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Relating Secondary Organic Aerosol Characteristics with Cloud Condensation Nuclei Activity

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Relating Secondary Organic Aerosol Characteristics with Cloud Condensation Nuclei Activity

A Dissertation submitted in partial satisfaction of the requirements for the degree of

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in

Chemical and Environmental Engineering

by

Xiaochen Tang

June 2013

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ABSTRACT OF THE DISSERTATION

Relating Secondary Organic Aerosol Characteristics with Cloud Condensation Nuclei Activity

by

Xiaochen Tang

Doctor of Philosophy, Graduate Program in Chemical and Environmental Engineering
University of California, Riverside, June 2013
Dr. David R Cocker III, Co-Chairperson
Dr. Akua Asa-Awuku, Co-Chairperson

A study on secondary organic aerosol (SOA) was conducted with a focus on correlating the chemical and physical characteristics with aerosol’s ability acting as cloud condensation nuclei (CCN). The work focuses on three types of aerosol: β-caryophyllene ozonolysis SOA, aliphatic amine SOA, and cigarette environmental tobacco smoke. The work on β-caryophyllene ozonolysis SOA enhances our understanding of the CCN activity of SOA formed with and without the presence of isoprene, by probing the effects of a series of environmental parameters on the formation and properties of SOA with more ambient-relevant precursor concentrations. This study demonstrates that aerosol formed from ozonolysis of a mixture of low and high molecular weight terpenes can be hygroscopic and can contribute to the global biogenic SOA CCN budget.

The aliphatic amine work explores the atmospheric behaviors of amines with typical atmospheric oxidants, e.g. nitrate radical, hydroxyl radical and ozone. This study shows that night time chemistry of aliphatic amines can produce secondary organic and inorganic aerosol mixtures, and the relative contribution of each component depends on the environment relative humidity. Thus, modelers need to include as much ambient data
as possible in order to mimic the amine behavior in the real atmosphere. The hygroscopicity of aliphatic amine secondary aerosol is also investigated, focusing on the correlation between complex composition and aerosol CCN activity. Despite of measurement artifacts, primary aliphatic amine aerosol is composed of highly volatile components with high hygroscopicity.

The third part of the work characterizes the environmental tobacco smoke (ETS) from research cigarettes, with an emphasis on enhanced condensational growth (ECG), represented by CCN activity and droplet formation properties. Changes in smoke particle size, chemistry, and volatility are correlated to changes in droplet behavior from offline and online chemical and physical measurements. The study shows that reference cigarette ETS are hygroscopic and will have similar lung deposition rates despite source.
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1 Introduction

1.1 Introduction of Dissertation

Atmospheric aerosols can be divided into two categories: primary aerosol and secondary aerosol. Primary aerosols are directly emitted from a variety of sources (e.g. dust, sea salt, combustion emission, etc.), while secondary aerosol are formed in the atmosphere through a series of atmospheric reactions and gas-to-particle partitioning. Aerosols scatter and absorb solar and terrestrial radiation, influence cloud formation by acting as cloud condensation nuclei (CCN) and participate in heterogeneous chemical reactions in the atmosphere, thereby affecting the abundance and distribution of atmospheric trace gases (Andreae and Crutzen, 1997; Haywood and Boucher, 2000). Evaluation of CCN activity of atmospheric aerosols requires knowledge of particle size and composition. However, due to the limited knowledge of aerosol sources, composition, properties, and mechanism of formation in the atmosphere, the effects of aerosols on climate are still far from being fully understood and quantified.

Atmospheric aerosols also have an important impact on human health (Pope and Dockery, 2006), e.g. they can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases (Bernstein et al., 2004; Finlayson-Pitts and Pitts, 1997). Adverse health effects from particulate matter (PM) are caused by the deposition of particles in the respiratory tract during inhalation. The water vapor uptake by hygroscopic components can alter dry particle size and deposition efficiencies (Blanchard and Willeke 1984; Broday and Georgopoulos 2001; Schroeter et al. 2001; Londahl et al. 2009; Varghese and
Gangamma 2009; Kane et al. 2010; Phalen et al. 2010). Therefore, the dose and deposition site of these aerosols are influenced by the growth of the particles. In the upper respiratory airways with high water vapor concentration, droplets may form and dry particles can effectively act as CCN as well.

Secondary organic aerosol (SOA) is an important contributor to atmospheric particulate mass (Seinfeld and Pankow, 2003). Goldstein and Galbally (2007) estimated SOA production of 510–910 Tg C yr\(^{-1}\) from 1300 Tg C yr\(^{-1}\), roughly a 50% yield, from volatile organic compounds (VOCs). SOA can be classified as biogenic or anthropogenic based on the major sources of the precursor VOC. Isoprene, monoterpenes and sesquiterpenes dominate the biogenic VOC emissions (Guenther et al., 1999; Guenther et al., 2000; Kanakidou et al., 2005), which may contribute to half of the global organic carbon (Hallquist et al., 2009b). \(\beta\)-caryophyllene (\(\beta\)-C, \(\text{C}_{15}\text{H}_{24}\)) is one of the most common and abundant sesquiterpenes and has been studied extensively. Previous studies have focused on \(\beta\)-C SOA formation, product detection and identification (Jaoui et al., 2003; Winterhalter et al., 2009; Griffin et al., 1999), but no previous \(\beta\)-C chamber experiments were not conducted in the presence of other terpene precursors. CCN activity of \(\beta\)-C SOA has been reported by only a few works, while almost all of them suggested not hygroscopic enough to be efficient CCN contributor.

On the other hand, low molecular weight aliphatic amines have been frequently detected from animal husbandry, fish processing, industry, etc. (Ge et al., 2011c). Thus, anthropogenic activities are responsible for the regional presence of both gas and particle phase amines at relatively high concentration. Atmospheric removal routes for amines
include reactions with acids (nitric or sulfuric acid) and/or oxidants (e.g. OH, \( O_3 \), and \( NO_3 \)) (Seinfeld and Pandis, 2006a; Finlayson-Pitts and Pitts, 2000; Silva et al., 2008). Multiple detection of particle phase amines in ambient samples validated the amine salt formation via acid-base reactions (Table 7 in Ge et al. (2011c)), while chamber studies showed that oxidation also lead to amine SOA formation. Consequently, there is high probability that inorganic and organic components co-exist in ambient amine-containing particles, especially in areas abundant with gas phase amines. However, the aerosol formation pathway and composition is subject to environmental conditions, such as relative humidity and oxidant species, which have not been thoroughly explored yet. CCN activity of amine SOA also needs characterization, for regional climate models to estimate effects of the amine aerosols.

This study provides new insights on both biogenic and anthropogenic SOA, by correlating chemical and physical properties with aerosol hygroscopicity. Ozonolysis of \( \beta \)-caryophyllene SOA is revisited in the large scale environmental smog chamber with the emphases on the effects of varying experimental parameters and precursor concentration on SOA CCN activity. SOA formation of aliphatic amines with atmospheric oxidants is also studied; aerosol forming potential, chemical composition and CCN activity is reported. Another facet of this study utilizes advanced chemical and physical characterization techniques to further characterize cigarette smoke. The following outlines each chapter in the dissertation.

Chapter 2 improves the current understanding of \( \beta \)-caryophyllene SOA CCN activity by conducting a series of chamber experiments with low precursor concentration.
Experimental parameters are varied to characterize the effects of precursor concentration, light intensity, hydroxyl radical concentration, and the presence of a lower molecular weight terpene precursor (isoprene). Changes in \( \beta \)-caryophyllene SOA chemico-physical properties (e.g., density, volatility, oxidation state) are explored with online techniques to improve our predictive understanding of \( \beta \)-caryophyllene CCN activity.

Chapter 3 characterizes environmental tobacco smoke (ETS) from research cigarettes to understand the effects of particle chemistry and hygroscopicity for enhanced condensational growth (ECG) by water vapor and wet particle deposition. Low nicotine (LN) and ultra-low nicotine (ULN) research cigarettes are tested with a Walton Smoking Machine (WSM); mainstream and sidestream ETS are produced and analyzed with combined online and offline measurement techniques. Changes in particle size, chemistry, and volatility are correlated to changes in droplet behavior from offline and online chemistry measurements.

Chapter 4 explores the aerosol formation from reactions between three aliphatic amines and HNO\(_3\)/O\(_3\)/NO\(_3\)/OH. Butylamine, diethylamine, and trimethylamine are selected as representatives of primary, secondary and tertiary amine, respectively. Effects of water vapor are also examined by conducting experiments under different relative humidity conditions (RH<0.1% to ~40%). The relative abundance of organic/inorganic components in the amine aerosol is reported, as well as the composition and chemical and physical characteristics. Results show that all three amines have a high potential to form secondary aerosol in reactions with NO\(_3\), while the reaction pathways are affected by the presence of water vapor. On the other hand, the OH photooxidation of amines has much
lower secondary aerosol yield and is independent of relative humidity, while ozonolysis produces negligible amount of aerosol.

Chapter 5 extends on the Chapter 4 study of the forming potential and composition of amine secondary aerosols to their CCN activity. The previous study proves that aliphatic amines can readily form secondary aerosol with complex components subject to the type of precursor amine and the oxidant, so different water-uptake abilities are expected for different amine aerosols. The results indicate that measured CCN activity corresponds to the relative contribution of inorganic/organic components in the aerosol phase, and aerosol volatility is correlated with parameterized hygroscopicity.

In addition, my research conducted at UCR has contributed to two additional peer-reviewed co-author publications. To our knowledge, it is the first time that the 5–8 nm particles emitted from ships was aptly synthesized on a laboratory scale, while CCN measurement indicated that neither laboratory generated nor ship emitted aerosol was hygroscopic (Zheng et al., 2010). A density estimation method proposed by Kuwata et al. (2011) was evaluated in Nakao et al. (2013) using a large database of density and elemental ratios (O/C and H/C) of SOA formed from the oxidation of 23 different volatile organic compounds (VOC) in the UCR/CERT chamber.
1.2 References


2 Are sesquiterpenes a good source of secondary organic cloud condensation nuclei (CCN)? Revisiting β-caryophyllene CCN

2.1 Introduction

Secondary organic aerosol (SOA) is an important contributor to atmospheric particulate mass (Seinfeld and Pankow, 2003). Atmospheric SOA can influence climate directly by absorbing and scattering light and indirectly via their ability to act as cloud condensation nuclei (CCN) and influence cloud formation. Goldstein and Galbally (2007) estimated SOA production of 510–910 Tg C yr\(^{-1}\) from 1300 Tg C yr\(^{-1}\), roughly a 50% yield, from volatile organic compounds (VOCs). Biogenic volatile organic compounds (BVOC) may contribute to half of the global organic carbon (Hallquist et al., 2009b) and isoprene, monoterpernes and sesquiterpenes dominate BVOC emissions (Guenther et al., 1999; Guenther et al., 2000; Kanakidou et al., 2005). Terpenes are atmospherically abundant and reactive, as reflected by ephemeral chemical lifetimes (~ several minutes, Goldan et al., 1993; Guenther et al., 1995; Neeb et al., 1997). Sesquiterpenes are the least abundant among the terpene classes but still play an important role in the tropospheric chemistry. Sesquiterpenes have highly reactive unsaturated double bonds and can form condensed phase products (Shu and Atkinson, 1995; Atkinson and Arey, 2003; Shu and Atkinson, 1994). Hence sesquiterpenes may have a similar large potential for SOA formation as monoterpenes; their contribution to global SOA formation may be as high as 9% (Donahue et al., 2005; Griffin et al., 1999; Dekermenjian et al., 1999; Bonn and Moortgat, 2003).
$\beta$-caryophyllene ($\beta$-C, $\text{C}_{15}\text{H}_{24}$) is one of the most common and abundant sesquiterpenes and has been studied extensively. It is emitted by pine trees (Helmig et al., 2007), orange orchards (Ciccioli et al., 1999) and several agricultural plant species such as potato plants, leaves of tobacco, sunflower, maize and cotton (Hansen and Seufert, 2003; Duhl et al., 2008). Ozone ($\text{O}_3$) readily attacks the double carbon bonds in $\beta$-C and the lifetime of $\beta$-C reacting with ozone is much shorter (~1 min) than with other oxidants in the troposphere (e.g. OH, NO$_3$) (Hoffmann et al., 1997). Ozonolysis is a significant pathway for ambient $\beta$-C removal; the relative contribution of $\text{O}_3$ reaction to tropospheric degradation is as much as 98% (Hoffmann et al., 1997). Even though the reported reaction rate of $\beta$-C dark ozonolysis varies (Ghalaieny et al., 2012; Shu and Atkinson, 1995), aerosol is readily formed in this chamber and in other previous studies (but not limited to; Ng et al., 2006; Winterhalter et al., 2009; Chen et al., 2012).

Previous studies have focused on $\beta$-C SOA formation, product detection and identification (Jaoui et al., 2003; Winterhalter et al., 2009; Griffin et al., 1999). Aerosol yield parameters (stoichiometric factor, $\alpha$, and equilibrium coefficient, $K_{om}$) for the photooxidation of $\beta$-C are 1.000 and 0.0416 (Griffin et al., 1999; Hoffmann et al., 1997), respectively. Jaoui et al. (2003) reported a number of products from $\text{O}_3$ oxidation (e.g., $\beta$-caryophyllone aldehyde, $\beta$-norcaryophyllone aldehyde, $\beta$-caryophyllonic acid, $\beta$-14-hydroxycaryophyllonic acid) with low vapor pressure that could contribute to formation of the secondary aerosols. Recently Li et al. (2011) reported formation of $\beta$-C SOA with low initial VOC concentration (1.7 to 46.4 ppbv) in the presence of seed aerosol ($\left(\text{NH}_4\right)\text{SO}_4$) and excess $\text{O}_3$. The elemental oxygen-to-carbon ratio ($\text{O/C}$) of first
generation products (0.13-0.29, Ding et al., 2011) were found to be lower than second generation products (0.2-0.5, Ding et al., 2011) identified in the aerosol phase. The work was followed by additional seeded $\beta$-C ozonolysis experiments of Chen et al. (2012) that confirmed that excess ozone concentrations were necessary to form secondary generation products with higher oxidation states and aerosol densities.

Furthermore, previous $\beta$-C chamber experiments were not conducted in the presence of other terpene precursors. Isoprene ($C_5H_8$) contributes up to 44% of total global VOC flux, $\sim$1500 Tg C (Guenther et al., 1995) and high concentrations of isoprene have been measured with $\beta$-C emissions (Fu et al., 2010; Lewandowski et al., 2008). Unlike sesquiterpenes, the O$_3$-isoprene reaction produces significant amounts of higher volatility products and thus the O$_3$-isoprene yield is much smaller. However, global emissions of isoprene are sufficiently large that the formation of SOA, even in small yields, may result in substantial contributions to condensed phase materials (Carlton et al., 2009). Reported SOA yield of the O$_3$-isoprene reaction is between 0.001 and 0.01 (Czoschke et al., 2003; Jang et al., 2002; Kleindienst et al., 2007). Kleindienst et al. (2007) observed lower aerosol mass with the presence of OH scavenger for SOA formed from O$_3$-isoprene reaction, which is consistent with the higher yield of isoprene photooxidation by H$_2$O$_2$ (0.009–0.036) (Kroll et al., 2006). Products of OH-initiated isoprene photooxidation have been detected in a considerable amount in the filters collected in Amazonia, Brazil (Claeys et al., 2004). In the same AMAZE-08 campaign, the estimated single hygroscopicity parameter, $\kappa$, of biogenic dominated SOA was $\sim$0.16±0.06 (King et al., 2010). Chamber study of King et al. (2010) showed that the CCN activity of seeded
isoprene SOA generated by irradiating H₂O₂ and isoprene was consistent with the Amazonian SOA (κ=0.10±0.03). It indicates that biogenic isoprene is a major source of SOA and can act as CCN to influence the climate in the forest region. The less volatile fraction of the isoprene SOA was also less CCN active (Poschl et al., 2010); similar to the less volatile and CCN active fraction of β-C SOA (Asa-Awuku et al., 2009). Thus the addition of reactive lower volatility materials to the β-C SOA may modify particle composition, density, volatility, and CCN characteristics and must also be explored.

To the best of our knowledge, only two studies have reported the CCN activity of β-C SOA (Asa-Awuku et al., 2009; Hartz et al., 2005). In both cases β-C SOA was formed in a 12 m³ chamber and was found to be less CCN active than monoterpene SOA, with activation diameter 152±26 nm at 1% supersaturation (ss) (Hartz et al., 2005; Asa-Awuku et al., 2009). Asa-Awuku et al. (2009) also found that the hygroscopic material in β-C SOA to be semi volatile, yet little or no information on β-C SOA characteristics such as O/C and density were measured with CCN properties.

SOA aging may lead to an increase of particle hygroscopicity and CCN activity (Jimenez et al., 2009). Asa-Awuku et al. (2009) reported significant aging of β-C ozonolysis SOA changed most CCN-relevant properties (e.g. activation diameter, water soluble fraction, droplet size) and resulted in increased CCN activity. However, Varutbangkul et al. (2006) observed the subsaturated hygroscopicity of SOA formed by photooxidation of β-C to decrease with aging, explained by the formation of higher-molecular weight and less hydrophilic oligomers. For isoprene SOA, little or no aging has been observed; no aerosol growth was reported for methyl vinyl ketone (MVK), the
most abundant first generation gas-phase product from isoprene oxidation reaction (Kroll et al., 2006). The aging of high and low molecular weight terpene precursor SOA is explored here.

