor and ambient lines. Voltage supplied to UV lamps were varied via programmable computer control to step through oxidant concentrations in the reactor. Ring flow was via a PTFE Teflon line and was used for gas-phase measurements. Center flow was a copper line that continuously pulled the sample for aerosol analysis. (b) Photograph of the reactor with a sun / rain cover and of the ambient aerosol inlet (right, covered by foil insulation) on the trailer roof during CalNex.
configuration, with no inlet, was chosen because of the observation of reduced SOA formation when any inlet and/or an inlet plate was used in a previous experiment (Ortega et al., 2013). The reactor output was measured by an AMS (described below), a scanning-mobility particle sizer (SMPS, TSI Inc., Model 3936 with TSI 3010 CPC), and an O₃ monitor (2B Technologies, Model 205). Fast switching valves were used to automatically alternate AMS and SMPS sampling between the reactor and unperturbed ambient sample line every 5 minutes. Bypass lines were used to maintain constant flow in both the reactor and ambient sample lines while instrumentation was sampling the other channel, to avoid artifacts due to particle or gas losses or re-equilibration that could occur if flow had been stagnant in the lines or modulated in the reactor. To maintain plug-like flow characteristics in the reactor, output flow was sampled from both a central stainless steel 1/4-inch OD tube at 2.0 lpm for aerosol measurements and a 3/8-inch OD PTFE Teflon perforated ring with 14-cm diameter for gas-phase measurements at 2.4 lpm. This setup allowed continuous measurements of both photochemically-aged and ambient aerosol.

The total flow rate through the reactor was 4.4 lpm corresponding to a residence time of 3 min. The reactor was used to expose ambient air to high levels of OH and O₃, produced when UV light from two low-pressure mercury lamps (model no. 82-9304-03, BHK Inc., with discrete emission peaks at 254 nm and 185 nm) initiated O₂, H₂O and O₃ photochemistry. This mode of operation is referred to as OFR185 (Li et al., 2015). We use the term “aging” to refer to the combined effect of OH, O₃, and light exposure in the flow reactor, although reactions in the reactor are understood to be dominated by OH under typical operating conditions (Peng et al., 2015). The intensity of aging was continuously stepped by computer-controlled lamp power supplies (custom made transformers from BHK Inc., controlled via Labview using a National
Instruments analog output board NI USB-6501), resulting in systematic stepping of lamp input voltage from 50–110 VAC. This voltage stepping modulates the photon flux and consequently the OH concentrations in the reactor (Li et al., 2015).

Oxidant concentrations in the reactor were stepped in 20-minute intervals, through six levels (including lights off, i.e. no added oxidants) comprising a two-hour cycle (Fig. 2). Only data from the last five minutes of each 20-minute period are used, to avoid including reactor transient periods. As lamp intensity increased, O₃ and OH concentrations increased in the reactor, resultant OA concentrations were measured from the reactor after oxidant perturbation as seen in Fig. 2. To account for particle losses in the reactor, reactor AMS concentrations have been corrected by comparing particles measured through the ambient inlet (averaging two concurrent ambient measurements just before and after lights off measurement) to the levels during the last 5 minutes of each period with lights off. This correction is applied over the sample period, in a time varying way and accounting for variations in UV intensity, resulting in an average correction of +5.8%.

The OH exposure (OH$_{exp}$, OH concentration integrated over the reactor residence time) achieved in this study is primarily a function of lamp photon flux (at 185 and 254 nm), residence time, and ambient H$_2$O concentration and OH reactivity (Li et al., 2015; Peng et al., 2015). OH$_{exp}$ was estimated using a calibration equation developed by multivariate fitting of the output from a kinetic model of reactor (OFR185) operation, and verified against data from several field and laboratory experiments including CalNex (Li et al., 2015). The equation uses ambient H$_2$O concentration, reactor output O$_3$ concentrations, flow rate, and ambient OH reactivity from collocated measurements (data from the Stevens Group, Indiana University). According to this equation, internal OH$_{exp}$ in the reactor typically ranged from 1.1×10$^{11}$–5.8×10$^{12}$ molec. cm$^{-3}$ s,
0.8 days–6.4 weeks of photochemical age assuming 24-hr average ambient OH concentrations of 1.5×10^6 molec. cm⁻³ (Mao et al., 2009). “Total photochemical age” refers to the sum of ambient photochemical age and reactor internally-generated photochemical age, used throughout this work unless otherwise specified. Ambient photochemical age is calculated by the ratio of 1,2,4-trimethylbenzene to benzene (Borbon et al., 2013), using collocated gas-phase measurements as described in Hayes et al. (2013). Subsequent figures use total photochemical age in day-units applying the average OH concentration of 1.5×10^6 molec. cm⁻³. During CalNex, OH concentrations averaged up to 4×10^6 molec. cm⁻³ during the daytime, from concurrent OH reactivity estimates. Since a significant part of SOA formation happens during the first few hours after emission, the 0.8 equivalent day minimum photochemical age would correspond to ~0.3 days at the peak OH observed during CalNex.

![Graph](image)

Fig. 2. A typical oxidant cycle showing steps in lamp intensity in the reactor. Top: reactor oxidant concentrations. Bottom: OA concentration for ambient and reactor output sampling.
Particle Measurements

Particle concentration and composition were analyzed with a high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, abbreviated as AMS hereafter; Aerodyne Research, Billerica, MA; DeCarlo et al., 2006; Canagaratna et al., 2007). The ambient measurement setup, instrument intercomparisons, scientific results, and their interpretation are reported in Hayes et al. (2013). The high-resolution (HR) fragmentation table (Aiken et al., 2008) and peak fitting (DeCarlo et al., 2006) were applied to the reactor measurements with no additional adjustments beyond those performed for the ambient CalNex data by Hayes et al. (2013). The elemental analysis of OA (O:C, H:C) was performed using the “improved-ambient” method published by Canagaratna et al. (2015) for both reactor and ambient measurements, which increases O:C on average by 27% and H:C on average by 11% over the previous “Aiken ambient” method (Aiken et al., 2008). Details of the quantification of AMS reactor measurements (i.e. collection efficiency, inlet and particle lens losses) and intercomparison with the SMPS are discussed in supplementary Section S1 (Figs. S1-S5). Hayes et al. (2015) performed a modeling study comparing the ambient AMS OA measurements with several box and 3-D SOA models. Here, we only discuss the modifications in post-processing and data analysis necessitated by the alternating sampling of the reactor output.

Fate of Low-Volatility Organic Gases in the Reactor

As organic gases are oxidized, they can form lower vapor pressure products, low-volatility organic compounds (LVOC). Semivolatile organic compounds (SVOC) will also be formed, but we focus this discussion on LVOC for simplicity. In the atmosphere, the dominant fate of these LVOC is condensation on aerosols, as OH lifetimes and dry deposition time scales
are slower (Donahue et al., 2013; Knote et al., 2015). However, given the limited residence time, high surface/volume ratio, and the high oxidant concentrations in the OFR, other fates can be competitive. LVOC in the reactor can either condense on aerosols, be lost due to condensation on the reactor walls, react further with OH resulting in condensable or non-condensable products, or exit the reactor in the gas phase to condense on the sampling line walls. Aerosol sampling instruments only measure the LVOC that condense on aerosols in the reactor. Given the short residence time and high OH$_{\text{exp}}$ of the reactor, SOA formation could be underestimated due to these competing fates. To account for vapor losses, we follow the method detailed in Palm et al. (2015), using McMurry and Grosjean (1985) for wall loss estimation. The method of Pirjola et al. (1999) is used for estimating organic gas condensation to aerosols based on the measured SMPS size distributions with the Fuchs-Sutugin correction for gas diffusion in the transition regime (Seinfeld and Pandis, 1998). It is assumed that products after five oxidation steps with OH at $k_{\text{OH}} = 1 \times 10^{-11}$ molec cm$^{-3}$ s$^{-1}$ are lost (fragmented and too volatile to condense). This is used to simulate a typical C$_{10}$ VOC oxidation in the reactor. Parameters used include the measured surface-area-to-volume ratio (A/V) of the reactor (25 m$^{-1}$), a coefficient of eddy diffusion $k_e$ approximated as 0.0036 s$^{-1}$, and a diffusion coefficient $D = 4 \times 10^{-6}$ m$^2$ s$^{-1}$, corresponding approximately to the diffusivity of a molecule with a mass of 200 g mol$^{-1}$.