O/C has been considered an important factor to characterize the oxidation state of SOA and particle hygroscopicity (Jimenez et al., 2009; Kroll et al., 2011; Chang et al., 2010; Massoli et al., 2010; Lambe et al., 2011). Recent studies also indicate the relative abundance of organic fragment ion signal m/z 44 (f_{44}) as a marker for oxygenated species (Canagaratna et al., 2007; Alfarra et al., 2007; Duplissy et al., 2011b; Aiken et al., 2008b). In Jimenez et al. (2009), ambient aerosols and chamber SOA from three different precursors showed the same trend of increasing hygroscopicity with increasing O/C. Duplissy et al. (2011b) also found strong correlation between hygroscopicity with f_{44} for SOA formed in an environmental chamber and from two field experiments. In this study, we characterize $\beta$-C SOA formed under different conditions and evaluate the effects of hydroxyl radical, light and addition of isoprene on SOA formation and CCN properties. We report density, volatility, O/C, and CCN activity to improve predictions for terpene SOA CCN systems.

2.2 Experimental Methods

This study was conducted in the University of California-Riverside/ CE-CERT indoor environmental chamber (Carter et al., 2005a). Two 90m³ Fluorinated Ethylene Propylene (FEP) copolymer Teflon® film reactors were suspended by a rigid steel framework within the temperature-controlled enclosure (temperature range 5–45°C,
normally set to 27°C for experiments). Both the chamber and the enclosure were continuously flushed with purified air (Aadco 737 series air purification system (Cleves, Ohio)). 115 W Sylvania black lights simulate solar irradiation and ultraviolet (UV) light within the reactor. β-C and isoprene were introduced to the chamber by passing a stream of pure nitrogen (N₂) over a known volume of liquid in a glass injection manifold. O₃ was formed using two Dalton ozone generators (Model Type: OZG-UV-01) and injected similarly with flushing pure N₂. Relative humidity (RH) inside the chamber was maintained at or below 0.1% RH. The reaction time for each experiment ranged from 6 to 8 hours. For experiments with photochemistry, black lights were turned on after injection of parent VOCs and oxidants.

Real-time particle density was measured using an Aerosol Particle Mass Analyzer (APM) (Kanomax model 3600) and SMPS (Scanning Mobility Particle Sizer) in series. Compared to traditional DMA (Differential Mobility Analyzer)-APM configuration, the APM-SMPS setup reduces sampling time, avoids the need to vary angular rotational speed and voltage applied to the APM, and increases the system signal to noise ratio. Density data was acquired every 75 seconds. Details of the instruments and theory are described elsewhere (Malloy et al., 2009c; Ehara et al., 1996b).

Particle volatility was monitored with a custom-built Volatility Tandem Differential Mobility Analyzer (VTDMA) (Burtscher et al., 2001; Rader and Mcmurry, 1986). The diameter of particles transmitted through the first SMPS (D₁) is selected to match the mode diameter of size distribution measured by a parallel SMPS. Then monodisperse particles are transported through a Dekati® thermodenuder (TD, residence
time: ~17 seconds, adjustable temperature). The diameter of particles leaving the TD ($D_f$) is then measured by fitting a log-normal size distribution curve from a second SMPS. Volume fraction remaining (VFR) is then calculated as the volume ratio before and after the TD, i.e., $VFR = (D_f/D_i)^3$. Note that the “volume” in VFR measurement is based on mobility diameter measurement which may include void space and void space is assumed negligible in SOA systems. The VTDMA was calibrated using the VFR of dry ($\text{(NH}_4\text{)}_2\text{SO}_4$ seed aerosol at room temperature as correction factors.

The evolution of particle elemental composition is tracked using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006a;Jimenez et al., 2003). The HR-ToF-AMS design is based on the on-line quantitative mass spectra measurements using a heated surface for particle vaporization followed by a standard 70 eV electron impact ionization and subsequent ion analysis with a time-of-flight mass spectrometer (Drewnick et al., 2005). The HR-ToF-AMS can provide quantitative data on both the non-refractory chemical species present in aerosol particles as well as the size of the particles (Jayne et al., 2000;Jimenez et al., 2003). Atomic O/C of SOA was calculated with elemental analysis of the HR AMS data (Aiken et al., 2007b).

Aerosol from the chamber was classified by a scanning mobility particle sizer (SMPS 3080), followed in parallel by a condensation particle counter (TSI CPC 3772) and a Droplet Measurement Technologies (DMT) Continuous-Flow Streamwise Thermal Gradient CCN Counter (CFSTGC) (Lance et al., 2006;Roberts and Nenes, 2005). The total aerosol concentration (CN) of the monodisperse particles was counted by the CPC.
and the CCN concentration was measured by the CCN counter. The DMA with the CCN counter was operated at a sheath-to-aerosol flow ratio of 10:1. The design and operating principles of the CCN counter are based on the model of Roberts and Nenes, 2005. Settings used in this study ranged from 0.2% to 1% and were calibrated using (NH₄)₂SO₄ aerosol (supplemental material). Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010) provides size resolved CCN activity using data from the CCN counter and SMPS. By keeping constant instrument settings during the scanning cycle of the SMPS, we obtain the time series of CN and CCN counts, then determine the CCN/CN ratio as a function of dry mobility diameter. This procedure is repeated over multiple settings, giving a characterization of the size-resolved CCN properties every 135 seconds (one cycle for SMPS). SMCA has been evaluated for calibration, laboratory and ambient aerosol, SOA filter samples, biomass burning aerosol (Asa-Awuku and Nenes, 2007; Asa-Awuku et al., 2008; Moore et al., 2010; Padro et al., 2007) and monoterpene SOA (Engelhart et al., 2008). The CCN counter is calibrated with atomized (NH₄)₂SO₄ solution (1g L⁻¹).

Measured and calculated activation diameters for (NH₄)₂SO₄ at multiple settings have been compared to theoretical values (Fig. S1). In this study, the activation diameters are converted to the single hygroscopicity parameter, κ, using κ-Köhler theory (Petters and Kreidenweis, 2007) as follows,

\[
\kappa = \frac{4A^3}{27\ln^2S_Cd_s^3} \quad \text{where} \quad A = \frac{4M_w\sigma_w}{RT\rho_w}
\]  

(1)

and \(M_w\) and \(\rho_w\) are the molecular weight and density of water, respectively, \(R\) the universal gas constant, and \(T\), the ambient temperature. \(\kappa\) assumes the surface tension of
the droplet is that of pure water, $\sigma_w = 72 \text{ mN m}^{-1}$. $S_c$ is the critical saturation for a dry particle of diameter $d_s$. In our experiments we determine the critical particle mobility diameter for instrument $S$ with SMCA.

2.3 Results and Discussion

2.3.1 SOA Formation, Density, and Volatility

In the absence of OH scavenger, the yield of $\beta$-C-O$_3$ SOA was $25\%-49\%$ for initial $\beta$-C concentration of 5 ppb and increased up to $40\%-71\%$ for 20 ppb $\beta$-C. This result is consistent with previously reported yield of $45\pm 2\%$ in Lee et al. (2006). To explore the role of hydroxyl radicals in the $\beta$-C-O$_3$ reaction, low (~1 ppm) and high (~11 ppm) concentrations of OH scavenger (2-butanol) were injected into the chamber before the start of the reaction. The concentration of 2-butanol ($C_{4}H_{10}O$) was quantified by comparing the reaction rate of OH-2-butanol with that of OH-$\beta$-C, with the reaction rate for the 2-butanol 100 times larger. The addition of 2-butanol at low concentrations (~1 ppm) did not affect the aerosol yield ($25\%-40\%, 41\%-49\%$) for both 5 and 20 ppb $\beta$-C. Adding high concentrations of 2-butanol (~11 ppm) to the system resulted in relatively lower yields ($15\%-33\%, 11\%-43\%$). Using Carbon Monoxide (CO) as the scavenger reduced the aerosol yield to the same extent. Our result is consistent with Chen et al. (2012), in which SOA yield of $\beta$-C dark ozonolysis in the excess of O$_3$ (200 ppb) was $21.9\% \pm 2.0\%$ for 3.3 ppb $\beta$-C and $46.1 \pm 4.2\%$ for 6.6 ppb with cyclohexane as OH scavenger. The decreased yields for the reactions free of OH radicals confirmed that OH radicals played a significant role in the $\beta$-C-O$_3$ reaction chain.
With the presence of ~1 ppm OH scavenger, 0.25 ppm and 0.7 ppm isoprene-O₃ SOA yields were both 4%, higher than literature values (0.0015 in Czoschke et al. (2003) and 0.002 in Jang et al. (2002)). Kleindienst et al. (2007) estimated the ozone-isoprene reaction yield to be 0.01, with complete suppression of OH-isoprene reaction, and even higher yield without the presence of OH scavenger. When 0.25 ppm isoprene and 5 ppb β-C were both precursors, the aerosol yield was close to isoprene SOA (~3%). When the precursor was 0.7 ppm isoprene and 5 ppb β-C, higher yield (6%) was observed. For low yielding SOA precursor, there is the possibility that not all systematic errors have been accounted for. Causes that may lead to the underestimation of isoprene-O₃ yield include: 1) no correction of aerosol chamber wall loss, 2) the use of unit density instead of real time measured density (~1.36 g cm⁻³ as reported in this study) 3) over estimation of reacted isoprene amount due to the lack of gas phase online measurements, and 4) different experimental conditions, for example, presence of seed aerosol (Czoschke et al., 2003).

Figure 1 shows the evolution of aerosol density, $\rho_a$, as a function of time for O₃ reactions. The $\rho_a$ of β-C SOA decreased moderately after initial particle formation (~0.10 g cm⁻³). Measured densities were insensitive to oxidant concentrations (O₃ or OH); the addition of the OH scavenger had negligible effect on β-C SOA. Average $\rho_a$ was 1.26±0.04 g cm⁻³ and 1.20±0.01 g cm⁻³ for β-C-O₃ reactions with precursor concentrations of 5 ppb and 20 ppb, respectively. This result agreed with the dependence of density on organic mass concentration in Chen et al. (2012) and the prediction of aerosol density from O/C and H/C AMS data sets (Nakao et al., 2012; Kuwata et al.,
2012). Higher density ($\rho_a = 1.36 \pm 0.02 \text{ g cm}^{-3}$) was observed for isoprene SOA and $\beta$-C-isoprene SOA, suggesting that isoprene-generated aerosol likely dominated the SOA formed from the mixed hydrocarbon precursors when isoprene accounted for >95 wt% in precursor mixtures.

Volutility measured by VTDMA also proved that isoprene-generated SOA determined volatility of the SOA mixture. It required ~100 minutes to reach steady state of gas-to-particle phase partitioning, but the aged $\beta$-C-isoprene oxidation products showed similar volatility to isoprene SOA, with no dependence of volatility on the initial isoprene concentration. Isoprene reacting with O$_3$ formed notably more volatile aerosol than 5 ppb $\beta$-C; VFR of isoprene SOA and $\beta$-C SOA at 50°C were ~0.85 and ~0.95, respectively. The volatility of $\beta$-C SOA was lower with the presence of the hydroxyl radicals (data not shown), suggesting the suppressed $\beta$-C-OH reaction could produce more volatile material than $\beta$-C-O$_3$ reaction. Increase in the initial precursor concentration (5 to 20 ppb for $\beta$-C and 0.25 to 0.7 ppm for isoprene) had different effects on the SOA VFR. For $\beta$-C, SOA formed with higher precursor concentration exhibited higher volatility (Fig. 2), consistent with Duplissy et al. (2008a) who suggested that at higher precursor concentration, more volatile, less oxygenated compounds could partition into the particle phase. The opposite trend was observed for isoprene. Higher isoprene concentrations formed low volatility products quickly and suggest an increased fraction of oligomer formation with higher isoprene precursor concentration.
2.3.2 AMS Chemical Composition

The chemical composition of the aerosol was characterized with online HR-AMS measurements. High resolution mass spectra of \( \beta \)-C SOA and isoprene SOA formed under different conditions can be found in supplemental material. Fig. 3a showed the O/C ratio as a function of reaction time for the studied SOA systems. For the same precursor concentration, O/C of the SOA was comparable with and without the UV lights (Table 1); in both cases, stable O/C suggested no apparent aging of the formed aerosol. Slightly larger O/C was observed for SOA formed from 5 ppb \( \beta \)-C (0.30±0.07) than 20 ppb (0.26±0.02). The inverse correlation between organic particle mass and oxidation state has also been observed in Chen et al. (2012). As pointed in Chen et al. (2011b), the O/C and H/C ratios for SOA measured by AMS is systematically too low. Without specific calibration for CO\(^+\) and H\(_2\)O\(^+\), the reported O/C of 0.28-0.37 corresponds to our result of 0.24-0.35 (Fig. 4b). When OH reaction pathway was suppressed with high concentration of OH scavenger (~11 ppm), SOA with lower O/C formed in the first 50 minutes and correspond to first-generation products of \( \beta \)-C ozonolysis (0.13–0.29; Ding et al., 2011). Then, first generation products convert to second generation products with higher O/C (0.2–0.5; Ding et al., 2011). Comparison of high resolution mass spectra suggested that contribution of oxygen-containing ion fragments (e.g. C\(_3\)H\(_3\)O\(^+\), CO\(_2\)\(^+\)) increased with the formation of second generation products. Complete scavenging of OH oxidation pathway had negligible effect on SOA oxygenation state for 5 ppb and 20 ppb \( \beta \)-C SOA, as well as 1 ppm scavenger (Fig. 4b). Molecules containing more oxygen atoms are heavier, so that O/C values corresponded to aerosol density, in a manner of high O/C versus high density.
Isoprene oxidation products showed even higher O/C (~0.5) than β-C SOA (Fig. 3a, Fig. 4b, Table 1), independent of initial isoprene concentration. Aerosol yield data suggested higher isoprene concentrations produce more isoprene-generated SOA to the mixture precursor system. Hence O/C of SOA formed from 0.7 ppm isoprene and 5 ppb β-C was analogous to that of single isoprene system (~0.5), while from 0.25 ppm isoprene and 5ppb β-C, O/C was only 0.33. Unlike the β-C-O₃ reaction, small amounts of OH scavenger in the mix-precursor system with 0.25 ppm isoprene resulted in more oxidized SOA (O/C ~0.4 compared to ~0.33), while no impact on the system with 0.7 ppm isoprene (still ~0.5) was observed. It is inferred that changes in the mix-precursor aerosol are caused by changes in isoprene-generated SOA properties (with lesser O/C material) as β-C-generated SOA is not affected by OH scavenger. Kleindienst et al. (2007) suggested that up to 50% of the formed aerosol in an isoprene-O₃ reaction derive from the OH channel without an OH scavenger present. Isoprene-OH reaction produced less oxidized SOA than isoprene-O₃ reaction; so as the fraction of OH-initiated SOA decreased, O/C of the formed aerosol increased as a result of the OH scavenger present.

Aiken et al. (2008b) suggested a linear correlation between the fraction of m/z 44 in total organics (f₄₄) and O/C in ambient data sets, \( f_{44} = (0.0382 \pm 0.0005) \times (O/C) + (0.0794 \pm 0.0070) \) (Fig. 3b). This correlation can be used to estimate elemental composition from unit-mass resolution data of ambient SOA. Here we applied this method to the SOA formed from β-C and isoprene with O₃. The squared correlation coefficient \( R^2 \) of \( f_{44} \) and O/C was lower than 0.55 for β-C-O₃ and isoprene-O₃ systems, except for the β-C-H₂O₂ system \( (R^2=0.84) \). \( f_{44} \) of β-C-OH SOA was much lower than that
of $\beta$-C-O$_3$ SOA (Fig. 3b) and close to that of ambient aerosol (Duplissy et al., 2011a) such that high $f_{44}$ presence may be a reason for the weak correlation of $f_{44}$ and O/C of chamber $\beta$-C SOA. Another difference between chamber SOA and ambient aerosol is that for chamber $\beta$-C SOA no time resolved change of $f_{44}$ and O/C was observed, however, $R^2$ improved with the presence of isoprene. This suggested that in ambient conditions, where lower molecular weight terpenes coexists with sesquiterpene and OH radical chemistry is prevalent, the $f_{44}$ with O/C correlation may hold for BVOC SOA.