At OH$_{\text{exp}}$ lower than $1 \times 10^{12}$ molec. cm$^{-3}$ s ($\sim$ 10 days) the dominant LVOC fate is condensation to the aerosol (see Fig. S6). At higher OH$_{\text{exp}}$, the fate of organic gases is dominated by loss to reaction with OH rather than condensing on aerosol. LVOCs lost to the walls or exiting the reactor play only a small role under the conditions of this study, due to the relatively high ambient aerosol surface area. The amount of SOA formed in the reactor is corrected for the fraction of SOA that condense on the aerosol by fitting a line to the calculated fraction of
LVOCs that condense on aerosol and dividing the measured SOA formed in the reactor by the fitted fraction of LVOCs that were lost by condensation on the aerosol (Fig. S6). This correction is a minimum at low to moderate ages, and highest at longest ages where net OA production is lowest (Sect. 3.2). Thus, the maximum net SOA production was typically corrected by a factor of 1.2. At increasing ages, where OA loss due to heterogeneous oxidation begins to dominate over gas-phase oxidation, it becomes unfeasible to apply the correction, as the net OA enhancement in the reactor is negative. Thus, correction is applied when reactor-measured OA is greater than ambient OA (EROA>1, ΔOA Mass>0, Sect. 3.2).

RESULTS
Observations

The time series of the reactor sample period is shown in Fig. 3a. The ambient aerosol during the first third (30 May–3 June 2010) of the measurement period is characterized by OA dominance, while the remaining two-thirds of the period (3–11 June 2010) is characterized by high concentrations of OA and nitrate, moderate sulfate and ammonium, and low chloride, with a marked diurnal cycle. This second period was strongly affected by in-basin pollution and is the most useful in terms of studying urban SOA formation (Hayes et al., 2013).

A 24-hour snapshot of the time series of ambient and reactor data is shown in Fig. 3b. This period is representative of the diurnal profiles observed from 3–9 June 2010. The oscillations (zig-zag pattern) in reactor output concentrations are due to OHexp stepping as shown in Fig. 2. Day and night periods are highlighted to indicate the period of inactive (20:00–8:00) and active ambient photochemistry (8:00–20:00) in Fig. 3b. Ambient nitrate and ammonium concentrations peak in early morning hours before sunrise, while OA peaks in the late afternoon,
Fig. 3. (a) Time series of reactor and ambient species mass concentrations during the sampling period. (b) Zoom on the time series of the species mass concentrations for one representative day. Daytime and nighttime are marked. (c) Average fraction contribution from organic, nitrate, sulfate, ammonium, and chloride to total AMS aerosol measurements for ambient and reactor (excluding dark reactor, “lights off” periods).

during the most photochemically active part of the day. Hayes et al. (2013) attributes this organic aerosol temporal pattern to the formation of fresh urban SOA as the LA-plume undergoes ~0.3 days of photochemical aging during transport to our field location, which is considered a receptor site as it experienced a strong impact from aged urban emissions. However, OA enhancement in the reactor peaked during night, ~12 h before the ambient OA peak. The nighttime reactor-aged OA mass peaks at approximately the same concentration as the following day’s ambient OA concentration, suggesting the reactor’s potential for estimating the next day’s
OA concentrations. Daytime reactor-aged OA mass shows very limited enhancement above the ambient OA mass, indicating that the precursors for SOA formation have been mostly depleted in ambient air. At the peak of the ambient photochemical age during daytime, only small amounts of precursors are available to contribute to further SOA formation from oxidation in the reactor, likely due to previous removal by photochemical oxidation and condensation. Figure 3c shows the average speciated contribution to total aerosol for ambient and the reactor (excluding dark reactor periods, where $\text{OH}_{\text{exp}} = \text{ambient}$), indicating overall enhancement of all species from reactor aging with very similar composition to ambient aerosol.

Observations of the OA size distributions indicate reactor aging does not significantly shift the size of the accumulation mode for the average of nighttime ambient and three different reactor age ranges (age ~ ambient, 3.7 days, and 23.5 days), from 2–9 June 2010 (Fig. S7). The reactor size distribution changes in intensity and shape are most pronounced during low ages (~3.7 days and lower), with an enhanced smaller size mode ($d_{\text{ca}} \sim 80$ nm). While many daytime/nighttime average size distributions and age ranges were explored, only ages at or below a few days at nighttime showed significant enhancement of small particle sizes. Highest ages (>14 days) show overall decrease in concentration across all size bins with the size of the accumulation mode unchanged from ambient within the uncertainty of the measurement. Given the high concentrations of large particles in this urban environment, we expect aging to enhance organic aerosol by condensation of semi- and low-volatile compounds on existing particles to dominate over new particle formation and growth. Reactor results are indicative of this process, although they also indicate the effect of new particle formation and/or of nanoparticle growth at lower OH exposures.
Aerosol Enhancements

Investigating reactor perturbation of ambient OA allows quantification of both relative and absolute OA changes vs. $\text{OH}_{\text{exp}}$. The relative OA enhancement ratio, $\text{ER}_{\text{OA}} = \text{reactor OA} / \text{ambient OA}$, and the absolute OA enhancement factor, $\Delta \text{OA Mass} = \text{reactor OA} - \text{ambient OA}$, are plotted vs. $\text{OH}_{\text{exp}}$ in Fig. 4a and Fig. 4b respectively for the sample period. OA mass is enhanced up to four times from ambient OA, with the majority of maximum $\text{ER}_{\text{OA}}$ peaking around a factor of two increase. OA enhancement peaks and plateaus between 0.8–6 days of OH aging, then decreases at higher aging, eventually showing net OA loss beyond two weeks of aging. When separated into daytime and nighttime $\text{ER}_{\text{OA}}$ and $\Delta \text{OA Mass}$ (Fig. 4), the qualitative trends are the same in both cases, but OA was more enhanced from reactor aging during nighttime by 5 $\mu$g m$^{-3}$, or a factor of 1.7x of ambient. A smaller enhancement is observed during the day 2–3 $\mu$g m$^{-3}$, or a factor of 1.2x of ambient The data for greater than 2 weeks of aging closely overlaps for day and night, with a decrease up to 2.5 $\mu$g m$^{-3}$, or a factor of 0.5x of ambient.

Fig. 4: (a) Relative OA enhancement ($\text{ER}_{\text{OA}} = \text{reactor OA} / \text{ambient OA}$) vs. estimated reactor photochemical age for the sampling period. (b) Absolute OA mass concentration enhancement ($\Delta \text{OA Mass} = \text{reactor OA} - \text{ambient OA}$) versus photochemical age. The data has been averaged into 6% quantiles for day and night measurements, with vertical error bars indicating standard errors.
The substantial difference between day- and nighttime enhancements can be explained as during the night the boundary layer is shallow and reactive precursors accumulate due to the absence of ambient photochemistry, with lower ambient photochemical ages of ~0.1 day (Hayes et al., 2015) and minimal loss mechanisms as the dominant urban VOCs do not react with O₃ or NO₃ (other than a small concentration of monoterpenes). In contrast, during the day reactive precursors in ambient air are depleted due to reaction with OH. Transport times from downtown LA, the dominant precursor source region impacting Pasadena, is ~0.5 days, with ambient photochemical ages reaching ~0.3 days. Thus most of the SOA precursors that can become SOA already have by the time the air was sampled in Pasadena and only about 20% more SOA could be produced from the precursors that remained. The trends in Fig. 4 indicate increased oxidation transitioning from a dominance of functionalization reactions and condensation at low-to-moderate exposures, to fragmentation-dominated reactions and evaporation of reaction products at the highest photochemical ages. Fragmentation can occur in the gas phase by reactions of SVOCs with OH, leading to non-condensable products and decreasing SOA formation. Fragmentation can also be due to heterogeneous oxidation of existing OA, producing more volatile species that may evaporate leading to OA mass loss. Discussion of the relative importance of these processes for this study is presented in Section 4.4 below.

Gas-Phase Observations: Odd Oxygen (Oₓ) Relation to SOA Formation

The day-night difference observed in both EROA and ΔOA mass merits examination of the relationship with ambient odd-oxygen, Oₓ (O₃ + NO₂). Ambient Oₓ correlates with freshly produced SOA in urban areas (Herndon et al., 2008; Wood et al., 2010; Hayes et al., 2013; Morino et al., 2014; Zhang et al., 2015), both resulting from recent photochemistry. For the reactor, oxidants
Fig. 5. Reactor OA mass enhancement vs. ambient $O_x$ (odd oxygen: $O_3$+NO$_2$) for all data in ~3.7 and ~23.5 day reactor age ranges during the sample period, colored by nighttime and daytime. Average for 10% quantiles are shown for ~3.7 days and ~23.5 days of photochemical age.

are generated internally and are not dependent on ambient $O_x$. As seen in Fig. 5, there is a steep inverse relationship between $\Delta$OA mass and ambient $O_x$ at low to moderate aging (~<4 days). As daytime ambient photochemical production of oxidants increases ($O_x$ >50 ppbv), the reactor’s SOA formation for moderate aging decreases to a near constant OA mass enhancement (2 $\mu$g m$^{-3}$). At high ages (>14 days), OA mass loss is fairly constant with ambient $O_x$, which is not surprising since the mechanisms responsible for OA depletion at long ages have little dependence on previous photochemical processing in the atmosphere. These results further confirm that as the degree of ambient photochemical processing of the sampled air increases
(during daytime), SOA production in the reactor becomes more limited, likely due to the depletion of reactive SOA precursors in ambient air, consistent with the conclusions from Fig. 4.