2.3.3 CCN Activity

$\beta$-C SOA was less CCN active than (NH$_4$)$_2$SO$_4$ ($\kappa$~0.6) but was more active than the previous measurements (Hartz et al., 2005; Table 1). In Huff-Hartz et al. (2005), the activation diameter at $ss$=1.0% was reported to be 152±26 nm for the SOA formed from 50 ppb $\beta$-C and 100 ppb O$_3$ (mixing ratio 1:2) in the presence of 2-butanol (6–13 ppm). Assuming constant surface tension and complete solubility, $\kappa$ was calculated to be 0.004. Asa-Awuku et al. (2009) reported smaller activation diameter at $ss$=1.02%, with 22 ppb $\beta$-C as precursor; activation diameter decreased from 90 nm to 70 nm within about 4 hours, with $\kappa$ increasing from 0.018 to 0.038. In summary, $\beta$-C SOA formed in the Carnegie Mellon University 12 m$^3$ chamber exhibited very low hygroscopicity ($\kappa$<0.04) and was not affected by the presence of OH scavenger. In our study, the mixing ratio of $\beta$-C to O$_3$ was around 1:10 (20 ppb $\beta$-C) or 1:40 (5 ppb $\beta$-C) with excess O$_3$ (initial concentration ranged from 100 ppb to 290 ppb). With ~11 ppm 2-butanol present, the activation diameter of dark ozonolysis SOA was much smaller, with a higher average $\kappa$ of 0.066±0.019 (Table 1b). In comparison with the previous studies, the decrease of
precursor concentration from 50 to 20 ppb or 5 ppb led to enhancement of the \( \beta \)-C SOA hygroscopicity, with an increase in \( \kappa \) by a factor of 16.5. This observation is consistent with Duplissy et al. (2008a) that showed the less oxygenated compounds formed at higher precursor concentration could result in less hygroscopic SOA. SOA was even more hygroscopic when no OH scavenger was present in the \( \beta \)-C-O\(_3\) reaction. \( \kappa \) ranged from 0.13 to 0.25 (Fig. 4a) and higher when precursor concentration was low (5ppb). Low concentration of OH scavenger also notably depressed CCN activity of \( \beta \)-C SOA (Table 1b, Fig. 4b), while lights had negligible effect. Asa-Awuku et al. (2009) confirmed that the hygroscopic fraction of \( \beta \)-C SOA was volatile. Here we can confirm that OH-participated reaction contributed to the formation of more volatile and more hygroscopic fraction of the \( \beta \)-C SOA. Gradual aerosol hygroscopic ageing was observed in the system with OH scavenger present. At the beginning of the experiment, \( \kappa \sim 0.03 \) was similar to Asa-Awuku et al. (2009). After 6 hours, the SOA became moderately active (\( \kappa \sim 0.09 \)). CCN activity of \( \beta \)-C SOA formed by OH photooxidation (\( \text{H}_2\text{O}_2 \) as hydroxyl radical source) was briefly examined. \( \beta \)-C-OH SOA showed lower hygroscopicity (\( \kappa = 0.100 \pm 0.018 \)) than \( \beta \)-C-O\(_3\) SOA, which suggests that OH indirectly promotes the formation of hygroscopic materials.

The hygroscopicity of isoprene SOA was lower than \( \beta \)-C SOA independent of initial isoprene concentrations (\( \kappa = 0.083 \pm 0.007 \) for 0.25 ppm and 0.138\( \pm 0.010 \) for 0.70 ppm; Table 1, Fig. 4a). As expected, CCN activity of mix-precursor SOA was between \( \beta \)-C SOA and isoprene SOA. A simple assumption can be made to estimate the contributions of hygroscopicity from isoprene and \( \beta \)-C like SOA. If additive,
\[ \kappa_{\text{mixture SOA}} = \kappa_{\text{isoprene SOA}} \cdot x + \kappa_{\beta-C \text{ SOA}} \cdot (1 - x) \]  

(2)

where \( \chi \) is the contribution of isoprene SOA. 5 ppb \( \beta\)-C SOA has \( \kappa \sim 0.22 \), 0.25 ppm isoprene SOA \( \kappa \sim 0.08 \), and the mix-precursor SOA have \( \kappa \sim 0.15 \). It is estimated that 50% of the aerosol exhibited \( \beta\)-C CCN behavior, when \( \beta\)-C accounted for <5% of the initial terpene concentration. Unlike density, volatility, or O/C, small amounts of \( \beta\)-C in the precursor mixture have significant contributions to the overall particle hygroscopicity.

The relationship between bulk chemical composition and \( \kappa \) was explored. Unlike chamber SOA from photooxidation of trimethylbenzene, \( \alpha\)-pinene and isoprene (Duplissy et al., 2008a; Jimenez et al., 2009), the O/C and \( \kappa \) of the \( \beta\)-C SOA (without OH scavenger) remained nearly constant during the dark ozonolysis process (Fig. 3a). Stable O/C values were observed after initial particle formation, indicating the products were not further oxidized (Sect 3.2). No correlation of O/C and \( \kappa \) has been observed for all conducted experiments (Figure 4b); \( R^2 \) value was consistently < 0.2. This data set suggests that a simple AMS O/C and \( \kappa \) empirical relationship can be complex and may not be used to predict \( \beta\)-C SOA systems. As suggested by Cappa et al. (2011), the observed hygroscopicity might be best modeled by both O/C and molecular size, especially in the case of OH aged systems.

Recent studies have proposed use of the bulk composition, \( f_{44} \) as a predictor of organic CCN (Duplissy et al., 2011b). \( f_{44} \) had little or no correlation to O/C or \( \kappa \) in the \( \beta\)-C system. Figure 5 shows \( R^2 \) of the hygroscopicity parameter \( \kappa \) versus different \( f_x \) for four types of experiments (\( \beta\)-C-O\(_3\) without scavenger, \( \beta\)-C-O\(_3\) with ~11 ppm scavenger,
isoprene-O₃, β-C-isoprene-O₃). The strongest correlation was observed for the system of β-C-O₃ with OH scavenger, in which $R^2$ between $\kappa$ and the fraction of $m/z$ 41, 42, 43, 44, 51, 67, 79 and 91 all exceeded 0.5. Except for m/z 43 ($C_2H_3O^+$) and m/z 44 ($CO_2^+$), all other abundant fragments consisted of one ion in the $C_xH_y$ ion family. For β-C-O₃ experiment, $f_{71}$ showed the strongest correlation with $\kappa$ among all $f_x$ ($R^2$~0.39). In comparison with the other two systems (isoprene-O₃, β-C-isoprene-O₃), no $f_x$ correlated with $\kappa$ with $R^2 > 0.39$. Linear correlations between $\kappa$ and $m/z$ of isoprene-O₃ SOA were the weakest but were improved by the presence of β-C. In conclusion, except for reaction systems with the additional presence of hydroxyl radicals, an empirical relationship with the mass fraction of fragment ions cannot be applied to predict β-C SOA CCN activity.

### 2.4 Summary and Implications

In this study, β-C-O₃ reaction was examined in regards to influences of OH scavenger, lights and another prominent biogenic VOC, isoprene. Chamber experiments were conducted at β-C concentrations of 20 ppb and 5 ppb with excess ozone. Higher precursor concentration lead to more volatile products condensing into the particle phase. The measured differences in SOA properties agreed with this theory. Compared with 5 ppb β-C, 20 ppb β-C with O₃ formed more SOA with lower density, hygroscopicity, O/C and higher volatility. Low concentration of OH scavenger (~1 ppm) had notable impacts on SOA volatility and hygroscopicity; when β-C-OH reaction was completely scavenged, SOA showed lower O/C, lower volatility and similar density. Results indicated that β-C-
OH reaction in the β-C-O₃ system promoted formation of highly oxidized and volatile aerosol. Loss of volatile components could explain the decrease of CCN activity in the OH-scavenged system. Given that β-C-H₂O₂ reaction does not produce more hygroscopic SOA than β-C-O₃ reaction, it supports the theory that OH reacts with key reactive intermediates to form second generation products with higher CCN activity.

This study suggests that β-C-O₃ SOA is a potentially important contributor to biogenic CCN. The hygroscopicity of β-C SOA (average κ ~0.2) formed from 5 or 20 ppb β-C was higher than previous β-C studies with higher precursor concentration (50 ppb) and ambient SOA (κ~0.13). Similar low κ values (<0.1) as previously reported were only obtained in the presence of high OH scavenger concentrations; hence OH measurements may be required for a direct comparison of experiments conducted in different chambers. The highly hygroscopic β-C-O₃ SOA should be considered in global models as a contributor of biogenic CCN.

Isoprene with ozone showed a much smaller yield than β-C, but isoprene SOA was more oxidized yet less hygroscopic than β-C SOA. In the ambient, isoprene may coexist with β-C in many locations with densely populated plants. Thus it is necessary to study the SOA properties with multiple precursors. β-C precursor with the presence of isoprene formed SOA that physically (density, volatility) exhibited properties similar to isoprene SOA (independent of initial concentrations 0.25 ppm or 0.70 ppm). Chemically (e.g. oxidation state), the mix-precursor aerosol behaved more like 0.70 ppm isoprene SOA because of the larger contribution of isoprene-generated SOA to total SOA mass. However, β-C SOA still dominated the hygroscopicity of the mix-precursor SOA even
when it was not the mass-predominant precursor. This result further emphasizes the significant role of β-C SOA as biogenic CCN in the ambient. O/C and $f_{44}$ of the β-C-O$_3$ and isoprene-O$_3$ SOA showed weaker correlations than ambient SOA. The correlations of κ and the most abundant mass-to-charge ratios were also insignificant in this study, making β-C SOA a unique system that cannot be easily predicted with AMS data and an empirical correlation. Our study concludes that SOA formed from multiple precursors instead of a single VOC species are complex and their water-uptake exhibit significant non-linear behavior.
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Table 2.1 Experimental conditions without OH scavenger

<table>
<thead>
<tr>
<th>β-caryophyllene (ppb)</th>
<th>Isoprene (ppm)</th>
<th>O₃ (ppb)</th>
<th>H₂O₂ (ppm)</th>
<th>Lights</th>
<th>Average O/C</th>
<th>Average κ</th>
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Table 2.2 Experimental conditions with OH scavenger

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<th>Isoprene (ppm)</th>
<th>O₃ (ppb)</th>
<th>2-butanol (ppm)</th>
<th>Lights</th>
<th>Average O/C</th>
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<td>0.138 ± 0.010</td>
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</tbody>
</table>
2.7 Figures

Figure 2.1 Particle density, $\rho_a$ (g cm$^{-3}$), as a function of reaction time. In each reaction, ozone was the oxidant and no OH scavenger was present unless specified (e.g. 5 ppb $\beta$-C w/ scavenger).
Figure 2.2 Time series of volume remaining fraction (VFR) of β-C SOA and isoprene SOA at 50°C. There was no OH scavenger in all the experiments shown in the graph.
Figure 2.3 a) Time series of O/C for dark experiments between O₃ and β-C/ isoprene. No OH scavenger was present in the reaction unless specified. b) Scatter plot of aerosol $f_{44}$ as a function of O/C with equation and $R^2$ of linear regression fit. The two dashed lines represent upper and lower bound of $f_{44}$-predicted O/C using the empirical correlation of $f_{44}$ and O/C described in Aiken et al. (2008b), $f_{44} = (0.0382 \pm 0.0005) \times (O/C) + (0.0794 \pm 0.0070)$. 
Figure 2.4 a) Time resolved $\kappa$ values for different reaction systems. Without OH scavenger, $\kappa$ of $\beta$-C SOA ranged from 0.13 to 0.25 (shade area) with no significant change during the period of each experiment. b) Plot of average $\kappa$ versus O/C using data in Table 1a and 1b.
Figure 2.5 Linear regression correlations (represented by $R^2$) between $\kappa$ and the abundant mass-to-charge ratios ($m/z$) of O$_3$-initiated SOA.
3 The effects of mainstream and sidestream environmental tobacco smoke composition for enhanced condensational droplet growth by water vapor

3.1 Introduction

Adverse health effects from particulate matter (PM) are caused by the deposition of particles in the respiratory tract during inhalation. The water vapor uptake by hygroscopic components can alter dry particle size and deposition efficiencies (Broday and Georgopoulos, 2001; Blanchard and Willeke, 1984; Varghese and Gangamma, 2009; Londahl et al., 2009; Kane et al., 2010; Schroeter et al., 2001; Phalen et al., 2010). Therefore, the dose and deposition site of these aerosols are influenced by the growth of the particles. Relative humidity (RH) in the lung is estimated at 99.5% RH (Anselm et al., 1990), and more recent work has calculated instantaneous values in the supersaturated range (up to 104% RH; Longest and Xi, 2008; Varghese and Gangamma, 2009; Longest et al., 2010) in the upper airways. At large RH, enhanced condensational growth (ECG) may occur, droplets may form (Longest et al., 2010) and dry particles will effectively behave as cloud condensation nuclei (CCN) within the respiratory system. Longest and Xi (2008) suggests that condensational growth may play a significant role in the deposition of cigarette smoke particles in the upper airways. Both size and composition influence the ability of particles to act as CCN (Andreae and Rosenfeld, 2008). The following study explores the aerosol composition of inhaled cigarette smoke in relation to ECG via the deposition of water vapor and CCN properties.
Cigarette smoke is an aerosol of liquid droplets (i.e., particulate phase) suspended in a mixture of gases and semi-volatile compounds (Ingebrethsen, 1986). More than 4000 components have been identified in tobacco smoke (Thielen et al., 2008), of which at least 50 are carcinogenic (Hoffmann and Hoffmann, 1993; Roberts, 1988). A number of potent lung carcinogens for humans, such as the polycyclic aromatic hydrocarbons (PAHs), tobacco-specific nitrosamines (TSNAs), phytosterols and the metals, are found only in the particulate phase (Hoffmann et al., 1996). The dry size of these particles in fresh inhaled smoke ranges from 0.1 to 1 μm in diameter and may reach the deep lung where the gas exchange takes place. Secondhand or environmental tobacco smoke (ETS) is aged and the combination of diluted “sidestream” smoke (released between puffs from the lit end of the cigarette) and “mainstream” smoke (exhaled by a smoker). Here we note, that the mainstream smoke is not humidified in the set-up; we characterize the water-uptake of the dry particle formed by the mainstream process. The mixture between sidestream and exhaled mainstream smoke in the environment after dilution and aging is often referred to as ETS and is a significant source of human exposure to fine particles (Klepeis et al., 2003).

The source and transformation during transport before inhalation are important for aerosol chemistry. Yadav et al. (2004) used a single particle time-of-flight mass spectrometer to show that the size and composition of fresh and aged smoke significantly differ. Sleiman et al. (2010) showed that additional products are formed during the photo-oxidative aging of ETS and suggested the water-soluble organic aerosol content is
enhanced in the presence of water vapor. Aerosol components that are water-soluble or surface active may affect the droplet growth rates.

The aged aerosol contributions to droplet growth from the respective mainstream and sidestream types of ETS are explored. Understanding the inhalation of smoke, specifically the links between the physicochemical properties and wet deposition rates are important. The goal of this study is to further characterize cigarette smoke, with an emphasis on wet enhanced condensational growth, represented by CCN activity and droplet formation properties. Changes in particle size, chemistry, and volatility are correlated to changes in droplet behavior from offline and online chemistry measurements.

### 3.2 Experimental Methods

A Walton Smoking Machine (WSM) produced mainstream and sidestream ETS. The operation and characterization of the instrument has been previously reported (Guerin et al., 1979; Chen et al., 1990). Two types of reference cigarettes, 1R5F and 3R4F (College of Agriculture, University of Kentucky), were tested with the WSM. The 3R4F is a low nicotine (LN) research cigarette and the 1R5F is an ultra low nicotine (ULN) research cigarette. Table 1 shows manufacturer specifications of both cigarettes. The ULN 1R5F reference cigarette produces significantly (~ 5 to 7 times) less particle, tar, and nicotine mass per cigarette than the LN 3R4F (Table 1, http://www.ca.uky.edu/ref cig/). Hence measurements in this study are normalized by
total number concentration for direct comparison of cigarette composition and contribution to water uptake ability. Two cigarettes of the same type were simultaneously smoked at the WSM. Testing followed the International Organization for Standardization (ISO) smoking protocol for smoking puff volume, duration, and frequency. The puff air volume was 35 cm$^3$ per puff; the duration was 2 s per puff and the frequency was 1 cycle per 60 s. As per ISO protocol, the vent blocking was 0% for WSM measurements. Mainstream smoke via the vent hole fitting of the WSM was collected in a 27 L stainless steel reservoir chamber. The chamber provided constant sample flow and consistent aerosol phase mixing conditions for subsequent particle sizing and hygroscopicity measurements. Hence the smoke produced and sampled by this method is representative of aged, non-humidified mainstream ETS. Sidestream ETS was funneled and diluted with compressed air by an ejector pump to simulate dilution conditioned secondhand smoke, which then was also collected in the stainless steel reservoir chamber.

Mainstream and sidestream ETS were size-selected with a scanning mobility particle sizer (SMPS, TSI 3080) and a condensation particle counter (CPC, TSI 3772). A Droplet Measurement Technologies Continuous-Flow Streamwise Thermal Gradient CCN Counter (CCNC) was operated in parallel with the CPC (Roberts and Nenes, 2005); CCNC counted the CCN concentration of size-selected aerosol while the CPC counted the condensation nuclei (CN) concentration. The CCNC instrument was calibrated with ($\text{NH}_4)_2\text{SO}_4$ aerosol. The critical diameter where CCN/CN=0.5, $d_{p50}$, of the ($\text{NH}_4)_2\text{SO}_4$ aerosol at the custom-set supersaturation (e.g. 0.6% and 1.0%) determined the varying instrument supersaturation $s$ (e.g., 0.54% and 0.85%). $s = S$ (saturation ratio) -1 and is
usually expressed as a percentage. The sample flow rates of CPC and CCNC were 1 and 0.5 L min\(^{-1}\), respectively. The sheath-to-aerosol ratio of both SMPS and CCNC instruments was 10:1. Previous work of Robinson and Yu (1998) suggest that \( s < 0.5\% \) is not large enough to activate cigarette smoke aerosol. In this study the CCNC \( s \) was set to be 0.54% and 0.85%, much smaller values and more likely to be instantaneous high RH in airways. At a constant CCNC supersaturation, \( s \), the activated fraction (CCN/CN) of the dry particle mobility size distribution was obtained every minute (~ one cycle of the WSM). \( d_{p50} \) was calculated using Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010). By applying the \( \kappa \)-Köhler theory proposed by Petters and Kreidenweis (2007), CCN activity of the smoke was represented using a single hygroscopicity parameter \( \kappa \), which gathers all the composition-dependent variables and can be determined experimentally from CCNC data (\( s \) and \( d_{p50} \)). \( \kappa \) can be used to describe hygroscopic particle growth at both subsaturated and supersaturated RH regimes (Petters and Kreidenweis (2007)).

In addition to dry \( d_{p50} \) and hygroscopicity information, the CCNC can also measure droplet growth size at the exit of the instrument column. The instrument optical particle counter provides size resolved droplet concentrations. The droplet growth information is assessed using the method of Threshold Droplet Growth Analysis (TDGA, e.g. Asa-Awuku et al., 2010;Padro et al., 2010). TDGA can directly assess the impact of organics on CCN growth kinetics by comparing the droplet sizes of activated aerosol particles with \((\text{NH}_4)_2\text{SO}_4\) particles at identical instrument \( s \). Wet diameters of particles with dry diameters equal to critical diameters (\( d_{p50} \)) are selected in this study.
The aerosol composition is characterized with online and offline methods in separate experiments. A catalytic stripper (CS) removed volatile components from smoke samples (Abdul-Khalek and Kittelson, 1995;Kittelson et al., 2005;Zheng et al., 2010;Stenitzer, 2003). Two different catalysts, Oxicat® and S-trap, remove hydrocarbon and sulfur components from the aerosol at 300 °C. Afterwards, a coil cools the sample to ambient temperatures. The flow rate through the CS is 1 L min⁻¹ for this study.

Smoke is sampled by an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS or HR-AMS) (Jimenez et al., 2003;DeCarlo et al., 2006a) at a rate of 1.3 cm³ s⁻¹. Unit mass resolution (UMR) data discerns differences in mass to charge (m/z) ion fragmentation. The elemental composition and oxidation state is examined with high resolution (HR) data analysis (Aiken et al., 2008b;Aiken et al., 2007b).

Offline filter measurements characterize the surface tension, water-soluble organic carbon (WSOC) and elemental carbon (EC) fraction of the organic aerosol. Filters are pre-weighed to estimate the total aerosol and organic mass (OM). Teflon Filters (PALL® Life Sciences, 47mm) were extracted in 18.2 MΩ of ultra pure water (Milli-Q Advantage A10 Ultrapure Water Purification System). Large insoluble particles were filtered from the solution using Whatman® 25 mm GD/X syringe filters, and then analyzed by a Sievers 900 portable Total Organic Carbon (TOC) Analyzer (GE) for dissolved organic carbon concentration. The water-soluble organic mass fraction, \( f_{WSOM} \), is inferred by multiplying the dissolved organic carbon concentration from TOC measurement by the organic mass to organic carbon (OM/OC) ratio defined by HR-AMS.
The EC/OC content was obtained by analyzing loaded quartz filter with a Sunset Laboratory (Forest Grove) Thermal/Optical Carbon Aerosol Analyzer. Surface tension values of the water extracted filter samples are measured with an Attension T-200 Pendant Drop Tensiometer.

3.3 Results and Discussion

3.3.1 Size Distribution, Volatility, and Organic Chemical Composition

Previous studies report particle sizes of cigarette smoke ranging from 0.1 to 1.5 μm, using various cigarette types, dilution ratio and measurement techniques (Chen et al., 1990; Bernstein, 2004). In comparison, we use the current, state-of-the-art real time particle sizing instrument, SMPS, which selects particles with size ~6 nm to 210 nm. Furthermore, the aerosols are from two low-nicotine research cigarettes. As a result, differences in cigarette smoke particle sizes and composition are expected. Results from the WSM are consistent with Chen et al. (1990) and show that after one puff, the composition and number of particles remains consistent for a given cigarette type. Both low and ultra-low nicotine smoke are formed with the aforementioned experimental set-up. Mainstream and sidestream ETS produce well-mixed and stable particle size distributions (Fig. 1). The particle number concentration was normalized by total concentration of each sample. For a given cigarette type, the gas to condensed phase partitioning from mainstream and sidestream ETS forms similar aerosol distributions. LN 3R4F ETS forms smaller particles than ULN 1R5F ($D_{p,\text{mode}} \sim 88$ nm, in mainstream and
sidestream ETS). 1R5F ETS forms aerosol distributions with larger modes, $D_{p,\text{mode}} = 113$ ± 4.1 nm and $D_{p,\text{mode}} = 88.2$ ± 3.2 nm in sidestream and mainstream modes, respectively. ULN cigarettes produce aerosol at larger sizes (Fig. 1). Differences in dry aerosol size distribution are due to variations in partitioning and condensation of volatiles into particle phase.

The majority of mainstream and sidestream ETS are organic and semi-volatile (Table 1, and Fig. 2). The EC/OC fraction constitutes less than 1% of the aerosol mass fraction. Catalytic stripper data in Figure 2 supports EC/OC measurements and shows that ~1% (by volume) of the material is non-volatile (evaporates at > 300°C) between 60 to 100 nm.

HR-AMS results compare the non-refractory and semi-volatile particulate composition formed by the two cigarette types in mainstream and sidestream ETS. Organics comprise more than ~95% of the total non-refractory and semivolatile aerosol mass. K$^+$ is the most prevalent inorganic ion mass fragment (< 3%) in both cigarettes. The OM/OC, O/C, and N/C ratios in mainstream smoke are larger than those in sidestream (Table 1); indicative of more oxidative materials present in the particulate phase of the main stream smoke due to higher combustion temperature. The properties of LN and ULN ETS are similar; however ULN mainstream aerosol contains slightly more nitrogen containing compounds than LN mainstream ETS in the particulate phase (Table 1). The inferred $f_{\text{WSOM}}$ ranges from 32 to 85%. 3R4F contains similar amounts of WSOC in side and mainstream ETS. 1R5F ETS contain more soluble mass; $f_{\text{WSOM}} = 45$ and 85% in mainstream and sidestream ETS, respectively (Table 1). For samples with 10.6 ppm
WSOC, the surface tension was 71.5 ± 0.7 mN m⁻¹ and similar to that of water at room temperature (72 mN m⁻¹). At higher concentrations (~39 ppm), the dissolved material only slightly depress surface tension (<5%). Hence water-soluble components of both main and sidestream ULN and LN smoke are non-surface active at ECG activation concentrations.

All experiments show abundance in the UMR m/z 43 fragmentation ion (Fig. 3 and Fig. 4). We normalized the signal intensity of all fragment ions by that of m/z 43. The fraction of m/z 43 ion in the total organic signal, f₄₃, equals 8.5 ± 0.1% in both LN and ULN mainstream ETS. HR analysis indicates that both oxidized (C₂H₅O⁺) and non-oxidized (C₃H₇⁺) species exist in the m/z 43 ion fragment. Significant differences are observed in the UMR and HR-AMS data. For example, the ratio (Rx) of LN to ULN mass spectra mainstream ETS at m/z 29 ion, R₂⁹ = 1.6 (Fig. 3); 3R4F forms 60% more aerosol fragments at m/z 29 (Formyl radical, CHO). However the majority of differences, Rx < 0.95 and > 1.10, are at m/z ions > 43 (Fig. 3). LN aerosol forms larger molecular weight fragments and aerosol than ULN. Prevalent Rx differs by 14 ions (e.g., R₅⁷, R₇¹, R₈₅); consistent with changes in CH₂⁺ and N⁺ fragments.

A comparison of LN 3R4F ETS shows f₄₄ ion in mainstream smoke is twice that in sidestream (Fig. 4). HR data shows key fragments have significantly more oxidized components. In LN mainstream and sidestream ETS, the oxidized contribution to UMR m/z 44 differs; the relative contribution of CO₂⁺ ions is more in mainstream (0.89±0.08) versus sidestream (0.66±0.03) LN smoke. In ULN sidestream m/z 44 ion fragment contains less oxidized CO₂⁺ (0.53±0.02).
3.3.2 CCN Activity and Droplet Formation

The ability of ETS to form droplets is less than that of inorganic salts (Fig. 5, Table 2). At $s = 0.85\%$ and $0.54\%$, $(\text{NH}_4)_2\text{SO}_4$ aerosol will form droplets at 30 and 38 nm respectively. These values respond to $\kappa \sim 0.6$. Calculation of $\kappa$ assumes no surface tension depression and complete solubility in the droplet, in which case $\kappa$ is inversely proportional to activation diameter ($d_{p50}$). Mainstream LN and ULN aerosol will form droplets at larger dry sizes (~50 and 70 nm) and are less hygroscopic than inorganic salts. The calculated $\kappa$ is consistent with values of organic and semi-volatile origin (Duplissy et al., 2008b; Poulain et al., 2010). The smoke formed in mainstream and sidestream smoke of LN cigarettes are of similar distribution and hygroscopicity ($\kappa \sim 0.15$) (Fig 1 and Table 2). The change in oxygenation (OM/OC, or O/C) of the bulk aerosol composition has little or no effect on bulk aerosol hygroscopicity. Figure 6 shows that the droplets formed at activation from 3R4F and 1R5F smoke grow to sizes, statistically similar to $(\text{NH}_4)_2\text{SO}_4$, and indicate similar growth kinetics. Despite being less hygroscopic ($\kappa < 0.6$, Table 2), organic ETS have the same droplet growth rates as soluble $(\text{NH}_4)_2\text{SO}_4$ particles.

The particle size distribution of the aerosol formed will determine the number of particles that experience ECG. Because the activation diameters for both cigarette types produce aerosol of similar hygroscopicity ($\kappa \sim 0.15$), ULN 1R5F cigarettes will produce more aerosol that activate and form droplets. At 0.54 and 0.85\% $s$, 58 and 79\% of the 3R4F mainstream and 68\% and 86\% of the 1R5F mainstream respectively experience ECG and will form droplets at larger $\mu$m sizes. The presented values are percentages of
the total aerosol distribution; as LN particles can produce 5 times more particulate matter than ULN cigarette types the absolute number concentrations must be accounted for (Table 1).

### 3.4 Summary and Implications

ETS aerosol is organic and is comprised of slightly soluble compounds. Particles exhaled through mainstream breath produce more oxidized aerosol. The single hygroscopicity parameter, $\kappa \sim 0.15$ is consistent for partially soluble organic aerosol and suggests that the smallest particles are unlikely to form droplets, and experience enhanced condensational growth (ECG) by water vapor. With this single hygroscopicity parameter, the water uptake of the aerosol can be estimated at sub and supersaturated RH levels. The aerosol that experience ECG in supersaturated regimes will grow to similar droplet sizes as soluble inorganic aerosol. The droplet growth kinetics of ETS is not dependent on solute composition for cigarette smoke particles tested in this study. Depression of surface tension is minor (<5%) for mainstream and sidestream smokes of both cigarette types. Slight changes in bulk aerosol composition do not significantly affect overall CCN activity; hence the wet deposition of mainstream and sidestream ETS in supersaturated regimes is expected to be similar. Our study shows that reference cigarette ETS are hygroscopic and will have similar lung deposition rates despite source. Additional study may be required for the diverse varieties of commercially available cigarettes. Significant changes in aerosol composition (beyond differences in nicotine
content) may alter ETS number, size, and composition. The fraction of particles that experience ECG must be treated differently in deposition models from those that do not. Particle size distribution and hygroscopicity must be considered to model inhalation, dry, and wet deposition rates of ETS. The single parameter, $\kappa \sim 0.15$, reported here can be used to approximate the importance of ECG for ETS.
3.5 References


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the chemistry of atmospheric organic aerosol, Nat. Chem., 3, 133-139, 10.1038/nchem.948, 2011.


growth kinetics of the water-soluble aerosol fraction in Mexico City, J Geophys Res-Atmos, 115, D09204, Artn D09204


Table 3.1 Aerosol Composition Characteristics of Cigarette Smoke. The aerosol phase is composed of semi-volatile organics, and EC makes up < 1% of the total organic carbon. O/C ratio of mainstream ETS is larger than sidestream smoke.

<table>
<thead>
<tr>
<th>Type</th>
<th>TPM(^a) [mg per cig.]</th>
<th>Tar(^a) [mg per cig.]</th>
<th>Nicotine(^a) [mg per cig.]</th>
<th>stream</th>
<th>O/C</th>
<th>N/C</th>
<th>OM/OC</th>
<th>( f_{PM2.5} )</th>
<th>EC/OC</th>
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<td>main</td>
<td>0.224 ± 0.001</td>
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<td>1.786 ± 0.073</td>
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<td>side</td>
<td>0.091 ± 0.001</td>
<td>0.031 ± 0.001</td>
<td>1.299 ± 0.005</td>
<td>0.85 ± 0.024</td>
<td>0.007</td>
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<td>9.4</td>
<td>0.73</td>
<td>main</td>
<td>0.212 ± 0.019</td>
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<td>1.616 ± 0.062</td>
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<tr>
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<td></td>
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<td></td>
<td>side</td>
<td>0.136 ± 0.003</td>
<td>0.038 ± 0.003</td>
<td>1.369 ± 0.007</td>
<td>0.32 ± 0.001</td>
<td>0.01</td>
</tr>
</tbody>
</table>

TPM = Total Particulate Mass

\(^a\)University of Kentucky (http://www.ca.uky.edu/ref cig/)

BDL = Below Detection Limits
Table 3.2 Aerosol activation and average single-parameter hygroscopicity data.

<table>
<thead>
<tr>
<th>Type</th>
<th>stream</th>
<th>$\kappa_{avg}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1R5F (ULN)</td>
<td>main</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>side</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td>3R4F (LN)</td>
<td>main</td>
<td>0.15 ± 0.01</td>
</tr>
<tr>
<td></td>
<td>side</td>
<td>0.15 ± 0.02</td>
</tr>
</tbody>
</table>
Table 3.3 List of abbreviations.

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CN</td>
<td>Condensation Nuclei</td>
</tr>
<tr>
<td>CCN</td>
<td>Cloud Condensation Nuclei</td>
</tr>
<tr>
<td>CPC</td>
<td>Condensational Particle Counter</td>
</tr>
<tr>
<td>EC</td>
<td>Elemental Carbon</td>
</tr>
<tr>
<td>ECG</td>
<td>Enhanced Condensational Growth</td>
</tr>
<tr>
<td>ETS</td>
<td>Environmental Tobacco Smoke</td>
</tr>
<tr>
<td>HR-ToF-AMS</td>
<td>High Resolution Time-of-Flight Aerosol Mass Spectrometer</td>
</tr>
<tr>
<td>or HR-AMS</td>
<td></td>
</tr>
<tr>
<td>ISO</td>
<td>International Organization for Standardization</td>
</tr>
<tr>
<td>LN</td>
<td>Low Nicotine</td>
</tr>
<tr>
<td>N/C</td>
<td>Nitrogen-to-Carbon ratio</td>
</tr>
<tr>
<td>O/C</td>
<td>Oxygen-to-Carbon ratio</td>
</tr>
<tr>
<td>OM/OC</td>
<td>Organic-Mass-to-Organic-Carbon ratio</td>
</tr>
<tr>
<td>RH</td>
<td>Relative Humidity</td>
</tr>
<tr>
<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
</tr>
<tr>
<td>ULN</td>
<td>Ultra-Low Nicotine</td>
</tr>
<tr>
<td>UMR</td>
<td>Unit Mass Resolution</td>
</tr>
<tr>
<td>WSM</td>
<td>Walton Smoking Machine</td>
</tr>
<tr>
<td>WSO OC</td>
<td>Water-Soluble Organic Carbon</td>
</tr>
<tr>
<td>WSOM</td>
<td>Water-Soluble Organic Mass</td>
</tr>
</tbody>
</table>
Figure 3.1 Particle Size distributions from mainstream and sidestream ETS. 1R5F cigarettes form particles of larger modes in both mainstream and sidestream ETS. Because the activation diameters for both cigarette types produce aerosol of similar hygroscopicity ($\kappa \sim 0.15$), ULN 1R5F cigarettes will produce more aerosol that activate and form droplets.
Figure 3.2 Exemplary volatility data from Catalytic Stripper measurements. Log normal particle distribution of ETS and nonvolatile aerosol are measured. The semivolatile distribution is inferred. Inset graph shows the semivolatile fraction as a function of particle mobility diameter. The majority of 3R4F aerosol is semivolatile and evaporates at temperatures below 300°C.
Figure 3.3 Exemplary $m/z$ 43 normalized UMR mass spectra of 3R4F (purple) to 1R5F (pink) mainstream ETS. Prominent peaks where the ratio LN 3R4F to ULN 1R5F mass spectra, $R$, is (a) $<0.95$ and (b) $>1.10$ are shown.
Figure 3.4 Exemplary m/z 43 normalized UMR mass spectra of ULN 3R4F main (purple) to ULN 3R4F (blue) sidestream ETS. The m/z 43 is the most abundant fragment in both cigarette types but is formed less in Main (8.5%) vs. Side (9.8%) stream smoke.
Figure 3.5 Activated fraction (CCN/CN) versus particle mobility diameter of mainstream ETS for $s_c$ at 0.85% (closed) and 0.54% (open). (NH$_4$)$_2$SO$_4$ calibration data (circles) is highly soluble in water and shown for comparison. LN 3R4F (triangles) have slightly smaller activation diameters, $d_{p50}$, compared to ULN IR5F (squares) aerosol. $\kappa$ (-0.15) of both cigarette types are consistent with partially soluble organic aerosol components.
Figure 3.6 Droplet growth of LN and ULN ETS. Both LN 3R4F (triangles) and ULN IR5F (squares) aerosol grow to similar sizes as (NH$_4$)$_2$SO$_4$ (circles) at activation in the CCNC instrument. This indicated similar growth kinetics. Despite being less hygroscopic ($\kappa < 0.6$, Table 2), organic ETS have the same droplet growth rates as soluble (NH$_4$)$_2$SO$_4$ particles. The shaded area is the region of measurement uncertainty ± 0.5 µm.
4 NO$_3$ radical, OH radical and O$_3$- initiated secondary aerosol formation from aliphatic amines

4.1 Introduction

Atmospheric aerosols can be divided into two categories: primary aerosol and secondary aerosol. Primary aerosols are directly emitted from a variety of sources (e.g. dust, sea salt, combustion emission, etc.), while secondary aerosol are formed in the atmosphere through a series of atmospheric reactions and gas-to-particle partitioning. Aerosols scatter and absorb solar and terrestrial radiation, influence cloud formation by acting as cloud condensation nuclei (CCN) and participate in heterogeneous chemical reactions in the atmosphere, thereby affecting the abundance and distribution of atmospheric trace gases (Andreae and Crutzen, 1997; Haywood and Boucher, 2000). Atmospheric aerosols also have an important impact on human health (Pope and Dockery, 2006), e.g. they can cause or enhance respiratory, cardiovascular, infectious, and allergic diseases (Bernstein et al., 2004; Finlayson-Pitts and Pitts, 1997). Due to the limited knowledge of aerosol sources, composition, properties, and mechanism of formation in the atmosphere, the effects of aerosols on climate and health are still far from being fully understood and quantified.