Urban SOA Formation Timescales from VOC Observations

To further constrain the timescales and precursors of urban SOA formation, ambient and reactor OA data are plotted together with ambient VOCs in Fig. 6. The maximum reactor OA enhancement has a similar diurnal profile to 1,3,5-trimethylbenzene (TMB). Both TMB and OA enhancement have diurnal profiles that are out of phase with ambient SOA. In contrast, the concentration of benzene shows little correlation with reactor SOA formation in the reactor. The lifetime of TMB by reaction with OH is nearly 2 orders of magnitude shorter, $\tau_{OH} \approx 3$ hours, $k_{OH} = 5.67 \times 10^{-11}$, than benzene, $\tau_{OH} \approx 6$ days, $k_{OH} = 1.22 \times 10^{-12}$ (Atkinson et al., 2006). The anti-correlation of TMB and reactor enhancement in OA and ambient SOA concentrations suggests that only in the absence of ambient photochemistry, substantial amounts of short-lived SOA precursors are present to produce most of the SOA formed in the reactor. Toluene, a VOC with a lifetime of 1.4 days and $k_{OH} = 5.63 \times 10^{-12}$ cm$^3$ molecule$^{-1}$s$^{-1}$ does not have the same diurnal structure as reactor OA and TMB (Fig. S8). The shape of the diurnal-scale time series in Fig. 6 and S8 can be explained as the sunrises ambient photochemistry begins at sunrise, very short lived precursors, such as TMB, begin decay rapidly due to gas-phase oxidation as well as boundary layer growth. As these gas-phase oxidation products condense, SOA forms and ambient OA reaches its daytime peak. At the daytime ambient OA peak, most of these short-lived precursors have been consumed, thus the reactor only forms an additional 1–2 $\mu$g m$^{-3}$ of SOA as opposed to the greater than 10 $\mu$g m$^{-3}$ possible when theses precursors are allowed to build in a shallow boundary layer and in the absence of photochemical sinks. Note that in the
afternoon the boundary layer is significantly deeper than at night, and thus the total afternoon SOA formation potential may not be that different than at night, even though the potential per unit volume of air is much smaller.

Fig. 6. Times series of benzene, 1,3,5-trimethylbenzene, ambient total oxygenated organic aerosol (OOA), reactor organic mass enhancement, and maximum reactor organic mass enhancement. Inset is a scatter plot of maximum reactor OA mass enhancement (for each OH$_{exp}$ cycle) vs. ambient 1,3,5-trimethylbenzene, with a linear ODR regression fit.

The inset in Fig. 6 is a scatter plot of maximum reactor SOA formation (per OH$_{exp}$ cycle) vs. TMB (slope $\sim$52, $R^2$=0.7). TMB’s SOA yield is on the order of 10% (Cao and Jang, 2007). Thus its concentration is insufficient to explain reactor SOA formation by a factor of $\sim$500, though it is not expected to be the sole SOA precursor. This correlation suggests species with a similar source footprint and lifetime as TMB produce most of the urban SOA. Such species
likely include semivolatile and intermediate volatility precursors (S/IVOC) that are rarely measured in ambient air (Dzepina et al., 2009; Zhao et al., 2014; Hayes et al., 2015). A comparison of observed reactor SOA formation with a model that uses all the measured VOCs is discussed in section 4.3 below.

OA Chemical Composition and Evolution with Aging

The evolution of OA chemical composition upon aging has been the subject of several studies, both for ambient (Heald et al., 2010; Ng et al., 2010; Kroll et al., 2011; Ng et al., 2011a) and reactor conditions (Kang et al., 2011; Ortega et al., 2013; Tkacik et al., 2014; Lambe et al., 2015). This evolution results in characteristic trends in specific diagrams: AMS fragments $f_{44}$ vs. $f_{43}$, and H:C vs. O:C. Both diagrams are shown for the CalNex ambient and reactor data in Fig. 7. $f_{44}$ is a tracer for aged OA (mostly CO$_2^+$), while $f_{43}$ (mostly C$_2$H$_3$O$,^+$ due to non-acid oxygenates, with some contribution from C$_3$H$_7$)$^+$ is a tracer of POA and freshly formed SOA (Ng et al., 2011a). In Figure 7a, ambient and reactor data evolve consistently and move up and to the left with aging, consistent with previous ambient field observations from multiple field campaigns (Ng et al 2010). As expected, reactor data with the highest age has the highest $f_{44}$. Positive Matrix Factorization (PMF) factors from Hayes et al. (2013) lay within ambient observations and data for lower OH$_{exp}$ in the reactor. Reactor data stays within the boundary of flow reactor results from Lambe et al. (2011a) and below the location of oxalic acid, as expected.

The Van Krevelen diagram (H:C vs. O:C) is shown in Fig. 7b and demonstrates results that are very consistent to those of the previous plot. The reactor data follows a similar trend to ambient data, with slopes of -0.64 and -0.68, respectively. A slope between -1 and -0.5 is consistent with the addition of acid and alcohol functional groups without fragmentation or the addition of acid groups with carbon–carbon bond breakage (Ng et al., 2011b). The consistency of
ambient and reactor OA aging suggest that the reactor produces similar SOA composition upon aging to that in the atmosphere within the LA-Basin.

Fig. 7. (a) Fractional contribution of m/z 44 ($f_{44}$) vs. m/z 43 ($f_{43}$) to OA for the ambient and reactor data in this work. The region of ambient observations from Ng et al. (2010), and for reactor laboratory observations and oxalic acid from Lambe et al. (2011a) are shown. (b) Van Krevelen diagram for ambient and reactor measurements for the sampling period. Functionalization slopes from Heald et al. (2010), and oxidation state from Kroll et al. (2011) are shown for reference. Elemental analysis has been calculated with the Improved-Ambient method from Canagaratna et al. (2015). Reactor measurements are colored by total photochemical age in days (at OH = $1.5 \times 10^6$ molec. cm$^{-3}$) and ambient PMF-derived HOA, SV- and LV-OOA factors are shown from Hayes et al. (2013).

Reactor O:C ratios increase with age and span a wider range than ambient observations (O:C up to 1.4). While O:C (and $f_{44}$) continually increased with additional OH$_{exp}$, peak reactor OA enhancement is observed at intermediate exposures and O:C ratios (0.8–6 days and O:C ~1.10–1.25), as seen in Fig. 8a. OA mass loss, i.e. ER$_{OA} < 1$, is observed together with the highest O:C ratios at the highest ages, which suggests OA fragmentation by heterogeneous oxidation results in the highest oxygen content remaining in the aerosol. With increasing age, H:C decreases continuously with OH$_{exp}$ (Fig. 8b), with H:C ~1.00–1.15 for the periods of maximum reactor OA enhancement. A qualitatively similar trend is observed in the reactor studies of Lambe et al. (2012) for SOA from OH oxidation of alkane precursors (Fig. 8a)
although starting with lower O:C and with a steeper slope at higher ages, and also by Ortega et al. (2013) for aging of biomass burning smoke.

Fig. 8. (a) Oxygen-to-carbon (O:C) and (b) hydrogen-to-carbon (H:C) elemental ratios for OA mass measured from the reactor vs. total photochemical age in days (at OH = 1.5×10^6 molec. cm^-3). Results using similar reactors for alkane oxidation from Lambe et al. (2012), and for aging of biomass burning smoke (Ortega et al., 2013) are also shown. (c) Average oxidation state (OSC= 2O:C – H:C) vs. OHexp. Data are colored by the relative organic enhancement (EROA = reactor OA / ambient OA).
Average carbon oxidation state (OS$_C$) has been proposed as a metric to characterize the formation and evolution of OA (Kroll et al., 2011). OS$_C$ can be approximated as $\sim 2 \times$O:C–H:C. Figure 8c shows OS$_C$ vs. photochemical age for ambient and reactor data. While ambient OS$_C$ is within the range of previous observed urban/anthropogenic OA, reactor OS$_C$ extends this significantly up to +2.0, consistent with ambient low-volatility OA observations up to +1.9 (Kroll et al., 2011). At the same OH exposure, higher OS$_C$ is observed for conditions of high reactor SOA production at intermediate ages. The highest values of OS$_C$ are observed for the highest ages, where heterogeneous oxidation leading to OA mass loss dominates. This indicates that heterogeneous oxidation adds substantial oxygen and reduces hydrogen from molecules to the particles to increase OS$_C$ despite overall mass loss.