Secondary organic aerosol (SOA) has been identified as a potentially important contributor to the atmospheric particulate mass (Seinfeld and Pankow, 2003). Goldstein and Galbally (2007) estimated SOA production of ~510–910 Tg carbon per year (C/yr) out of the 1300 Tg C/yr of VOCs emitted, which accounts for about half of the VOC
emissions to the atmosphere. Inorganic compounds (e.g. ammonium sulfate, nitrate, sea salt and wind-blown dust) also comprise a relatively large fraction of fine particle mass (25-50%, Gray et al., 1986). As derivatives of ammonia, amines have a similar acid-neutralizing capability to form inorganic salts and have been measured in both gas and particle phases. Ge et al. (2011c) summarized a series of studies and identified a total of 154 amines in the atmosphere, derived from anthropogenic and biogenic sources. For example, anthropogenic sources of amines include animal feeding operations (Luebs et al., 1973; Lunn and Vandevyver, 1977), food processing (Passant et al., 1993; Tsuji, 1971), and combustion (Joseph and Browner, 1980; Rosenberg, 1984), etc.. Measured gas-phase amine concentration at different sampling sites varied from ppt level to more than a few hundred ppb, with high concentrations of aliphatic amines being detected around animal feedlots. Rabaud et al. (2003) detected numerous amines in the air at a dairy with concentrations up to 560 µg/m³ (187 ppb) for butylamine (BA). Schade and Crutzen (1995) determined that amine emissions from animal husbandry was composed of three methylamine derivatives, with trimethylamine (TMA) present in the highest concentration. On the other hand, the presence of amine in the particle phase has been indicated by a series of single particle laser desorption/ionization-mass spectrometry (SPLDI-MS) studies (Murphy and Thomson, 1997; Glagolenko and Phares, 2004; Zhang et al., 2012).

Atmospheric removal routes for amines include reactions with acids (nitric or sulfuric acid) and/or oxidants (e.g. OH, O₃, and NO₃) (Seinfeld and Pandis, 2006a; Finlayson-Pitts and Pitts, 2000; Silva et al., 2008). Multiple detection of particle
phase amines in ambient samples validated the amine salt formation via acid-base reactions (Table 7 in Ge et al. (2011c)), while chamber studies showed that oxidation also lead to amine SOA formation. Malloy et al. (2009d) proved that reactions between primary amines and NO$_3$ were sufficiently fast to be competitive with acid-base reactions, resulting in aerosol dominated by organic compounds. Rapid reaction was also observed between trimethylamine and nitrate radicals, forming a large amount of secondary organic aerosol (Silva et al., 2008). Consequently, there is a high probability that inorganic and organic components co-exist in ambient amine-containing particles, especially in areas abundant with gas phase amines. Direct dissolution of amines into existing wet particles under humid conditions is also highly likely, due to their water solubility. A series of studies have reported the strong dependence of mass of particle-phase amines, especially TMA, on relative humidity (Glagolenko and Phares, 2004; Zhang et al., 2012; Rehbein et al., 2011). Presence of water may also involve radical oxidation and may impact the reaction pathway and aerosol yield to some extent (von Hessberg et al., 2009; Jonsson et al., 2006). Previous chamber studies have not reported the effect of humidity on amine aerosol formation and characteristics, so the relative importance of humidity is still poorly understood.

Identification and quantification of aminium salts have been performed using a series of online and offline instruments: Aerodyne Time of Flight Aerosol Mass Spectrometer (cToF-AMS) (Murphy et al., 2007; Sorooshian et al., 2008), High Resolution ToF-AMS (HR-ToF-AMS) (Malloy et al., 2009d; Sun et al., 2011; Ge et al., 2012), Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) (Smith et
al., 2010), ion chromatography (Erupe et al., 2010; VandenBoer et al., 2012) and Particle Into Liquid Sampler- Ion Chromatography (PILS-IC) (Murphy et al., 2007; Sorooshian et al., 2008; Sun et al., 2011). The difficulty in using the AMS as a tool to quantify amine aerosol is that response factors for different amine salts vary significantly (Silva et al., 2008), thus the AMS can only be used to identify amine-related ion peaks and obtain ion fragment information. PILS-IC, on the other hand, can speciate and quantify the calibrated aminium ions (cations) as well as nitrate and sulfate ions (anions) while independent of amine salt species and ionization efficiencies. To improve our understanding of amine atmospheric reactions and the chemical nature of formed aerosol, both AMS and PILS-IC are indispensable.

This study focused on aerosol formation from three amines: butylamine (BA), diethylamine (DEA) and trimethylamine (TMA), selected as representatives of the primary, secondary and tertiary amine species. We reported the relative abundance of organic/inorganic components in the chamber aerosol. We also examined composition and characteristics of amine aerosol formed under different relative humidities, in order to study the effect of water vapor in the reactions.

4.2 Experimental Setup

All experiments were conducted in the mezzanine chamber at the Center for Environmental Research and Technology, College of Engineering, University of California, Riverside (CE-CERT/UCR). The schematic of the chamber and instruments can be found in the supplementary material (Fig. S1). The CE-CERT mezzanine chamber
consists of a 12.5 m\(^3\) 50.8 \(\mu\)m FEP Teflon\(^\circledR\) film reactor installed in a 2.5 m\(\times\)3 m\(\times\)7.8 m enclosure. The enclosure interior is covered with reflective aluminum sheeting and six fans are installed underneath. The light source for photooxidation experiments is 170, 40W black lights with peak intensity of 350 nm (350 BL, SYLVANIA). Before and during every experiment, the reactor is flushed with purified air (Aadco 737 series air purification system). Background particle concentration was below the detection limit (0.2 cm\(^{-3}\)). Relative humidity (RH) inside the chamber was maintained at or below 0.1% RH unless chamber was humidified before a reaction. Particle-free water vapor was generated by bubbling purified air through distilled water and then passing the air through a 1 \(\mu\)m particle filter. Water vapor concentration is determined by two submerged heaters, which control the distilled water temperature. The ultimate relative humidity (RH) in the chamber is monitored using the LI-COR\(^\circledR\) LI-840A CO\(_2\)/H\(_2\)O Analyzer.

Four types of amine reactions were explored in this study: 1) photooxidation in the absence of NO\(_x\) with H\(_2\)O\(_2\) as hydroxyl radical source, 2) dark oxidation reactions with nitrate radical (introduced as N\(_2\)O\(_5\)), 3) dark reaction with O\(_3\), and 4) neutralization reactions, i.e. amines reacting with nitric acid (HNO\(_3\)). Both dry and humid experiments were conducted for reactions between amine and OH/NO\(_3\) radicals. Initial concentrations in each experiment were 100 ppb amine (TMA, DEA or BA), ~300 ppb HNO\(_3\), 300 ppb N\(_2\)O\(_5\)/O\(_3\) or 1 ppm H\(_2\)O\(_2\). Amines were introduced into the chamber by passing a stream of purified air over a known volume of liquid in a heated glass injection manifold. The same method was applied for both H\(_2\)O\(_2\) and HNO\(_3\) injections. N\(_2\)O\(_5\) was synthesized from the reaction of O\(_3\) with NO\(_2\) and was collected in a glass vial soaked in liquid
nitrogen. Upon injection, the glass vial was warmed to room temperature to vaporize the solid N$_2$O$_5$. N$_2$O$_5$/O$_3$ gas of known partial pressure was introduced into a calibrated bulb and then flushed into the chamber the same way as H$_2$O$_2$. For all experiments, O$_3$/N$_2$O$_5$/H$_2$O$_2$/HNO$_3$ was injected after complete mixing of the target amine in the chamber.

A custom built scanning mobility particle sizer (SMPS) was used to monitor particle size distribution between 27 and 685 nm, similar to that described by Cocker et al. (2001a). Calibration of SMPS particle sizing was periodically performed using aerosolized polystyrene latex (PSL) particles of three sizes (90, 220, and 350 nm) (3000 series Nanosphere Size Standards, Thermo Scientific).

Real-time particle density was measured using an Aerosol Particle Mass Analyzer (APM) (Kanomax model 3600) and SMPS in series. Briefly, the mobility aerosol density is determined from the mass selected by the APM and the peak diameter from the SMPS located directly downstream of the APM. Density data was acquired every 75 seconds. Details of the instruments and theory are described elsewhere (Malloy et al., 2009b; Ehara et al., 1996b).

Particle volatility was monitored with a custom-built Volatility Tandem Differential Mobility Analyzer (VTDMA) (Burtscher et al., 2001; Rader and Mcmurry, 1986). The diameter of particles transmitted through the first SMPS ($D_i$) is selected to match the mode diameter of size distribution measured by a parallel SMPS. Then monodisperse particles are transported through a Dekati® thermodenuder (TD, residence time: ~17 seconds, adjustable temperature). The diameter of particles coming out of the
TD \( (D_f) \) is then measured by fitting a log-normal size distribution curve from a second SMPS. Volume fraction remaining (VFR) is then calculated as the volume ratio before and after the TD, i.e., \( \text{VFR} = (D_f/D_i)^3 \). Note that the “volume” in VFR measurement is based on mobility diameter measurement which may include void space and void space is assumed to be negligible in SOA systems. The VTDMA was calibrated using the VFR of dry \((\text{NH}_4)_2\text{SO}_4\) seed aerosol at room temperature.

The evolution of the particle elemental composition is tracked using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006a; Jimenez et al., 2003). The HR-ToF-AMS design is based on the on-line quantitative mass spectra measurements using a heated surface for particle vaporization followed by a standard 70 eV electron impact ionization and subsequent ion analysis with a time-of-flight mass spectrometer (Drewnick et al., 2005). The HR-ToF-AMS can provide quantitative data on both the non-refractory chemical species present in aerosol particles as well as the size of the particles (Jayne et al., 2000; Jimenez et al., 2003).

Semi-continuous detection of the amine salts was enabled by a custom made Particle-into-Liquid Sampler coupled to dual ion chromatographs (PILS-ICs), which was configured as previously described (R.J. et al., 2001; Orsini et al., 2003). Two annular denuders (University Research Glassware) preceded the PILS to remove gas phase parent and products, one coated with citric acid and the other with sodium carbonate. Sample air was pulled through denuders and PILS at approximately 16 L min\(^{-1}\). Particles passed through the denuders and were transmitted to the mixing chamber where dissolved in Millipore water stream (18.2 MΩ) and turned into droplets. The steam droplets impinged
onto the impaction plate and were flushed off by a constant flow of lithium bromide water of known concentration, which served as an internal standard. The lithium bromide solution carried the sample to ion chromatographs for online analysis. Flow rates through the ion chromatographs were determined by a peristaltic pump and were verified before every experiment. Details of the ion chromatography separation and analysis can be found in Praske et al. (2013, in preparation). Briefly, separation can be achieved for the following ten analytes with relatively high resolution: lithium (used as an internal standard), ammonium ($\text{NH}_4^+$), methylamine ($\text{MA}^+$), dimethylamine($\text{DMA}^+$), trimethylamine($\text{TMA}^+$), ethylamine($\text{EA}^+$), diethylamine ($\text{DEA}^+$), triethylamine ($\text{TEA}^+$), triethylamine-$\text{N}$-oxide ($\text{TEAO}^+$), and butylamine ($\text{BA}^+$). The cation and anion IC eluent solution is 3 mM nitric acid/3.5% (v/v) acetonitrile solution and 3.2 mM sodium carbonate/1.0 mM sodium bicarbonate solution, respectively. The PILS-ICs system sampled directly from the chamber and was pre-calibrated for all potential amine species prior to each experiment. The PILS-ICs started sampling before the addition of the amines and continued till the end of the experiment. The volume of the sample loop allows for the IC to fill every 15 minutes. Hence each sample represents the average composition of chamber aerosol in the previous 15 minutes. Even though oxidation products of amine (e.g., amide, imine) may also form salts, here we focus on the formation of aminium nitrate salts, cations and anions of which can be detected and speciated by IC.
4.3 Results and Discussion

4.3.1 Aerosol forming potential of three amines under dry conditions

Aerosol yield, $Y$, as defined in Odum et al. (1996) is the ratio of total aerosol mass ($M_0$) to the consumed mass of reactive organic gas ($\Delta$ROG). In this study, $\Delta$ROG equals the amount of injected amines (100 ppb), assuming complete consumption as a result of excessive oxidants. This assumption has been validated by adding more oxidants after peak number concentration was observed – there was no further growth of particles. $M_0$ was calculated by multiplying aerosol volume (converted from SMPS-measured particle number concentration, assuming spherical particles) by measured aerosol density at the end of each experiment. Chamber wall loss of particle number and mass was accounted for assuming 1st order wall loss kinetics (Cocker et al., 2001a) when calculating aerosol yield. Reaction rate with NO$_3$ was very fast for all three amines, with particle nucleation and coagulation completed within 10 minutes after the injection of N$_2$O$_5$. The photooxidation by OH was slower; the maximum number concentration occurred about an hour after black lights were turned on and continuous growth of aerosol volume was observed during the whole experiment (~3-4 hours).

For BA and DEA, negligible amount of aerosol was formed in the ozonolysis reactions ($Y<1\%$, Table 1), while ~15 $\mu$g m$^{-3}$ aerosol was yielded in the TMA-O$_3$ reaction, similar to the result in Silva et al. (2008). Thus, reaction with O$_3$ is not an important aerosol-producing pathway for aliphatic amines. On the other hand, NO$_3$ and OH–initiated reactions produced significant amounts of aerosol, with the NO$_3$ oxidation having greater aerosol yield than the OH oxidation (Table 1). With NO$_3$ and OH, tertiary
amine (100 ppb TMA) showed the largest aerosol formation potential (1.06 with NO₃, 0.52 with OH) while BA (100 ppb) had the lowest aerosol formation potential (0.62 with NO₃, 0.07 with OH). We only report yield with a single precursor concentration (100 ppb), and do not intend to extrapolate a yield curve in this study.

4.3.2 Salt formation in dry experiments

4.3.2.1 Salt mass fraction in bulk aerosol

In our previous work (Silva et al., 2008; Malloy et al., 2009d) we used AMS mass fragments for nitrate ion as an indicator that salt formation from amines was a minor pathway. To better quantify the products of acid-base reactions in these experiments, PILS-ICs system was deployed to get semi-realtime concentration of aminium nitrate salts. We calculate salt fraction ($f_{salt}$) by dividing salt mass (sum of cation and anion mass) by total aerosol mass (volume × density). The data from the SMPS was averaged every 15 minutes to synchronize with the PILS-ICs data. As expected, no aminium nitrate salts were detected in any photooxidation experiment due to lack of acid source, which is consistent with Murphy et al. (2007). Therefore, the remainder of this section discusses the aerosol and salt formation in dry reactions with the nitrate radical.

_TMA_

Reactions between TMA and NO₃ produced organic aerosol, which is consistent with Silva et al. (2008) and further verified by PILS-ICs and SMPS data in our study. The total concentration of MA⁺, DMA⁺, TMA⁺ and NO₃⁻ ions is below 10 μg m⁻³, accounting for <6% of the total aerosol. Salt fraction decreased slightly with time from 5.6% to 2.5%
(Fig. 1a). Therefore, acid-base reactions under dry conditions are not favorable for TMA. Ge et al. (2011a) estimated that the solid/gas equilibrium dissociation constant ($K_p$) of trimethylaminium nitrate (TMA•HNO$_3$) was one order of magnitude higher than ammonium nitrate at 298.15 K. This suggests that thermodynamically, it is less likely for TMA to form nitrate salt compared with ammonia. Meanwhile, the atmospheric ammonia concentration is also orders of magnitude higher than TMA concentration, so secondary oxidation processes are expected to be the dominant atmospheric pathway of TMA. Thermodenunder results show that the VFR of TMA- NO$_3$ aerosol was slightly lower than TMA-OH aerosol at 100 °C and may be due to the presence of semi-volatile TMA nitrate salt.

**DEA**

A mixture of organic and inorganic compounds was formed in the reaction between DEA and NO$_3$. The composition of the inorganic salt was mainly DEA$^+$ and NO$_3^-$, while a small amount of EA$^+$ was observed (<1 μg m$^{-3}$). The estimated $K_p$ of diethylaminium nitrate (DEA•HNO$_3$) is three orders of magnitude lower than TMA•HNO$_3$ at 298.15K (Ge et al., 2011a), suggesting that DEA•HNO$_3$ is more likely to be present in the particle phase. Approximately 40% of the total aerosol mass was estimated to be composed of inorganic salt ~30 minutes after N$_2$O$_5$ was injected. The contribution of salt increased to 59% in the first two hours after N$_2$O$_5$ was injected, and then decreased to 48% (Fig. 2a). Accounting for the measurement uncertainty of PILS-IC, the salt fraction calculated based on the last sample is still lower than the previous samples. Simultaneously, the VFR of formed aerosol increased continuously after two
hours (Fig. 2b). It can be concluded that, approximately two hours from the beginning of the reaction, formation of the less-volatile SOA became more significant than the formation of the inorganic salt (DEA•HNO₃). Thus, the decrease of volatility can support the observation of decreasing salt fraction.

**BA**

Butylaminium nitrate dominated the formed aerosol in the BA-NO₃ reaction. In the first 15 minutes, it accounted for ~63% of total aerosol mass, and retained a relatively constant fraction in the first 2 hours (~78%, Fig. 1c). Therefore, the acid-base reaction dominated over secondary oxidation chemistry for BA. As salt was the dominant component in the BA aerosol, the aerosol mass spectrum appeared very similar to that of pure butylaminium nitrate (Fig. S2a, b). Compared with organic-dominating aerosols, this mass spectrum is very simple and similar to the butylamine mass spectrum in McLafferty (1993). The yield of the NO₃-initiated reaction was notably higher than the photooxidation reaction (0.62 versus 0.07, Table 1), likely due to the formation of butylaminium nitrate.

### 4.3.2.2 Chemical composition of salt-containing amine aerosol

Analysis of high resolution AMS data provided empirical evidence for a high abundance of salts. The HRNO₃ family only contains fragments from nitrate and can be used as an indirect method to evaluate the salts formed during the experiment. Fig. S2 (c) shows the average fraction of HRNO₃ signal in the total signal ($f_{HRNO3}$) of butylaminium nitrate salt, as well as the real-time $f_{HRNO3}$ of aerosol formed in BA-NO₃ reaction, which
was within the ±10% range of the BA•HNO₃ salt $f_{HRNO3}$. Similarly, the $f_{HRNO3}$ of DEA-NO₃ aerosol equaled 77% of that of DEA•HNO₃ salt.

4.3.3 Effects of water vapor on aerosol formation

4.3.3.1 OH photooxidation

The effect of humidity on SOA yield was negligible for OH-initiated reactions (Table 1). When calculating aerosol yield, the density of aerosol formed from dry photooxidation experiments was applied to avoid bias when using APM-SMPS for humid amine experiments. The patterns of mass spectra of aerosol formed in humid and dry experiments are analogous to each other, suggesting similar reaction mechanisms in dry and humid experiments (Fig. 3).

4.3.3.2 Reaction with NO₃

Reported aerosol yield in humid experiments (Table 1) was also calculated using density of aerosol formed in dry experiments. Humid BA+ NO₃ reactions produced more aerosol than dry experiments which was not the case for TMA and DEA; water vapor suppressed aerosol volume in reactions between TMA/DEA and NO₃. Additional experiments have been conducted and testified the repeatability of the results.

In humid chamber experiments, water will react with the original oxidant (N₂O₅) as well as the nitrate radical (NO₃) to produce nitric acid (HNO₃) according to the following reactions:

\[ \text{N}_2\text{O}_5 (g) + \text{H}_2\text{O} (g,l) \rightarrow 2\text{HNO}_3 (g,l) \]  \hspace{1cm} (1)

\[ \text{NO}_3 (aq) + \text{H}_2\text{O} (l) \rightarrow \text{HNO}_3 (aq) + \text{OH} (aq) \]  \hspace{1cm} (2)
where g, l and aq stands for gas, liquid and aqueous phase, respectively. More nitric acid production drives the acid-base reaction equilibrium towards the formation of aminium nitrate salt, resulting in a larger amount of particle-phase inorganic salts in the formed aerosol. However, the gas-to-particle partitioning of aminium salts is still determined by their thermodynamic properties.

**TMA**

There was a small amount of salt formed in the TMA-NO$_3$ reaction at RH ~10%. However, when RH in the chamber increased to ~22%, a higher salt fraction was detected while the secondary aerosol was still dominated by organics (Fig. 1a). Detailed mechanism is proposed in a parallel paper (Price et al., 2012, in preparation). The salt fraction decreased with time from 19% to 14%, likely due to the repartitioning of aminium nitrates to gas phase. At the same time, VFR (at 100 °C) of the bulk aerosol continuously increased, but remained lower than the VFR of aerosol in the dry experiment. It agreed well with the PILS-ICs data, and suggested that volatility of aminium salts was higher than the organic products.

Abnormally high signal intensity of $m/z$ 58 has been observed in humid TMA experiments using the HR-AMS. Large signal of $m/z$ 58 has been reported previously with a cToF AMS used to detect trimethylaminium nitrate salts (Murphy et al., 2007), and C$_3$H$_8$N$^+$ has been used as a tracer-ion for amine-type compounds (Sun et al., 2011). The low ionization potential of TMA was believed to be responsible for the proposed surface ionization. Hence, we did not present mass spectrum of “humid” TMA aerosol here. There were no similar effects on the detection of DEA and BA aerosol in humid
experiments, but the ionization efficiency of amine nitrate salts remains uncertain due to potential surface ionization effects on the AMS vaporizer (Silva et al., 2008).

DEA

DEA-NO₃ aerosol formed at RH ~37% was composed of >50% salt (Fig. 1b) and showed high volatility with VFR close to zero at 100 °C. Salt mass concentration and fraction kept increasing, as well as the HRNO₃ family intensity detected by AMS. The accumulation of DEA•HNO₃ and ethylaminium nitrate (EA•HNO₃) in the aerosol phase suggested that water vapor enhanced the condensation/formation of inorganic salt. Comparing aerosol mass spectra with that formed in the dry experiment, major m/z peaks overlapped and most showed similar intensity, except for several high m/z peaks (58, 86, 94, 100 and 111, Fig. 4a). The higher abundance of large ions (containing 5-6 carbon atoms) suggested that water vapor promoted formation of products with higher molecular weight. Alpha cleavage is likely responsible for yielding the (M-13)^+ fragment (m/z 58) for DEA nitrate salt.

BA

PILS-ICs determined that less amount of BA nitrate salt was formed under humid conditions than in dry experiments, while the mass of BA•HNO₃ salt formed at higher RH (~30%) was 2/3 of that formed at lower RH (~10%). However, the aerosol volume at higher RH (~30%) was 1.9 times the volume of aerosol formed in the dry experiment, resulting in much lower BA nitrate salt fraction in the total aerosol (~18%, Fig. 1c). Nevertheless, BA salt fraction at RH ~10% appeared the same as that in dry experiments because the aerosol volume and salt mass at RH ~10% decreased by the same extent
compared with dry experiments. Large amount of ammonium ion (NH$_4^+$) was only detected in the RH ~30% experiment, which accounted for 20-27% of total aerosol mass. It suggested that there might be additional reaction routes forming NH$_4$NO$_3$ in the aqueous phase in the more humid (RH~30%) experiment, which can explain the decreased BA salt contribution to the total aerosol and the increase of aerosol yield. Meanwhile, the simple pattern of the mass spectra of aerosol formed at both RH~10% and RH~30% revealed that the formed aerosol was still dominated by inorganic salt.

When chamber RH was ~30%, almost all components of the aerosol formed in the BA-NO$_3$ reaction evaporated at 35 °C (VFR <0.03). The extremely high volatility at 35 °C prevented accurate measurement of aerosol density using the APM-SMPS system (which slightly heats aerosol during measurement). Caution should be used with APM measurements for such highly volatile aerosol.

### 4.4 Conclusion

This study investigated the aerosol formation from reactions between three aliphatic amines (TMA, DEA and BA) and O$_3$/OH radical/NO$_3$ radical, as well as the effect of water vapor on aerosol composition and characteristics. Low molecular weight aliphatic amines are the most common and abundant gas phase amines in the atmosphere, however, even TMA, the most abundant aliphatic amine, has a flux several orders of magnitude lower than ammonia. Therefore, aerosol formation from aliphatic amines may only have comparatively significant impacts in specific regions with concentrated amines.
Night time chemistry of amines with the predominant radical source NO$_3$ is examined, showing that all three amines have the potential to form secondary aerosol. PILS-ICs was utilized to detect and quantify inorganic nitrate salts in the secondary aerosol. Results show that DEA and BA are capable of forming significant amount of stable inorganic salt with precursor concentration at ppb level. TMA oxidation, which has attracted attention in the last decade, tends to form non-salt secondary organic aerosol under dry conditions. Compared with NO$_3$-initiated reactions, OH photooxidation of amines in the absence of NO$_x$ yields a smaller amount of secondary aerosol composed of only organic components; no aminium nitrate salts are formed as a result of the absence of NO$_x$.

Water vapor in the atmosphere is inevitably involved in the gas- and aerosol-phase reactions and affects gas-to-particle partitioning of parent and products. As N$_2$O$_5$ and the nitrate radical are both very soluble and can react quickly with water to form nitric acid, we see enhanced nitrate salts formation in humid experiments. Mass spectra of dry and humid experiments suggest that water vapor enhanced formation of more products with high molecular weight in DEA-NO$_3$ reaction while it had a negligible effect on BA-NO$_3$ reactions. The accumulation of diethylaminium nitrate throughout the experiment may also result from the presence of water vapor. For BA, RH~10% leads to same fraction of salt, while RH~30% leads to much higher aerosol volume and smaller salt contribution. As no nitric acid is produced in the dry or humid OH-initiated experiments, the aerosol formation is not affected by the presence of water vapor. Due to the high volatility of aminium nitrate salts, difficulty in utilizing APM-SMPS technique
increased the uncertainty of aerosol and salt yield. This should also be considered when using an APM in studies involving volatile species.

This study adds to our understanding of atmospheric reactions of amines, especially the chemistry of OH and NO$_3$-initiated reactions. The formation of SOA and inorganic nitrate salts from gas phase amines depends strongly on the availability of amine, HNO$_3$ and atmospheric oxidants, as well as relative humidity. For amines with atmospheric relevant concentration, we expect similar reaction pathway and aerosol composition, as long as the oxidants are in excess. Meanwhile, future work should focus on the aerosol formation of amines in the presence of ammonia at atmospheric relevant concentration, as well as reactions under high relative humidity (RH>50%). When the environment relative humidity is higher than the RH of deliquescence, aminium salts may exist as solution instead of solids, leading to various changes of reaction pathway and aerosol properties. The competition between amine and ammonia also affects the atmospheric processes. Thus, except for the measured SOA to salt ratio in the chamber experiments, modelers need to include as much ambient data as possible in order to mimic the amine behavior in the real atmosphere.

Secondary aerosol from amine sources can be highly hygroscopic and CCN active due to the formation of salts. As the contribution of organic and inorganic components in the particle varies with the types of precursor amines and the oxidants, we expect to find different water-uptake abilities for different amine aerosols. Further work is also needed to look into the aerosol formation mechanisms of the aliphatic amines, because of their
large aerosol yield, important role in particle nucleation and potential impacts on cloud formation and global climate.
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### 4.6 Tables

Table 4.1 List of performed experiment conditions, aerosol yield and density.

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<thead>
<tr>
<th>Oxidant</th>
<th>Amine (100 ppb)</th>
<th>RH (%)</th>
<th>Yield</th>
<th>Density (μg m⁻³)</th>
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<td></td>
<td>30</td>
<td>0.07</td>
<td></td>
</tr>
<tr>
<td>N₂O₅ (~ 300 ppb)</td>
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<td>1.40 ± 0.03</td>
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<td>1.36 ± 0.05</td>
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4.7 Figures

Figure 4.1 Time series of salt fraction in the dry and humid experiments of a) TMA+ NO$_3$, b) DEA+ NO$_3$, and c) BA+ NO$_3$.
Figure 4.2 a) Time series of aerosol mass, salt mass and salt fraction for DEA-NO$_3$ reaction; b) VFR of aerosol formed in the dry DEA-NO$_3$ reaction at 100 °C.
Figure 4.3 Mass spectra of DEA (panel a) and BA (panel b) aerosol formed in humid and dry photooxidation experiments.
Figure 4.4 Mass spectra of DEA (a) and BA (b) aerosol formed in humid and dry NO₃-initiated experiments.
CCN activity of aliphatic amine secondary aerosol

5.1 Introduction

Aerosol can directly or indirectly affect the earth’s radiative balance and forcing of the climate system thus they can contribute significant uncertainty to climate predictions. Direct effects result from the scattering and absorption of solar and thermal radiation by aerosol particles, whereas indirect effects result from acting as cloud condensation nuclei (CCN) and participating in heterogeneous chemical reactions. According to IPCC (Intergovernmental Panel on Climate Change) 2007, the response of cloud characteristics and precipitation processes to increasing anthropogenic aerosol and CCN concentrations represents one of the largest uncertainties in our current understanding of climate change.

The relative contribution of inorganic/organic components plays a vital role in the determination of bulk CCN activity of ambient aerosol. The aerosol composition is complex. 25-50% of fine particle mass is comprised of inorganic compounds (Gray et al., 1986), such as ammonium sulfate, nitrate, sea salt, wind-blown dust, etc. Organics make up ~20-90% of the global aerosol composition in the troposphere (Kanakidou et al., 2005). Only 10% of the organic composition has been speciated and quantified using gas chromatography with mass spectrometry (Finlayson-Pitts and Pitts, 1986; Rogge et al., 1993; Saxena and Hildemann, 1996), thus little is known about the particle chemical and physical properties. Therefore, parameterizations are used to effectively represent the water uptake potential of atmospheric aerosols, among which the hygroscopicity
parameter (Petters and Kreidenweis, 2007), $\kappa$ has been used more and more frequently in recent studies (e.g. Moore et al., 2012; Mikhailov et al., 2013; Tang et al., 2012a; Asa-Awuku et al., 2011; Jimenez et al., 2009). Application of $\kappa$ allows direct evaluation of aerosol CCN activity while avoiding the knowledge of aerosol properties, such as density, molecular weight and surface tension. In Petters and Kreidenweis (Petters and Kreidenweis, 2007), $\kappa$ values representative of atmospheric particulate matter is derived as 0.1~0.9 using previous ambient studies (Fitzgerald et al., 1982; Hudson and Da, 1996; Dusek et al., 2006). This wide range indicates that there is large variance in aerosol composition and solubility. In other words, the relative contribution of soluble and non-soluble components varies widely. Among inorganics in the atmospheric aerosol, several principal components are highly soluble and hygroscopic, such as ammonium sulfate and nitrate, $\kappa$~0.6 and 0.67, respectively; whereas moderately hygroscopic organic species have CCN activities corresponding to $0.01< \kappa <0.5$ (Petters and Kreidenweis, 2007).

Particle phase amines have been repeatedly detected in field campaigns at different locations, summarized by Ge et al. (2011c). Chamber studies also confirmed both acid-base reactions and oxidation processes can lead to formation of amine secondary aerosol (Silva et al., 2008; Murphy et al., 2007; Malloy et al., 2009d). Amines may also enhance or affect nucleation and particle growth, even more than ammonia (Loukonen et al., 2010; Berndt et al., 2010; Wang et al., 2010a; Wang et al., 2010b). To date few studies have examined the CCN activity of amine aerosol formed from reactions with atmospheric oxidants or nitric acid.
Solubility of multiple aliphatic aminium nitrates has been summarized in Table 5 in Ge et al. (2011b), which are comparable with or higher than that of ammonium nitrate. Presence of particulate amine has been reported to be coincident with enhanced water uptake of aerosol from a bovine source (Sorooshian et al., 2008); it can be hypothesized that aminium nitrates are highly hygroscopic, similar to ammonium nitrate. Thus, the presence of aminium nitrate salts in the ambient has the potential to impact regional air quality and CCN concentrations.

This work focuses on the CCN behavior of trimethylamine and butylamine secondary aerosols. Tang et al. (2013b) reports the aerosol formation potential and the chemical nature (inorganic/organic) for these two aliphatic amines, as well as the effect of environment relative humidity on the reaction pathway and aerosol composition. Here we investigated the CCN activity of aerosol formed from dry and humid reactions with nitrate radical (NO$_3$) and hydroxyl radical (OH).