DISCUSSION

Evolution of Net Urban OA with Photochemical Age

The identity of the SOA precursors responsible for urban SOA formation remains unclear. Combustion emissions such as those from vehicles are thought to be a major source of urban SOA (e.g. Hayes et al., 2015), and urban non-combustion sources of SOA precursors, if important, are finely spatially intermingled with combustion sources. CO is often used as a tracer of the initial concentration of urban SOA precursors in an airmass and thus allow an implicit correction for dilution occurring in parallel with aging. For this reason, the ratio of OA to CO concentration (above background level) vs. photochemical age is often used to investigate the evolution of urban SOA (de Gouw et al., 2005; DeCarlo et al., 2010).
Fig. 9. Ratio of OA to excess carbon monoxide (above background levels) vs. total photochemical age in days (at OH = $1.5 \times 10^6$ molec. cm$^{-3}$) for ambient and reactor data. Also shown is the value for LA Basin outflow from aircraft measurements from the NOAA WP-3D during CalNex (Bahreini et al., 2012b). See Hayes et al. (2013) for a discussion of the determination of CO background levels. Averages for quantiles of ambient (7%), reactor (7%), reactor dark (25%, internal OH$_{exp}$ = 0) and reactor vapor loss-corrected (12%) data are shown. A fit to reactor data is also shown (see text for details). Results from field studies in the northeastern US and Mexico City are shown in the background (DeCarlo et al., 2010).

Fig. 9 shows the results of this analysis for our reactor and ambient measurements.

Background CO during CalNex-LA is on average ~105 ppb (ranging from 85—125 ppb, Hayes et al., 2013). A range of ± 20 ppb uncertainty in background CO, results in an average ± 6 μg m$^{-3}$ ppm$^{-1}$ uncertainty in OA/ΔCO. Ambient photochemical age is calculated from the VOC ratio method as in Hayes et al. (2013). Reactor total photochemical age is the sum of ambient photochemical age (of the air ingested into the reactor at each time) and reactor age. The range observed in previous field campaigns in the Northeastern US and Mexico City are shown for
LA Basin outflow data are also shown, from aircraft measurements aboard the NOAA WP-3D during CalNex (Bahreini et al., 2012b), averaged for 1–2 days of photochemical age, falling in the middle of the range of previous ambient observations.

Fig. 9 shows the data averages for 7% quantiles of total photochemical age, to better illustrate the average trends of the observations without the higher noise level of 2.5 min. measurements. All data points for the sample period are shown for ambient and reactor measurements in Fig. S9a for reference. An increase in OA/ΔCO with aging is observed for ambient and reactor dark data (where reactor age = ambient photochemical age in the absence of internal reactor OH\textsubscript{exp}), consistent with previous studies and as discussed in Hayes et al. (2013; 2015). Reactor data are shown without and with the vapor loss-correction applied (see Sect. 2.3). The reactor data is consistent with SOA formation being dominated by shorter-lived precursors, as little increase in OA/ΔCO is observed after about a day of total age, consistent with the SIMPLE parameterization of urban SOA (Hodzic and Jimenez, 2011; Hayes et al., 2015).

To further illustrate the lifetimes of important urban SOA precursors, OH-decay curves of gas-phase benzene, toluene, and 1,3,5-trimethylbenzene (TMB) are overlaid in Fig. S9a with data from Fig. 9. The timescale of SOA formation is in between those of TMB and toluene decays, mostly shorter than toluene decay and definitely shorter than benzene decay, again consistent with the previous discussion.

We note that in Fig. 9 aging of CO (decay of CO from reacting with OH in the reactor or atmosphere) was not included in the evolution of OA/ΔCO analysis, as the purpose of ΔCO is to serve as an inert tracer of the urban SOA precursors emitted into each airmass. However, when comparing with aged pollution observed in the field after e.g. a week of transport, the aging to the urban CO needs to be taken into account. This is shown in Fig. S9b, and indicates that
ambient observations of very aged pollution would not show a decrease in OA/ΔCO due to photochemistry since the decreases in OA and CO at long photochemical ages have similar timescales. We note that a decrease in the OA/ΔCO ratio for ambient aged pollution may still be observed for other reasons such as wet deposition (Dunlea et al., 2009). Production of CO from urban VOCs is expected to be less than 1/10 of the directly emitted CO (Hallquist et al., 2009) and is neglected here.

Fit to the Observed Ambient and Reactor Evolution

The evolution of urban SOA vs. photochemical age follows a similar trend in different field studies with a rapid increase in the first day followed by a plateau at longer ages. Previously, this evolution has been fit with the SIMPLE parameterization, a 2-parameter model in which a single VOC precursor (VOC*) is oxidized with a single rate constant with OH to produce non-volatile SOA. This parameterization has been shown to fit ambient data as well or better than more complex models (Hodzic and Jimenez, 2011; Hayes et al., 2015). However, the evolution past the initial ~2 days is almost completely unconstrained by ambient observations, due to the difficulty of identifying urban pollution-dominated air masses after advection for several days, and of determining ΔCO when it is of the order of the uncertainties in the CO background. The reactor data from our study offer a unique opportunity to extend the model fit to much longer photochemical ages. The fit in Eqn. 1 was modified from Hayes et al. (2015)’s 2-parameter model for this purpose, where (POA+BGSOA)/CO is the primary OA plus background SOA, constrained at 16 μg m⁻³ ppm⁻¹ (Hayes et al., 2015), VOC*/CO is the VOC* emission ratio, and t is photochemical age, using measurements at local temperature and pressure.
\[
\frac{OA}{\Delta CO} = \left( \frac{POA + BGSOA}{CO} + \frac{VOC^*}{CO} \left[ 1 - e^{-\left( \frac{t}{\tau_1} \right)} \right] e^{-\left( \frac{t}{\tau_2} \right)} \right)
\]  

(1)

Fitting the reactor data in this way requires the addition of a 2nd timescale to account for loss of OA at long ages, as done in Eqn. 1. Fitting all ambient plus vapor loss-corrected data results in \(\text{VOC}^*/\text{CO} = 56\pm5 \ \mu\text{g m}^{-3} \ \text{ppm}^{-1}, \ \tau_1 = 0.3\pm0.1 \ \text{days}, \ \text{and} \ \tau_2 = 50\pm10 \ \text{days} \) (Fig. 9, all data points, i.e. before averaged into quantiles is in Fig. S9a). In this parameterization, \(\tau_1\) is the timescale for urban SOA formation and \(\tau_2\) is the timescale for net OA mass loss due to fragmentation, likely dominated by heterogeneous oxidation.

Comparison of Reactor output to Urban SOA Model Results

It is of interest to compare the SOA formation constrained from our reactor and ambient data to SOA models used in 3D modeling studies, as those models remain poorly constrained (e.g. Hayes et al., 2015). Here we used two of the model variants recently described in Hayes et al. (2015), and compare to our data in Fig. 10. The first model variant is a “traditional model” with SOA formation from VOCs using pre-2007 yields (Koo et al., 2003), which has been shown before to underpredict urban SOA formation by over an order-of-magnitude (Dzepina et al., 2009; Morino et al., 2014; Hayes et al., 2015). This comparison is still of interest as several SOA models still use this approach (e.g. Morino et al., 2014; Baker et al., 2015; Hayes et al., 2015).

The second model variant represents SOA formation from VOCs and primary semivolatile and intermediate volatility precursors (P-S/IVOC; Robinson et al., 2007), and has been shown to predict SOA formation adequately at short timescales (<1 day) but to overpredict at long ages (Dzepina et al., 2011; Hayes et al., 2015). SOA formation from VOCs uses the Tsimpidi et al. (2010) formulation, including “aging” of the SOA, and using the high NOx yields since the observed SOA formation mostly occurs in the urban environment where RO2 react mainly with NO (Hayes...
et al., 2015). SOA from P-S/IVOCs is represented using the Robinson et al. (2007) parameterization. Recent results suggest that P-S/IVOC are needed to explain SOA formation observed in ambient air during CalNex (Zhao et al., 2014; Hayes et al., 2015), consistent with other locations (Dzepina et al., 2009; Hodzic et al., 2010).