5.2 Experimental Setup

Three series of experiments were performed for TMA and BA: OH photooxidation, NO$_3$-initiated reaction, and acid-base reaction. The initial concentration of each reactant in the experiment was: precursor amine (TMA or BA) 100 ppb, HNO$_3$ ~300 ppb, or N$_2$O$_5$ 300 ppb, or H$_2$O$_2$ 1 ppm. Both dry and humid (relative humidity < 40%) experiments were conducted for reactions between amine and OH/NO$_3$ radicals. All experiments were conducted in the 12 m$^3$ environmental reactor chamber at the Center for Environmental Research and Technology, College of Engineering, University of
California, Riverside (CE-CERT/UCR). Details of the chamber facility can be found in Tang et al. (2013b). Relative humidity (RH) inside the chamber was maintained at or below 0.1% RH during dry experiments. In humid experiments, water vapor was generated by bubbling purified air through distilled water and then passing the air through a 1 mm particle filter; RH was monitored using a LI-COR® LI-840A CO₂/H₂O analyzer. Details for experimental protocol and setups are described in the preceding paper (Tang et al., 2013b). A series of chemical and physical characterization instruments were deployed for the study of aerosol properties.

A custom built scanning mobility particle sizer (SMPS) was used to monitor real time particle size (27-685 nm) and volume distribution (Cocker et al., 2001a). A Volatility Tandem Differential Mobility Analyzer (VTDMA) was also custom built and used for online volatility measurement. It consists of two differential mobility analyzers (DMA), one condensational particle counter (CPC) and one Dekati® thermodenuder (TD, residence time ~17 s). The first DMA size-selects particles that transmit through the TD with diameter \( D_i \), while the second DMA and CPC measures the diameter of particles coming out of the TD \( D_f \) by fitting a log-normal size distribution curve. Volume fraction remaining (VFR) is calculated as the volume ratio of particles before and after passing through the TD with temperature \( T \), i.e. \( \text{VFR}=\left(\frac{D_f}{D_i}\right)^3 \).

Chemical composition of chamber SOA was tracked using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006a;Jimenez et al., 2003). Non-refractory chemical species in the aerosol phase can be
quantified, providing chemistry information of bulk aerosol as well as elemental composition.

Quantification of particle phase inorganic salts was enabled by a custom made Particle-into-Liquid Sampler coupled to dual ion chromatographs (PILS-IC), the configuration of which was described elsewhere (Orsini et al., 2003; Weber et al., 2001). In Brief, PILS dissolves particles in hot water steam and turns them into droplets, and then the collected steam droplets is carried by lithium bromide solution into IC for online analysis of cations and anions. Details of the IC separation and analysis can be found in Praske et al. (in preparation).

The CCN activity and supersaturated hygroscopicity is measured with a Droplet Measurement Technologies (DMT) Continuous-Flow Streamwise Thermal Gradient CCN Counter (CFSTGC) (Lance et al., 2006; Roberts and Nenes, 2005). Aerosol from the chamber was classified by a commercial SMPS (TSI 3080), followed in parallel by a condensation particle counter (CPC, TSI 3772) and the DMT CCN counter. The total aerosol concentration (CN) of the monodisperse particles was counted by the CPC and the CCN concentration was measured by the CCN counter. The DMA used with the CCN counter was operated at a sheath-to-aerosol flow ratio of 10:1. Instrument \( ss \) settings used in this study ranged from 0.2\% to 1\% and were calibrated using atomized \((\text{NH}_4)_2\text{SO}_4\) aerosol. Scanning Mobility CCN Analysis (SMCA) (Moore et al., 2010) provides size resolved CCN activity using data from the CCN counter and SMPS. By keeping constant instrument supersaturation \((ss)\) during the scanning cycle of the SMPS, we obtain the
time series of CN and CCN counts, and then use an inversion procedure to determine the CCN/CN ratio as a function of dry mobility diameter. The critical diameter, which corresponds to the CCN/CN ratio of 0.5, is determined for each ss. This procedure is repeated over multiple ss, giving a characterization of the size-resolved CCN properties every 135 seconds.

5.3 Theory

5.3.1 κ of multi-component aerosol system

We use the κ-Köhler theory (Petters and Kreidenweis, 2007) to convert the measured activation diameters to the single hygroscopicity parameter, κ, using as follows,

\[ \kappa = \frac{4A^3}{27\pi^2 S_c d_s^2} \]  

(1)

\[ A = \frac{4M_w \sigma_w}{RT \rho_w} \]  

(2)

where \( M_w \) and \( \rho_w \) are the molecular weight and density of water, respectively, \( R \) the universal gas constant, and \( T \), the ambient temperature. κ-Köhler theory assumes the surface tension of the droplet is that of pure water, \( \sigma_w = 0.072 \) N m\(^{-1}\). \( S_c \) is the critical saturation for a dry particle of diameter \( d_s \). In our experiments we determine the critical particle mobility diameter for instrument ss with SMCA.

For the multi-component aerosol system, the Zdanovskii, Stokes, and Robinson (ZSR) (Zdanovskii, 1984; Stokes and Robinson, 1966) mixing rule is employed to predict the CCN activity, based on the assumption that water uptake by each individual
component of a particle is independent and additive. Therefore, the overall $\kappa$ value is the sum of $\kappa$ values of each individual component weighted by its volume contribution to the total aerosol.

Here we assume there are only two components, inorganic and organic in the aerosol phase of the amine oxidation products. Applying the ZSR rule as in Petters and Kreidenweis (2007), the $\kappa$ value of the bulk aerosol can be estimated as follows:

$$\kappa = \sum_i \varepsilon_i \kappa_i = \varepsilon_s \kappa_s + \varepsilon_o \kappa_o$$

where $\varepsilon_i$ is volume fraction of the inorganic/organic components in the aerosol; “s” and “o” subscripts refer to salt and organic components, respectively. $\kappa_s$ is calculated from the mass fraction, $m$, and density, $\rho$ as

$$\varepsilon_s = \frac{\nu_s}{\nu_s + \nu_o} = \frac{m_s/\rho_s}{m_s/\rho_s + m_o/\rho_o}$$

$$\varepsilon_o = 1 - \varepsilon_s$$

5.3.2 Maintaining constant $ss$ in CCN column

As shown in Roberts and Nenes (2005), the centerline supersaturation of CCN counter is controlled by the flow rate ($Q$) and temperature difference ($\Delta T$) between the top ($T_1$) and bottom ($T_3$) of the column, if the absolute pressure in the column is constant (Fig. S1, Eq. 6). Selecting various combination of $Q$ and $\Delta T$ will be able to not only change $ss$ but also maintain same or very similar $ss$. Normally, change of $ss$ is achieved by keeping constant inlet flow rate (0.5 L min$^{-1}$) and varying $\Delta T$. In fact, $T_1$ is always
identical to the aerosol sample temperature, which is constant for all experiments. Therefore, change of $\Delta T$ is determined by that of $T_3$, temperature at the bottom of the column. Larger temperature gradient along the CCN column is required for higher $ss$, which also causing the activated aerosol exiting the CCN column hotter.

To examine the artifact caused by the high temperature during the measurement, the temperature gradient inside the CCN column will be varied while keeping the centerline $ss$ constant.

$$ss \propto \frac{\Delta T}{Q}$$  \hspace{1cm} (6)

$$\Delta T = T_3 - T_1$$  \hspace{1cm} (7)

5.4 Results and Discussion

5.4.1 TMA

TMA photooxidation without the presence of NO$_x$ forms organic aerosol with low hygroscopicity, $\kappa \sim 0.18$ (Table 1). Similarly, dry reactions between TMA and NO$_3$ produced organic-dominant secondary aerosol with comparable hygroscopicity ($\kappa \sim 0.20$, Table 1). In humid TMA-NO$_3$ experiments, inorganic salts are formed (Tang et al., 2013a). For example, the salt mass fraction stabilizes after ~2 hours of reaction at ~15% for RH ~22% experiment (Tang et al., 2013), CCN activity of the humid aerosol with increased salt fraction has $\kappa \sim 0.28$. The formed inorganic salt was believed to be TMA•HNO$_3$, because under humid conditions, N$_2$O$_5$ and NO$_3$ radical will form nitric...
acid which can be directly neutralized by TMA. Observation of both TMA$^+$ and NO$_3^-$ ions from PILS-IC system confirmed the hypothesis. Hence, it is reasonable to estimate the CCN activity of organic components in the two-component TMA aerosol by applying ZSR mixing rule on $\kappa$-Köhler theory.

Table 2 showed the measured $\kappa$ value of TMA•HNO$_3$ (0.72±0.04) as well as the density, mass fraction and calculated volume fraction. The calculated $\kappa$ value for organic components in the humid TMA-NO$_3$ aerosol is 0.19, similar to that of the dry TMA-NO3 aerosol, suggesting that despite of the salt-forming reaction pathway, mechanism for formation of TMA SOA is analogous in dry and humid reactions.

5.4.2 BA

Similar low hygroscopicity values were observed for BA SOA formed from dry and humid OH photooxidation ($\kappa$~0.24, Table 1). The CCN activity of BA-OH SOA did not change with time during the experiments. This is consistent with findings in Tang et al. (2013a) that AMS mass spectra patterns were alike for dry and humid BA-OH reactions. Even though there were no obvious differences in experimental conditions for several dry BA-NO$_3$ experiments, differences existed for $\kappa$ values of dry BA-NO$_3$ aerosol, the range of averaged $\kappa$ within 0.15 to 0.35. Hygroscopicity of formed aerosol is unstable at the beginning of the reaction, with the change of $\kappa$ within ±0.1, which may be due to the non-uniform aerosol composition.

Aerosol formed in humid experiments showed higher $\kappa$ values. Higher hygroscopicity values are due to the formation and presence of inorganic salts in the
particle phase (Tang et al., 2013a). Other than the formation of butylaminiun nitrate (BA•HNO₃) via direct reaction of BA+ HNO₃, additional pathway also lead to another salt, ammonium nitrate (NH₄NO₃). Fig. 1 showed ratio of mass concentration (µg m⁻³) of two cations, NH₄⁺ and BA⁺ in the total BA aerosol mass concentration (µg m⁻³) using data collected by PILS-IC and SMPS. It can be seen that with higher relative humidity, the relative contribution of ammonium ion (NH₄⁺) in the total aerosol increased, while that of butylamine ion (BA⁺) followed the opposite trend. As κ of NH₄NO₃ is larger than that of BA•HNO₃ (0.74 vs. 0.53, Table 1), aerosol containing more NH₄NO₃ exhibited higher CCN activity.

Difference in aerosol composition also affected aerosol volatility, represented by volume fraction remaining (VFR) in Fig. 2. Dry aerosol (RH<0.1%) showed the lowest volatility, with VFR ~1 at thermodenuder temperature T= 35 ºC. Comparing VFR of aerosol formed under three different relative humidities (RH<0.1%, ~12%, and ~23%) at T= 50 ºC, volatility corresponded to the increase of relative humidity, while continuously decreased during each experiment. Furthermore, experiment conducted under RH~35% resulted in the most volatile aerosol, VFR of which was close to zero even at T= 35 ºC. Given the observation made from the RH~12% and ~35% experiments that the inorganic components dominated secondary aerosol formed in humid BA-NO₃ experiments, it can be deduced that the inorganic salts are highly volatile.

Standard deviation of κ values for humid BA-NO₃ aerosols increased notably compared with that for dry aerosol. Chemical composition ages with time for BA-NO₃
systems and $\kappa$ values decrease as well. In addition, measured $\kappa$ values vary for changes in $ss$. Basically, $\kappa$ measured at higher $ss$ (i.e. the $ss$ settings > 0.6%) was smaller than those measured at lower $ss$ (i.e. the $ss$ settings \leq 0.6%), and the discrepancy was observed from the beginning to the end of the experiment. As stated in Petters and Kreidenweis (2007), the hygroscopicity parameter $\kappa$ is only dependent on aerosol composition, not on the value of $ss$. Thus, there must be inconsistence in aerosol composition when measured at high and low $ss$.

Aerosol formed from both dry (RH<0.1%) and humid (RH~30%) experiments between BA and NO$_3$ were re-examined at $ss \sim$0.37 using the same CCN counter. Varied temperature difference ($\Delta T$) of the CCN column was listed in Table 3, as well as the calculated $\kappa$ values. For both types of aerosols, $\kappa$ measured at $\Delta T$=7, 14 and 17 °C were relatively consistent, with standard deviation ±0.03 (dry) and ±0.04 (humid), and showed a slight decrease at the beginning of the experiments. However, when $\Delta T$=21 °C and $Q$=167 cm$^3$ min$^{-1}$, it is impossible to determine the critical diameter needed for calculating $\kappa$ because the CCN/CN ratio was below 0.2 and did not reach a plateau. It suggested that BA aerosol was unable to activate inside the CCN column, as a result of the high temperature and longer retention time. Secondary gas to particle partitioning is temperature dependent; with high temperatures favoring gas phase constituents. Thus, shrink of particle size caused by evaporation of volatile compounds is assumed to be responsible for the failure of activation.
However, temperature sensitivity of atomized NH$_4$NO$_3$ aerosol was also tested with $\Delta T= 7$ and $21 \, ^\circ C$, no difference was observed between critical diameters under two conditions. Similar measurements were done for BA•HNO$_3$ as well, only 10% difference of $\kappa$ was discovered.

### 5.5 Summary

The formation of aliphatic amine secondary aerosol is complex and the reaction pathways can lead to the formation of organic and inorganic components. Changes in the single hygroscopicity parameter $\kappa$ reflect changes in aerosol chemical composition. The CCN activity for amine secondary aerosol is dependent on the oxidation pathway. NO$_3$ radical acid pathways produce more CCN active aerosol than OH radical systems, especially in humid (RH > 30%) conditions. The tertiary amine precursors form less volatile material that can be described by a two component inorganic/organic hygroscopicity model. Variability in amine hygroscopicity, especially for primary aliphatic amines is due to the presence of volatile components. Tertiary aerosol does not exhibit variance and primary aliphatic amine hygroscopicity is more susceptible to changes in temperature and RH.

### 5.6 References


5.7 Table

Table 5.1 $\kappa$ values of aerosol formed from reactions with OH (H$_2$O$_2$ as source), NO$_3$ (N$_2$O$_5$ as source) and HNO$_3$.

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<thead>
<tr>
<th>Amine</th>
<th>Oxidant</th>
<th>RH (%)</th>
<th>$\kappa$</th>
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<td>36</td>
<td>0.25±0.03</td>
</tr>
<tr>
<td></td>
<td>N$_2$O$_5$</td>
<td>12</td>
<td>0.19±0.04</td>
</tr>
<tr>
<td>BA</td>
<td></td>
<td>23</td>
<td>0.48±0.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.33±0.08</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>0.49±0.08</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Amine</th>
<th>Oxidant</th>
<th>RH (%)</th>
<th>$\kappa$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TMA•HNO$_3$</td>
<td></td>
<td></td>
<td>0.72±0.04</td>
</tr>
<tr>
<td>BA•HNO$_3$</td>
<td></td>
<td></td>
<td>0.53±0.03</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td></td>
<td></td>
<td>0.74*</td>
</tr>
</tbody>
</table>

* Petters and Kreidenweis, 2007
Table 5.2 Mass and volume fraction, density, and hygroscopicity of inorganic/organic components in the humid (RH ~ 22%) TMA-NO₃ aerosol.

<table>
<thead>
<tr>
<th></th>
<th>Mass fraction</th>
<th>Density (g cm⁻³)</th>
<th>Volume fraction</th>
<th>Hygroscopicity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt</td>
<td>0.15</td>
<td>1.25*</td>
<td>0.165</td>
<td>0.72±0.02</td>
</tr>
<tr>
<td>Organics</td>
<td>0.85</td>
<td>1.4 **</td>
<td>0.835</td>
<td>0.19±0.00</td>
</tr>
<tr>
<td>Bulk aerosol</td>
<td>1</td>
<td>1</td>
<td>0.28±0.02</td>
<td></td>
</tr>
</tbody>
</table>

* Salo et al., 2011.
** Tang et al., 2013.
Table 5.3 Values of temperature difference ($\Delta T$) and flow rate ($Q$) inside the CCN column and the resulted real ss (%)..

<table>
<thead>
<tr>
<th>$\Delta T$ (°C)</th>
<th>Flow Rate, $Q$ (cm$^3$ min$^{-1}$)</th>
<th>ss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>500</td>
<td>0.37</td>
</tr>
<tr>
<td>14</td>
<td>250</td>
<td>0.39</td>
</tr>
<tr>
<td>17</td>
<td>206</td>
<td>0.38</td>
</tr>
<tr>
<td>21</td>
<td>167</td>
<td>0.37</td>
</tr>
</tbody>
</table>
Figure 5.1 Fraction of $\text{BA}^+$ (a) and $\text{NH}_4^+$ (b) mass measured by PILS-IC in the total aerosol mass for the BA-NO$_3$ experiments under three different relative humidities (RH<0.1%, ~10%, ~30%).
Figure 5.2 Volume Fraction Remaining (VFR) of BA-NO$_3$ aerosol formed under various relative humidity at different thermodenuder temperature.
Figure 5.3 $\kappa$ values measured at similar ss (~0.37%) with various temperature difference ($\Delta T$) inside the CCN column. Open symbols refer to dry reaction (RH<0.1%), and closed symbols refer to the humid one (RH~30%).
Supplemental Material

Figure S1 Schematic of CCN column showing temperature difference (ΔT) and aerosol flow direction.
6 Summary of Dissertation

The overall objective of this study was to advance the understanding of secondary aerosol influences on air quality, climate and health. The goal was achieved by studying the aerosol forming potential of sesquiterpene and aliphatic amines, the aerosol properties, and their CCN activity. Using advanced characterization tools on cigarette tobacco smoke provided insights on the effects of smoke composition on the enhanced condensational growth (ECG) under supersaturated conditions. The parameterized hygroscopicity can be used to approximate the importance of ECG for tobacco smoke.