![Diagram](image.png)

Fig. 10. Comparison of reactor data with model results for evolution of OA/ΔCO vs. total photochemical age in days (at OH = 1.5×10^6 molec. cm^-3) with (a) traditional SOA formation model, high NOx, Robinson + Tsimpidi model from Hayes et al. (2014). Also shown is the summary of urban aged ratios from de Gouw and Jimenez (2009). (b) High NOx, Robinson + Tsimpidi model from Hayes et al. (2015) run with one-half IVOCs per the results of Zhao et al. (2014). (POA+BGSOA)/ΔCO is 21 μg m^-3 ppm^-1, which somewhat is higher than the value of 16 μg m^-3 ppm^-1 previously reported by Hayes et al. (2013). This difference is due to the different methods used to estimate the background SOA. Briefly, in this work as well as in Hayes et al. (2015), the background SOA is estimated to be equal to the minimum low-volatility oxygenated organic aerosol (LV-OOA) concentration in the diurnal cycle. Whereas in Hayes et al. (2013), the background SOA was estimated to be equal to the mean LV-OOA concentration for photochemical ages less than 1.2 h.
Figure 10a shows the comparison of the SOA models against our ambient and reactor results. The traditional model predicts SOA a factor of 10 lower than our observations, consistent with previous studies. The updated model performance is mixed: the magnitude of SOA formation at short times (<1 day) is somewhat slower but similar to the ambient data. SOA formation at long ages (>1 day) is significantly overpredicted by a factor of ~3. This model does not include heterogeneous oxidation reactions leading to fragmentation which could decrease predicted OA at high photochemical ages, resulting in a wider discrepancy at very long ages (>10 days). Figure 10b shows the same comparison using lower IVOCs as suggested from field measurements (Zhao et al., 2014). The same model was used, but with the initial concentrations of primary IVOCs decreased by one-half to better match the ambient observations of Zhao et al. (2014), as described by Hayes et al. (2015). Decreasing IVOCs brings down overall SOA predictions, increasing the discrepancy at shorter ages and still overestimating SOA concentrations compared to reactor measurements at the longest ages. This result suggests that the reduced IVOC concentrations cannot account for all model discrepancies. It is of interest to compare the reactor results with those of other SOA mechanisms in the future.

Evolution at High Photochemical Ages

The photochemical evolution of OA at long ages is of high interest as it partially controls the background of OA at remote locations where it may influence climate more strongly, due to the higher sensitivity of clouds to aerosols at low aerosol concentrations (Reutter et al., 2009). Heald et al. (2011) noted that a process that consumed OA with a timescale of ~10 days was needed in order to avoid overpredictions of OA in remote air. Heterogeneous oxidation is thought to play an important role for long photochemical ages, while being too slow to compete
at timescales of a day or so (DeCarlo et al., 2008; George and Abbatt, 2010). Fig. 11a compares our CalNex results to heterogeneous OH oxidation of ambient air from George and Abbatt (2010) using a similar oxidation flow reactor (TPOT), but with gas-phase SOA precursors removed by a denuder. Note that no SOA formation is observed for the George and Abbatt case due to the use of a denuder, and thus only the data for ER_{OA} < 1 can be approximately compared. The two datasets show a similar trend with the start of a net decrease around 2 weeks of oxidation and a similar evolution. A decrease in SOA yields at high ages (>7 days) was also observed by Lambe et al. (2012), in experiments where SOA was formed from gaseous precursors. However it is likely that the decrease in that study is dominated by gas-phase fragmentation of condensable species leading to lack of SOA formation, rather than by SOA formation followed by its heterogeneous oxidation (e.g. Fig. S6).

To evaluate directly whether heterogeneous oxidation could explain the gain of oxygen observed in the aerosol, we follow the method outlined in appendix A of DeCarlo et al. (2008). Fig. S10 shows an estimate of the total number of OH collisions with OA in the reactor vs. total photochemical age. Heterogeneous oxidation calculations use volume equivalent diameter (d_{ve}) of 285 nm as calculated using the peak of the mass distribution and estimated particle density from AMS components, assume every collision results in reaction (\gamma = 1). The measured net oxygen added (\Delta \text{Oxygen in OA} = O_{\text{atoms,reactor}} - O_{\text{atoms,ambient}}) vs. OH_{\text{exp}} is also shown. If it is assumed that each OH collision with OA results in one O atom addition, the number of O atoms added is underpredicted by a factor of 10 at ages ~ 1 day, decreasing to a factor of 2 at ~10 days, and lower values at high ages (>10 days). This analysis supports that heterogeneous oxidation is not dominant in forming SOA at low-to-intermediate ages, but it likely plays a role in OA evolution at the highest photochemical ages in the reactor.
An alternative explanation for the loss of OA at high photochemical ages is that the reaction of semivolatile gas species with OH (leading to fragmentation and thus non-condensing species) can lead to OA evaporation as the semivolatile species in the particles evaporate to re-establish equilibrium partitioning. However, most of OA has too low volatility to evaporate in response to the removal of semivolatile species from the gas phase. Fig. S11 shows the volatility distribution estimated for CalNex OA using concurrent thermal denuder measurements (Huffman et al., 2008; Faulhaber et al., 2009). As observed in other locations (Cappa and Jimenez, 2010), only ~20% of the OA is susceptible of evaporation upon removal of the gas phase. Losing ~60% of the OA would be the equivalent of heating to 100°C in a thermal denuder. Thus, there is not enough semivolatile material available to account for that degree of loss observed in our reactor measurements. We note that some models predict SOA that is too volatile (Dzepina et al., 2009), and if applied in a flow reactor context they may wrongly predict a large effect from semivolatile evaporation. Additionally, timescales for ambient OA evaporation upon removal of gas-phase organics from field measurements has been shown to be slow and size dependent, with fast evaporation up to only ~20% of OA mass happening on the order of ~100 min, followed by much slower evaporation of the order of days (Vaden et al., 2011). Given the short residence time utilized in the reactor during this study (< 5 minutes), there is not significant time to allow for substantial repartitioning of OA in equilibrium with semivolatile gas-phase organics.
Fig. 11. (a) Relative organic aerosol enhancement ($ER_{OA}$) from all reactor data in this study (including 6% quantiles) and from a heterogeneous oxidation study (George and Abbatt, 2010) plotted vs. total photochemical age in days (at $OH = 1.5 \times 10^6$ molec. cm$^{-3}$). (b) $SOA/\Delta CO$ vs. photochemical age for our study and for aging of vehicle exhaust with a similar reactor at a tunnel near Pittsburgh, PA (Tkacik et al., 2014). Results from field studies in the northeastern US and Mexico City are shown in the background (DeCarlo et al., 2010).
Comparison to a recent Reactor Study in a Tunnel

It is of interest to compare the evolution of urban SOA vs. photochemical age determined in this work with a recently published study with a similar flow reactor in a vehicle tunnel in Pittsburgh, PA (Tkacik et al., 2014). Whether urban SOA is formed predominantly from vehicle emissions has been the subject of recent debate (Ensberg et al., 2014). The data are compared in Fig. 11b as SOA/ΔCO, where ambient POA and background OA have been subtracted from our reactor data to compare to Tkacik et al. (2014)’s SOA-only measurement. Since the tunnel data has not been corrected for vapor losses in the reactor, we only show uncorrected CalNex reactor data for this comparison.

The tunnel experiment shows qualitatively similar results, with an initial increase to a peak of the same order, followed by a decrease in SOA/ΔCO at high ages. The initial SOA rise and peak occur at higher OH$_{exp}$ than observed in CalNex ambient data and in previous ambient urban studies, as well as our flow reactor data. The difference at low ages between the tunnel and the other studies may be due to several reasons:

1) Possible OH$_{exp}$ overestimation in the tunnel study. OH$_{exp}$ in flow reactors can be reduced by 1-2 orders of magnitude by high levels of OH reactivity from high concentrations of very fresh emissions, such as those present in the tunnel environment (Li et al., 2015; Peng et al., 2015). OH$_{exp}$ was corrected for OH suppression in the tunnel study using laboratory experiments with NO levels similar to the tunnel. However, the OH reactivity of NO$_x$ is expected to decay much faster than that of VOCs and their reaction products. Thus the OH suppression in the tunnel study was likely underestimated (Peng et al., 2015) as OH suppression from VOCs was not considered. Since OH suppression is largest at low OH$_{exp}$ that effect may account for the
deviation observed at low ages while having a much smaller effect on the tunnel data at high ages.

(2) There may be substantial losses of semivolatiles in the inlet of the tunnel study. In contrast, our flow reactor was operated without an inlet to minimize the loss of semivolatiles, based on an observation in a previous study of a substantial reduction in SOA formation when any inlet or an inlet plate was used (Ortega et al., 2013). Since semivolatile primary species are larger molecules with faster OH rate constants (Ziemann and Atkinson, 2012), that could explain the lack of SOA formation at ages below a day, compared to the large amount of SOA formed for those ages in the ambient CalNex observations (Hayes et al., 2013; 2015). However the fact that the magnitude of eventual SOA formation is larger in the tunnel study argues against this possibility. Thus it is most likely that the observed difference between the tunnel and our study is due to overestimation of OH$_{\text{exp}}$ at lower ages in the tunnel study.

A recent study examining the ambient SOA results from CalNex concluded that either vehicle emissions are not the dominant source of SOA in the LA Basin, or that the ambient SOA mass yields are much larger than what has been derived experimentally (Ensberg et al., 2014). Given the similar magnitude of SOA formation in the tunnel vs. ambient data and the fact that most urban CO arises from motor vehicles, as well as the likely overestimation of OH$_{\text{exp}}$ at low ages in the tunnel study, the combination of both studies strongly suggests that motor vehicles are the dominant source of urban SOA, and that the SOA yields from vehicle emissions are much larger than estimated from measured VOCs as by Ensberg et al. (2014). The contribution of typically unmeasured S/IVOCs to SOA may explain the missing vehicle SOA, as discussed in section 4.3.
SUMMARY AND CONCLUSIONS

Real-time measurement of SOA formation and OA aging was carried out with a photochemical oxidation flow reactor coupled to an AMS and SMPS during the CalNex field campaign and targeted urban emissions. This work represents the first applications of an oxidation flow reactor to ambient urban air, to our knowledge. Continuous ambient air sampling through the reactor provides complementary information to the analysis of ambient data at the site, and provides constraints on the evolution of urban SOA at long ages that are very difficult to observe with ambient measurements. Additionally, these uninterrupted reactor measurements over a two-week period allowed for observations over a prolonged period of stagnant air accumulating urban emissions.

OA enhancement peaked between 0.8–6 days of atmospheric equivalent aging ($\text{OH}_{\text{exp}} = 1.0–5.2 \times 10^{11}$ molec. cm$^{-3}$ s). Reactor OA mass showed net destruction decreasing below ambient concentrations after two weeks of atmospheric equivalent aging ($\text{OH}_{\text{exp}}$ above $2 \times 10^{12}$ molec. cm$^{-3}$ s) suggesting a shift from chemistry dominated by functionalization/condensation to one dominated by heterogeneous oxidation leading to fragmentation/evaporation, but with functionalization still occurring. Comparison to reactor experiments of heterogeneous oxidation of ambient air shows similar trends to those observed for high ages in this study. High OA enhancement was observed at night ($\text{ER}_{\text{OA}} \sim 2$, delta OA $\sim 5\mu$g/m$^3$) with reactor-aged OA mass peaking at concentrations similar to peak daytime ambient OA mass. Reactor-derived OA mass enhancement correlates with 1,3,5-trimethylbenzene, and has an inverse relationship with $O_x$ and ambient OOA, suggesting that short-lived precursors ($\tau_{OH} \sim$ few hours) dominate SOA formation in the LA-Basin.
The chemical evolution of OA in the reactor was examined with a Van Krevelen diagram (H:C vs. O:C). Reactor-aged OA produces a similar slope (~0.65) to that observed in ambient OA, thus is consistent with the reactor producing similar functionalization to ambient oxidation. While total OA mass was observed to decrease at very high OH exposures, O:C continued to increase. Oxidation state of carbon peaked at high values (OS_{C}~2 at highest OH_{exp}), similar to ambient observations of low volatility OA.

Modeling results indicate predicted maximum SOA from traditional models is a factor of 10 less than the maximum OA mass enhancement observed from aging ambient air in the reactor, consistent with previous comparisons using ambient data. Updated VBS-based models including both VOC and S/IVOC overpredict SOA formation by a factor of 2–3 at intermediate to high ages. If the IVOC emissions are reduced by a factor of 2 in the updated model to fit recent CalNex observations, the discrepancy between model and observation is reduced but these models cannot capture the reduction of SOA mass concentration that is observed with the OFR at longer OH exposures.

Evolution of the ratio of OA/ΔCO vs. photochemical age shows the reactor produces results consistent with the ambient data. At ages beyond those reliably observed for ambient OA, the reactor observations show a leveling and then decrease in OA/ΔCO. A fit of this data results in a timescale of SOA formation ~0.3 days and fragmentation-dominated heterogeneous oxidation and net mass loss with a timescale of ~50 days. The fit derived in this work may be useful in future studies, e.g. as a check on proposed model-parameterizations of urban SOA formation. Comparison to a similar reactor experiment aging vehicular emissions in a tunnel shows consistent results with our study, especially if a likely overestimation of OH_{exp} at low ages in the tunnel is taken into account. The combination of both studies strongly suggests that vehicle
emissions do dominate urban SOA formation and their SOA formation potential is higher than when only VOCs are considered.

This study shows that oxidation flow reactors are useful tools as part of ambient field studies, as they allow real-time measurement of SOA formation potential and oxidation across a wide range of photochemical ages. These results help constrain SOA models not only for the growth phase of the SOA but also for the decay phase, when further aging removes SOA mass. Future studies should apply this technique in other cities and other environments such as forested regions and the outflow from polluted continents, in order to further constrain the SOA formation potential and timescales for different sources and regions.

SUPPLEMENTAL INFORMATION

Quantification of AMS Reactor Data

All aspects of quantification of AMS data are the same as described by Hayes et al. (2013). Here we describe only those aspects where additional analysis or corrections are needed specifically for the reactor output data.

AMS Collection Efficiency

Quantification of AMS concentration data requires a correction for particle bounce at the vaporizer, referred to as the collection efficiency (CE; Canagaratna et al., 2007). The composition-dependent CE formulation of Middlebrook et al. (2012) was used by Hayes et al. (2013) to estimate CE for the ambient data, leading to good intercomparisons with multiple collocated instruments as documented by that study. The same methodology has also been applied to reactor output measurements.
Fig. S1a shows the time series of reactor and ambient aerosol concentrations and estimated CE. Ambient CE periodically rises above 0.5 due to larger fractions of ammonium nitrate aerosol, which leads to reduced particle bounce (Middlebrook et al., 2012). The reactor typically formed additional ammonium sulfate and ammonium nitrate beyond ambient concentrations at the same time as ambient levels peak for those compounds, thus the reactor CE profile has a very similar temporal structure to ambient. However, Fig. S1b shows that the estimated CE increases at the highest reactor OH$_{\text{exp}}$, due to additional ammonium nitrate formation in the reactor with increased photochemical age.

![Fig. S1. (a) Estimated AMS collection efficiency (CE) and corresponding AMS mass concentration time series for ambient and reactor data (after applying CE correction). (b) Estimated CE vs. OH exposure (OH$_{\text{exp}}$) in the reactor for all reactor measurements and averages for 7% quantiles.](image)

Highly acidic particles, as indicated by the ammonium balance, can also lead to increased CE in the AMS (Middlebrook et al., 2012). The ammonium balance method compares the measured ammonium to that required to fully neutralize observed sulfate, nitrate, and chloride (Zhang et al., 2007), as shown in Fig. S2. Ambient and reactor results have near identical slopes that are indistinguishable from the one-to-one line within the uncertainties of the measurements,
signifying full neutralization for both. Furthermore, this comparison indicates that the reactor is producing similar inorganic composition to that observed in the atmosphere as nitric acid and sulfuric acid gases are formed in the reactor and fully neutralized by ammonium forming ammonium nitrate and ammonium sulfate. Thus no correction of CE due to the presence of highly acidic particles are needed in this study.

![Graph showing measured vs. predicted ammonium assuming full neutralization (Ammonium balance) for ambient and reactor data. Linear orthogonal distance regression fit lines, slope and R² for each are also shown.](image)

Fig. S2. Measured vs. predicted ammonium assuming full neutralization (“Ammonium balance”) for ambient and reactor data. Linear orthogonal distance regression fit lines, slope and R² for each are also shown.

Comparison of AMS and SMPS measurements for ambient and reactor data, shows that ambient data falls along a one-to-one line, indicating both instruments are measuring the same amount of mass within the uncertainties (Fig. S3a). Reactor output data has a slightly higher slope of 1.14, i.e. the AMS measures ~14% higher mass than the SMPS from the reactor and also shows a cluster of points where SMPS>AMS due to periods where substantial mass is formed at small particle sizes (see below). Both slopes are within the combined uncertainties of the two measurements. Fig. S3b shows the relative increase in aerosol concentration in the reactor (i.e.
ratio of reactor to ambient concentrations) for the SMPS vs. AMS which also compare well, on average (slope = 1.05), but with considerable scatter, most of which is likely due to additional measurement noise introduced from ratioing multiple short measurements. Evaporation of freshly formed NH₄NO₃ in the longer residence times in the SMPS (compared to the faster AMS analysis) where the sheath flow may have reduced NH₃ and HNO₃ gas concentrations, has been observed with this experimental setup, and may be a cause of the slightly larger slope for reactor output conditions. An small underestimation of AMS CE for the reactor conditions could also result in this observation.

Fig. S3. (a) Scatter plot of AMS mass vs. mass estimated from SMPS measurements for ambient and reactor data, with linear orthogonal distance regression fit slope and R² for each. A one-to-one line and +/-15% region is shown for reference. (b) Relative enhancement ratio from AMS and SMPS data with raw data, 20-minute averaged smooth data, linear orthogonal distance regression, line, fit slope and R² for each.

It is also possible that the AMS relative ionization efficiency (RIE) of organic species is lower for more oxidized species (Jimenez et al., 2003; D. Murphy, pers. Comm. 2015), although no clear evidence has been reported for ambient data (e.g. Docherty et al., 2011). If that effect played a dominant role here, we would expect the reactor slopes to be lower, rather than slightly
higher than 1. Thus we conclude that any RIE changes are small and cannot be separated from other effects such as small changes in CE, nitrate evaporation in the SMPS, or differences in particle transmission (next section).

Accounting for Particle Mass below the AMS Lens Transmission

As the reactor exposed ambient air to high levels of OH and O₃, new particle formation and growth was sometimes observed. To fully account for the mass of all particles formed in the reactor, it is necessary to quantify the mass of small particles below the AMS lens transmission size (Zhang et al., 2004). SMPS data was used to estimate the total mass concentration below the AMS size cut. First, particle transmission from plumbing line losses was corrected using the Particle Loss Calculator (von der Weiden et al., 2009) for this experimental plumbing and flowrate configuration for both reactor and ambient SMPS data, with transmission curves as shown in Fig. S4. Second, the measured SMPS mass that is below the AMS transmission curve was estimated using a published AMS lens transmission parameterization (Knote et al., 2011) multiplying the SMPS size-dependent mass by the size-dependent AMS lens fractional loss (1-transmission). Figure S5a shows a time series of estimated reactor and ambient mass missed by the AMS due to transmission losses. Since corrections needed to account for the contribution of these small sizes to total mass is small for ambient data (on average 1.7%), Hayes et al. (2013) did not apply a correction to AMS ambient data. Fig. S5b shows the estimated fraction of the reactor output mass that is below the AMS lens transmission size vs. total photochemical age in days (at OH = 1.5×10⁶ molec. cm⁻³). An average of 6.2% of the total reactor output mass is estimated to be below the AMS lens transmission, with no dependence on photochemical age except possibly at the highest values (>20 days of age).
Fig. S4. Estimated particle transmission of inlet plumbing vs. particle diameter for reactor and ambient sampling lines for both AMS and SMPS measurements, calculated using the particle loss calculator of von der Weiden et al. (2009).

Fig. S5. (a) Time series of SMPS mass measured below the AMS lens transmission size for ambient and reactor measurements. (b) Percent of estimated mass not measured by AMS, due to on particle losses in sampling lines and the AMS lens transmission at small sizes, for the reactor vs. total photochemical age in days (at $OH = 1.5 \times 10^6$ molec. cm$^{-3}$), where all data is colored by $\Delta$OA mass with average 5% quantiles and standard error bars.
Fig. S6. Modeled fate of low volatility organic gases (LVOCs) formed in the reactor vs. OH\textsubscript{exp} including wall loss, reaction with OH, condensation on aerosol, and exiting the reactor, with a fit for the fraction condensing on aerosols in the reactor.

We note that the AMS measurements from the reactor may be biased ~6% low, on average, and sometimes as much as 20%. This non-measured mass likely has a large OA fraction (see Fig. S7). Thus, reactor-reported mass enhancement above ambient may be underestimated by these amounts. Given the 6.2% AMS underestimation from particle transmission of small sizes in the reactor, and the apparent 14% overestimation in the AMS vs SMPS comparison, but overall good agreement in the relative enhancement of total aerosol between both instruments, we have not corrected for these differences as the net correction would be small and within the uncertainties of the measurement, while the correction process would introduce additional noise.
Fig. S7. AMS mass size distribution (vs. vacuum aerodynamic diameter, $d_{va}$) for reactor and ambient OA, averaged from 20:00 on 2 June 2010 – 00:20 on 9 June 2010 for average nighttime ambient and reactor with no internal OH$_{exp}$ (dark reactor), and for ~3.7 days and ~23.5 days aging.

Fig. S8. Times series of benzene, 1,3,5-trimethylbenzene, and toluene on top panel. Time series of ambient OOA, reactor OA mass enhancement, maximum reactor mass enhancement, and $O_x$ on bottom panel.
Fig. S9. Ratio of organic aerosol to excess carbon monoxide (above background) vs. total photochemical age in days (at \( \text{OH} = 1.5 \times 10^6 \text{ molec. cm}^{-3} \)) for (a) the same data as Fig. 9, showing all data used to produce averages for quantiles of ambient and reactor vapor-loss corrected data. Also shown are the expected decays of benzene, toluene, and 1,3,5-trimethylbenzene in the reactor vs. total photochemical age in days (at \( \text{OH} = 1.5 \times 10^6 \text{ molec. cm}^{-3} \)), using reaction rates from Atkinson et al. (2006). (b) The same data as Fig. 9, showing reactor vapor loss-corrected data, but where excess CO is decreased by reaction with OH in the reactor, including means for 12% quantiles. Results from field studies in the northeastern US and Mexico City are shown for comparison to previous observations (DeCarlo et al., 2010). A fit to the data when CO is assumed to react with OH is shown.
Fig. S10. Measured oxygen added to OA in the reactor vs. total photochemical age in days (at OH = 1.5×10^6 molec. cm^-3), along with a log normal fit to the ΔOxygen data. Reactor data is colored by OA mass enhancement. The estimated number of OH collisions with OA is shown, based on the methodology outlined in appendix A of DeCarlo et al. (2008).
Fig. S11. Top panel: Mass fraction remaining (MFR) for OA vs. thermal denuder temperature for this CalNex-LA dataset, using the methods described in Huffman et al. (2008; 2009). Bottom panel: estimated volatility distribution of particle- and gas-phase species, calculated from the thermal denuder profile using the method of Faulhaber et al. (2009), on bottom panel.
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CHAPTER IV
CONCLUSION

My doctoral research focused on examining the potential for SOA formation, through oxidation of source emissions and atmospheric pollutants in ambient airmasses. The research was essentially an \textit{in-situ} kinetics experiment performed on the atmosphere, with the intent of giving a more realistic comparison between airmasses in different environments and their potential to form aerosol downwind. The goal was to perform aerosol aging experiments akin to laboratory-based chamber experiments in the field.

To achieve these goals, I modified, developed, and applied a field deployable tool to quantify SOA formation potential in near-real time. Modifying the original PAM chamber, described in Kang et al., (2007), for field deployment by decreasing size, increasing rigidity, and functional control, this upgraded reactor ran tandem with a AMS. Together with particle size distribution measurements (TSI, Inc. Scanning Mobility Particle Sizer; SMPS) and gas-phase precursors measurements. Through collaborations, comparisons with a Proton Transfer Reaction Mass Spectrometer (PTR-MS) and Gas-Chromatography Mass Spectrometry (GC-MS), during multiple field deployments of the reactor provided the opportunity to fully explore the link between Volatile Organic Compounds (VOCs) and SOA formation in the atmosphere.

As a ‘proof of concept’ and with the aim of improving our instrumental design, I have participated in two major measurement campaigns, including an international field campaign at the interface of rural and urban environment (DAURE, Montsey, Spain), and a domestic industrial epicenter (SHARP, Houston, TX), not reported in detail in this thesis. After further optimization, including converting to a metal reactor shell, running with open-flow through configuration,
upgrading of multiplexing/switching value system for simultaneous AMS measurements, computer controlled UV lamps, oxidant scrubber and denuder development for sampling, post-processing analysis code development, and data acquisition systems, the reactor was deployed in two lucrative campaigns of data reported here. The reactor upgrades allowed real-time aging measurements of biomass burning emissions and the urban environment of the Los Angeles Area. Together with measurements reported in this dissertation, my research has facilitated recent field work including reactor aging of biogenic emissions (not reported here) and presents a suite of datasets to explore SOA formation from the range of air masses and ambient conditions.

Focusing on the biomass burning study, numerous experimental innovations were established. As the first real-time flow reactor aging experiment of a complex emissions, such as smoke, with continual scanning of $OH_{\text{exp}}$, an open-flow-through configuration minimizing semivolatile losses, multiplexing AMS and PIT-MS measurements allowed for concurrent observations of unprocessed and aged smoke. With fast photochemistry, short residence time, and controllable OH concentrations, the reactor provided the platform for multiple burn experiments per day and scanning of a large range of $OH_{\text{exp}}$ during each experiment. Over a range of biomass fuel types, the reactor allowed for investigation of OA enhancement and chemical evolution as a function of age in as novel technique to augment traditional measurements.

From unprocessed smoke measurements compared to reactor aged smoke, VOC mass spectral evolution indicated aromatics and terpenes decreased with increasing $OH_{\text{exp}}$, while formic acid and other unidentified compounds increased. Although the total VOC concentration decreased with $OH_{\text{exp}}$, some gas-phase oxidation products increased with photochemical processing. Further probing of gas-phase SOA precursors and products from this study and future biomass burning
deployments is important for identifying these compounds and understanding mechanisms governing photochemical processing.

Organic aerosol enhancement from aging of smoke in the reactor resulted in a wide range of enhancement, 0.6–2.3, spanning from substantial SOA production to net OA mass loss. With an average enhancement factor of $1.42 \pm 0.36$, considerable SOA was produced from smoke aging. The variability in observed in this study is consistent with previous investigations of both field and laboratory studies of biomass-burning aging. OA mass losses observed in certain fuels is conceivably from heterogeneous oxidation and volatilization (Molina et al., 2004) or oxidation of gas-phase semivolatiles leading to fragmentation and evaporation of particle-phase species that were in equilibrium with the aerosol phase (Donahue et al., 2012; Lambe et al., 2012). In this study, fuels with higher POA emissions resulted in less relative OA enhancement from photochemical aging. We confirm the net SOA to POA ratio of biomass burning emissions is far lower than that observed for urban emissions, as reported elsewhere (DeCarlo et al., 2010; Hayes et al., 2013), and is attributed to the higher organic ratio of urban emissions (Heald et al., 2008). The ratio of net SOA to CO (used to monitor the evolution of SOA) is similar between both sources and can often be higher for biomass burning emissions (Cubison et al., 2011; Jolleys et al., 2012).

Most fuels showed maximum ER$_{OA}$ (deviation from 1) around three days of photochemical age ($OH_{exp} \sim 3.9 \times 10^{11}$ molecules cm$^{-3}$ s$^{-1}$), then leveled off and remained constant even with increased $OH_{exp}$. VOCs measured with the PIT-MS do not correlated with the enhancement of OA, suggesting the importance of primary intermediate volatility and semivolatile gases as SOA precursors. Observations verify that while heterogeneous processes can be important in conditions where gas-phase oxidation cannot occur, that gas-phase oxidation will be more effective most of the time at increasing OA mass with photochemical age (Donahue et al., 2012).
Consistent chemical transformations were observed from aging in every burn experiment, such as m/z 28 and 44 enhancement (CO\(^+\) and CO\(_2\)^+ increase), notably even in fuels that undergo a net mass decrease from aging. The slope \(f_{44}\) vs OH\(_{\text{exp}}\) varies with each fuel type (as the smoke from each of the fuels is oxidized) and this rate appears to increase with initial contribution of m/z 44 to POA. The contribution of m/z 60 to OA, the levoglucosan-like fragment, \(f_{60}\), remains constant or significantly decreases with increased photochemical age (persisting above the background biomass burning-free level of 0.3%).

For all biomass fuel experiments, the oxygen-to-carbon ratio of POA spanned 0.15–0.5, with aged OA O/C ratios enhanced up to 0.87, and the O/C of added mass (when there was net enhancement) ranged from 0.4–1.0. The relationship of O/C with OH\(_{\text{exp}}\) for most aged smoke show similar increasing slope to alkane precursor SOA (Lambe et al., 2012). As overall \(\text{ER}_{\text{OA}}\) and O/C from aging correlates with degree of oxidation of POA, characteristics both intrinsic, i.e. chemical composition, and extrinsic, i.e. correlation with POA concentration, emerge as important predictors of SOA formation from aging biomass-burning emissions. As photochemical age increases, Van Krevelen diagrams of H/C vs. O/C result in different slopes for each different fuel, implying distinctive functionalization for each biomass.

Deploying the reactor to aging biomass burning emissions shows photochemical aging of smoke from can account for a significant enhancement of initial emitted OA mass. The secondary processes, which include functionalization and fragmentation reactions, need to be included in regional and global climate models, as well as predictive air quality forecasting to improve our constraints on aerosol in climate, global OA budgets, as well as support air quality policy, forecasting, and mitigation in regions susceptible to wildfires or controlled burning.
Highlighting the urban emission study, real-time measurements of net SOA formation and OA aging were successfully examined with an OFR coupled to an AMS and SMPS during the CalNex field campaign, targeting LA-Basin emissions. This work details one of the first fruitful applications of the reactor in conjunction with a full suite of in-situ aerosol instrumentation at a large scale field project during a multi-platform investigation. Complementing already established gas- and aerosol-phase instrumentation and other methods of determining SOA contributions to fine particulate matter concentrations, continuous ambient air sampling through the reactor allowed with a multiplexing system facilitated ambient and aged measurements in real-time. Computer-controlled scanning of oxidant concentrations provided continuous scanning of OH$_{\text{exp}}$, with oxidation of ambient air typically from 0.87 days – 6.4 weeks of age. The reactor measurements were virtually uninterrupted over a two week period enabling observations over different meteorological conditions and emissions.

Organic enhancement of these urban emissions peaked between 0.8–4 days of aging (OH$_{\text{exp}} = 1.0–5.2 \times 10^{11}$ molec. cm$^{-3}$ s$^{-1}$). Suggesting a shift from chemistry dominated by functionalization/condensation to fragmentation/evaporation dominated oxidation reactions but with functionalization still occurring, reactor OA mass decreased below ambient concentrations after two weeks of atmospheric equivalent aging, OH$_{\text{exp}}$ above $2 \times 10^{12}$ molec. cm$^{-3}$ s$^{-1}$. Highest SOA formation, OA enhancement, was observed during nighttime with reactor-aged OA mass peaking at concentrations similar to the following daytime ambient OA mass peak. While inorganic (sulfate, nitrate, and ammonium) aerosol formation shows a similar shape with OH$_{\text{exp}}$, values do not decrease below ambient levels at the highest OH$_{\text{exp}}$.

Examining the change in ratio of OA with excess CO concentrations (above background) indicate the reactor produces comparable results as observed in ambient SOA formation. At
photochemical ages beyond that observed in ambient OA, the reactor shows a leveling off and then
decrease in OA/ΔCO with increased age. A fit of this data results in two timescales, one of SOA
formation ~0.5 days and one of fragmentation-dominated heterogeneous oxidation up to ~30 days.
These fits and timescales should be applied in future studies and in updated model-
parameterizations of urban SOA formation.

Comparing to flowtube studies of heterogeneous oxidation of ambient air (George and
Abbatt, 2010), similar trends are observed with plateau then decrease below ambient at highest
OH_{exp}, but with higher relative OA enhancement achieved in this study. Comparing reactor-aged
tunnel vehicular emissions (Tkacik et al., 2014), the relative shape of OA increase and then
decrease, moving from functionalization to fragmentation as oxidation moves from SOA
formation to OA aging, is observed in both studies. However, the time to peak OA formation is
much longer in the tunnel vehicle emission aging study. This discrepancy suggests the importance
of semivolatiles both in reactor design and deployment, as well as in urban SOA formation.
Reactor OA mass enhancement correlates with 1,3,5-trimethylbenzene, suggesting that precursors
with similar emission footprints and reactivity, short-lived (τ_{OH} ~ few hours), dominate SOA
formation in the LA Basin.

Modeling SOA formation results show maximum SOA from traditional models is much
less than the maximum OA mass enhancement observed from reactor-aging. An updated VBS-
based model (Hayes et al., 2014) overpredicts SOA formation. This difference may be due to
intermediate species from traditional VOCs, POA evaporation, and SOA precursors not included
in models. As the reactor forms significant SOA at night, when oxidation of VOCs is slower (only
by available O_3 and NO_3), reactor SOA production may be less dominated by partially oxidized
VOCs and likely by evaporated POA or un-accounted for reactive SOA precursors emissions. This study emphasizes the importance of heterogeneous oxidation leading to OA fragmentation at longer photochemical ages (beyond a week), a mechanism that warrants inclusion in up-to-date SOA models.

Examining aging effects on chemical composition, in a Van Krevelen diagram (H/C vs O/C), reactor-aged OA yielded a similar slope as observed in ambient OA (both \(~0.6\)) consistent with the addition of acid groups with carbon–carbon bond breakage, or acid and alcohol functional groups without fragmentation. This is suggests the reactor produces comparable functionalization reaction to ambient oxidation. While reactor-aged OA mass decreases at very high OH-exp, O/C continues to increase. Maximum net SOA production was observed at intermediate OH exposures and O/C ratios, a consideration for future deployments, instrument development and model verification.

Photochemical aging of urban emissions can contribute significant OA beyond that formed immediately downwind of fresh sources, particularly if the air has not been exposed to very much photo-oxidation (such as at night) or with an unventilated boundary layer (typical nighttime inversion). Nighttime observations deliver important insights into the potential for SOA formation in the absence of rapid photochemistry, as well as into the precursors and processes are dominating ambient SOA formation during daytime. An inverse relationship between reactor SOA formation (at night) and ambient SOA formation (during day) highlight important connections between the arrival/timing and distribution of emissions, day/night transport, and SOA formation in urban and urban-impacted regions that control where, when, and how much SOA is formed. SOA formation and processing observed in this study include functionalization and fragmentation reactions, and can be attributed to short-lived reactive gas-phase organic compounds and heterogeneous
oxidation leading to fragmentation, that need to be included in climate and air quality modeling efforts to improve constraints on global and regional OA budgets.

Results from both the biomass burning and urban emission studies illuminates the reactor’s predictive potential and highlight its usefulness as a tool for real-time measurement of SOA formation and oxidation across a wide range of photochemical ages.
REFERENCES