Chapter 2 evaluated the influence of experimental parameters on the chamber-formed β-caryophyllene ozonolysis SOA properties and especially the CCN activity. The β-C SOA CCN activity reported in this study is much higher than previous studies (κ < 0.1) that use higher precursor concentration in smaller environmental chambers; similar results are only achieved with significant use of OH scavenger. No direct correlations are observed with β-C aerosol ion fragment fraction (f_i) and κ, while the addition of isoprene improves the CCN predictive capabilities with bulk aerosol chemical information. Results also show that aerosol formed from a mixture of low and high molecular weight terpene ozonolysis can be hygroscopic and can contribute to the global biogenic SOA CCN budget.

Chapter 3 investigated the effect of mainstream and side stream smoke composition for water uptake and droplet growth abilities. More than 99% of the
mainstream and sidestream ETS mass is semivolatile aerosol and non-elemental carbon, of which more than 95% is organic. The water-soluble organic comprises 30-85% of the aerosol mass fraction and has no effect on surface tension when dissolved in water. The O/C and N/C from HR-ToF-AMS data show that more oxidized components are present in mainstream smoke. Differences in the bulk aerosol composition have little effect on the overall water uptake. The two types of cigarettes produce aerosols of similar hygroscopicity (with $\kappa \sim 0.15$ or less) in mainstream and sidestream smoke. Droplets grow at the same rate within the CCN instrument. However, ULN reference cigarettes that produce dry particles at larger sizes are more likely to experience ECG.

Chapter 4 evaluated the yield, chemical nature and chemicophysical properties of secondary aerosol formed from three aliphatic amines (TMA, DEA, and BA) with atmospheric oxidants. Results show that all three amines have a high potential to form secondary aerosol in reactions with NO$_3$, while the reaction pathways are affected by the presence of water vapor. On the other hand, the OH photooxidation of amines has much lower secondary aerosol yield and is independent of relative humidity, while ozonolysis produces negligible amount of aerosol. DEA and BA are capable of forming a significant amount of stable inorganic salt at ppb level concentrations, while TMA tends to form mostly non-salt secondary organic aerosol under dry conditions. Secondary aerosol from OH oxidation is composed of organic components only, due to the lack of acid source. This study suggests that night time chemistry of aliphatic amines can produce secondary organic and inorganic aerosol mixtures, and the relative contribution of each component depends on the environment relative humidity.
Chapter 5 extended Chapter 4, focusing on evaluating the CCN activity of the aliphatic amine SOA. The formation of amine secondary aerosol is complex; reaction pathways can lead to the formation of both organic and inorganic components. Changes in the single hygroscopicity parameter $\kappa$ reflect changes in aerosol chemical composition. The CCN activity for amine secondary aerosol systems can range from $\kappa$ 0.2 to 0.74; amine secondary aerosol can be hygroscopic if formed under humid conditions. Tertiary amine (TMA) secondary aerosol can be described by a two-component inorganic/organic hygroscopicity model; the BA-NO$_3$ aerosol cannot. Variability in amine hygroscopicity, especially for primary aliphatic amines is due to the presence of volatile components. Therefore, measured hygroscopicity of tertiary amine aerosol does not exhibit variance while that of primary aliphatic amine aerosol is more susceptible to changes in temperature.

Continuing work on the composition and reaction pathway for aliphatic amine secondary aerosols is necessary in order to fully understand the aerosol hygroscopicity and appropriately estimate the climate effects. The behavior of aliphatic amines with the presence of ammonia should also be investigated to more accurately mimic the real environment and estimate the role of aliphatic amines in the atmosphere.
APPENDICES
Appendix A

Density and elemental ratios of secondary organic aerosol: application of a density prediction method

1. Introduction

Aerosol contributes to climate change and adversely affects air quality (Seinfeld and Pandis, 2006b). SOA volume concentration in environmental chambers or flow tube reactors are often quantified using a scanning mobility particle sizer (SMPS) based on particle electrical mobility diameter. Current air quality regulation for aerosol is based on mass concentrations (e.g., National Ambient Air Quality Standards for annual PM$_{2.5}$ concentration < 15 g/m$^3$), hence particle effective density is necessary to convert SOA volume concentrations to mass concentrations. Density must be estimated when a direct measurement is not available; however, the estimation of the density of organic aerosols is highly uncertain, mostly due to lack of chemical identification (Hallquist et al., 2009a).

Kuwata et al. (2012) proposed an estimation method for density of organic material based on elemental ratios (O/C and H/C); important applications include determination of organic aerosol density using elemental ratios determined by an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) (DeCarlo et al., 2006b; Aiken et al., 2007a). Considering the recent wide-spread use of elemental analysis in the aerosol science community, the estimation method has the potential to be applied to a large number of laboratory and field studies. However the experimental verification of the semi-empirical relationship was limited to a selective few biogenic systems (isoprene, -pinene, central Amazon Basin) as well as a field measurement in northern California (Setyan et al., 2012); therefore, further verification covering an expanded range of systems is needed. This study aims to evaluate the applicability of the Kuwata et al (2012) estimation method to 22 different SOA forming
systems, including oxidation of aromatic hydrocarbons, phenolic compounds, and biogenic compounds.

2. Experimental

2.1 Environmental chamber

All experiments were conducted in the UC Riverside/CE-CERT environmental chamber described in detail in Carter et al. (2005b). In short, this facility consists of dual 90 m³ Teflon® reactors suspended by rigid frames in a temperature controlled enclosure (27 ± 1 °C) continuously flushed with dry purified air (a dew point below -40 °C) air generated by an Aadco 737 series (Cleves, Ohio) air purification system. Blacklights (272 bulbs, 115 W Sylvania 350 BL, NO₂ photolysis rate 0.4 min⁻¹) are used as the light source for all the photooxidation experiments reported herein; ozonolysis experiments were carried out in the dark.

2.2 Gas and particle analysis

The Agilent 6890 Gas Chromatograph – equipped with a flame ionization detector was used to measure concentrations of precursor hydrocarbons and an inert tracer (perfluorohexane) unless noted otherwise (Table S1). Analytical conditions are described elsewhere (Nakao et al., 2011ab).

Particle effective density was directly measured with an Aerosol Particle Mass Analyzer (APM, Kanomax) (Ehara et al., 1996a) coupled to a custom-built Scanning Mobility Particle Sizer (SMPS) (Cocker et al., 2001b) in series. A detailed description of the APM-SMPS system and data algorithms are described elsewhere (Malloy et al.,
Chemical composition of SOA was monitored by HR-ToF-AMS (DeCarlo et al., 2006b); the elemental ratios (O/C, H/C) of SOA were acquired by the elemental analysis (EA) described by Aiken et al. (2008a). The ion species list in the high-resolution data analysis toolkit, PIKA (v1.08), was modified to fit all significant ions with m/z less than 100. The high resolution fragmentation table was modified to account for different \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) for different systems as discussed in section 4.1.

2.3 Chamber experiments

The reactants used for the chamber experiments are summarized in Fig. 1. NO (UHP grade, Matheson) was used for NO\(_x\) photooxidation experiments. All other chemicals were purchased from Sigma-Aldrich at the highest purity available. All experiments were performed under dry (RH<0.1%) conditions. The experimental procedure has been described elsewhere (Nakao et al., 2011ab; Tang et al., 2012b). Reactants were oxidized under the following three conditions: 1) photooxidation in the presence of NO\(_x\), 2) photooxidation using H\(_2\text{O}_2\) (50wt% solution in water) as a radical source, or 3) dark ozonolysis. The reaction conditions and wall-loss corrected SOA concentration is summarized in the supplementary material (Table S1).

3. Density prediction method

Previous methods to estimate material density require information on chemical structures (e.g., Girolami, 1994), which is practically infeasible for SOA consisting of many unknown species (Hallquist et al., 2009a). Recently, Kuwata et al. (2012) proposed a semi-empirical relationship between organic material density \(\rho_{\text{org}}, \text{g/cm}^3\), O/C, and H/C as follows:
The relationship was optimized for 31 individual atmospherically relevant organic species with known densities, and was further evaluated against chamber results using two reactants ( -pinene and isoprene) and an Amazon field data set. The stated accuracy of the prediction is within 12% (Kuwata et al., 2012). To visualize density prediction in terms of elemental ratios, a Van Krevelen diagram (H/C vs. O/C) with density contour is shown in Fig. 2. Note that oxidation state of carbon (OSc) and density isopleth are nearly parallel in the region for typical SOA (around 1.2~1.5 g/cm$^3$), which suggests that chemical processing without change in OSc (e.g., hydrolysis) would have minor impact on density prediction. Two curved lines denote the range of elemental ratios of ambient organic aerosol deconvoluted by PMF (Positive Matric Factorization) (Ng et al., 2011), suggesting that density of low volatility oxygenated organic aerosol (LV-OOA) can reach 1.8 g/cm$^3$.

Uncertainties of elemental analysis of HR-ToF-AMS data includes the quantification of (H$_2$O$^+$)$_{org}$ and (CO$^+$)$_{org}$. Although both ions possibly have significant contribution to bulk elemental ratios, the contribution of organics to H$_2$O$^+$ is uncertain due to other sources of H$_2$O$^+$ (moisture in the air, unevaporated water, and/or inorganics), and CO$^+$ peak is typically overwhelmed by neighboring N$_2$$^+$ peak. The default assumption is that (CO$^+$)$_{org}$ is equal to (CO$_2^+$)$_{org}$ and (H$_2$O$^+$)$_{org}$ is 22.5% of (CO$_2^+$)$_{org}$ (Aiken et al., 2008a). Kuwata et al. (2012) applied calibration factors of (CO$^+$)$_{org}$/(CO$_2^+$)$_{org}$ and (H$_2$O$^+$)$_{org}$/(CO$_2^+$)$_{org}$ fragment ratios for HR-ToF-AMS measurement determined by Chen
et al. (2011a). The impact of \((\text{CO}^+)_{\text{org}}\) and \((\text{H}_2\text{O}^+)_{\text{org}}\) on elemental ratios and density prediction is discussed in the following section.

4. Results and Discussion

4.1 Measurement of SOA density and elemental ratios

When ambient aerosols are analyzed by a HR-ToF-AMS, a number of sources may contribute \(\text{H}_2\text{O}^+\) fragment (Aiken et al., 2008); however, since the chamber experiments in this study were carried out under dry conditions without seed particles, measured \(\text{H}_2\text{O}^+\) is predominantly from organics. Measured \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) is shown in Fig. 3 (relative ionization efficiency of \(\text{H}_2\text{O}^+\) and \(\text{CO}_2^+\) is assumed to be 2.0 and 1.4, respectively; Aiken et al., 2008). \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) values were generally observed to be higher than the default assumption, which significantly affect elemental ratios. \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) tended to increase as the number of alkyl substituents on aromatic ring increases (trimethylbenzene highest). This trend was due to nearly constant \((\text{H}_2\text{O}^+)_{\text{org}}\) fraction and decreasing \((\text{CO}_2^+)_{\text{org}}\) fraction as the number of substituent increases (not shown). The decreasing trend of \((\text{CO}_2^+)_{\text{org}}\) fragment fraction is consistent with higher formation of less reactive ketones than reactive aldehydes (benzene vs. trimethylbenzene; Sato et al., 2012). The observed \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) was grouped according to the number of alkyl substituents and the average values of each group are applied to elemental analysis. Note that although the higher \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) values results in higher \(\text{H}/\text{C}\) and \(\text{O}/\text{C}\), since \(\text{H}_2\text{O}^+\) does not affect oxidation state of carbon, \((\text{H}_2\text{O}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) calibration has a minor impact on density prediction (Fig. 2).
Chen et al. (2011) quantified \((\text{CO}^+)_{\text{org}}\) utilizing difference of PToF (Particle Time-of-Flight) of other ions with \(m/z\) 28 (\(\text{N}_2\) and gas-phase \(\text{CO}\)). However, since most of the AMS data in this study was acquired without PToF, and Chhabra et al. (2011) reported \((\text{CO}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) for SOA from toluene/\(m\)-xylene/phenolic compounds were 0.9 ~ 1.3, reasonably close to the default value, 1, this study kept the default value for \((\text{CO}^+)_{\text{org}}/(\text{CO}_2^+)_{\text{org}}\) of 1.

Observed SOA density and elemental ratios are shown in Fig. 4 (literature values under similar experimental conditions are shown for comparison, Kuwata et al., 2012; Chhabra et al., 2010; Ng et al., 2007; Chen et al., 2011a) and Table S1. Results were grouped by each reactant without regard for oxidation conditions in the following discussion. Although different experimental conditions might significantly influence elemental ratios and density, no systematic dependence of density and elemental ratios on oxidation conditions is observed within the data set. Shilling et al. (2009) observed loading dependence of density and elemental ratio with particularly stronger loading dependence for <10 \(\mu\)g/m\(^3\), using a steady-state continuous flow chamber that provided large amount of integrated signal at low mass-loading. However, since this study was generally performed under higher mass loading compared to Shilling et al., mass loading effect was observed to be minor.

SOA density ranged between 1.21 and 1.48 g/cm\(^3\), with phenol yielding the highest SOA density (average: 1.42 g/cm\(^3\)) and \(\beta\)-caryophyllene the lowest (average: 1.22 g/cm\(^3\)). The measured density and O/C followed a similar trend; density (and O/C)
decreased slightly as the carbon number of reactants increased, except for isoprene. The different trend for isoprene SOA indicates that bulk composition of isoprene SOA formation is significantly different from aromatic SOA. The trend of H/C was opposite to O/C. These observations support previous findings of the correlation between density and the extent of oxidation of SOA (Katrib et al., 2005).

O/C of aromatic SOA and corresponding phenolic SOA were similar (Fig. 4). If additional oxygen in reactant (e.g., phenol vs benzene) results in additional oxygen in condensing species, O/C ratio of phenolic SOA is expected to be higher than corresponding aromatic SOA (e.g., ~17% higher for phenol SOA than benzene SOA assuming condensing products have six carbons). A possible explanation is that aromatic SOA is mostly consisted of multigenerational reaction products (two or more oxidation steps), and hence the presence of additional oxygen in reactants (e.g., phenol) only shortened the reaction steps needed to reach condensing products.

4.2 Density prediction vs. measurement

Predicted densities are compared with measured densities in Fig. 5. The predictions agreed with measurements within 12% except for C6 aromatic/phenolic compounds (benzene, phenol, and catechol). The overprediction of C6 SOA density suggests that C6 SOA contains less density-enhancing structural features such as hydrogen bonds or ring structures (Girolami, 1994). A characteristic of C6 SOA is its higher CO$_2^+$ fragment signals in AMS spectra compared to SOA from methylated aromatics, which suggest higher contribution of carboxylic acids and possibly oligoesters (from reactions of carboxylic acids and alcohols) in C6 aromatic SOA (Sato et al., 2012;
benzene vs. 1,3,5-trimethylbenzene). Oligoester formation could result in loss of hydrogen bonding, and hence lower density. Further chemical analysis using different techniques would be needed to verify the hypothesis.

As reported by Kuwata et al. (2012), the effect of nitrogen or sulfur containing species on the density prediction needs further investigation. For all the experiments in this study, effect of nitrogen is expected to be minor since N/C ratios of SOA were 0.00–0.01 (Table S1). No reactant in this study includes sulfur and thus the effect of sulfur is not probed.

5. Conclusion

A recent study proposed a semi-empirical relationship between organic aerosols density, O/C, and H/C (Kuwata et al., 2012). This study applied the semi-empirical relationship to the extensive data set of elemental compositions and densities of SOA formed by the oxidation of 22 different reactants including terpenes, aromatic hydrocarbons, and phenolic compounds, in an environmental chamber. The semi-empirical relationship successfully predicted density of SOA within 12% error except for overprediction for C6 aromatics (benzene, phenol, and catechol). This study further extended the range of application of the prediction method to include anthropogenic systems.
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7. Figures

Figure A.1 Reactants used for chamber experiments
Figure A.2 Van Krevelen diagram with density and oxidation state of carbon (OSc) contours
Figure A.3 (H$_2$O$^+$)$_{org}/$(CO$_2$$^+$)$_{org}$ fragment ratio of SOA observed by the HR-ToF-AMS
Figure A.4 Effective density, H/C, and O/C of secondary organic aerosol as functions of carbon number of parent species
Figure A.5 Comparison of predicted and measured density of secondary organic aerosol. Dotted lines indicate ±12% lines.
Appendix B

Characterization of a method for aerosol generation from heavy fuel oil (HFO) as an alternative to emissions from ship diesel engines

1. Introduction

Freshly emitted particulate matter (PM) is ideal for in vivo and in vitro health effect studies. While researchers have relatively easy access to on-road engine and chassis dynamometer PM, it is difficult to directly explore the health impacts of PM from ships. Few manufacturers (Man B&W, Wartsila, and Mitsubishi) control more than 80% of ship engine market share and even they have very few engine dynamometers and scientists are rarely granted access to such extraordinary facilities (Kasper et al., 2007). When direct engine PM emissions are not available, health scientists may use bulk PM samples. The National Institute of Standards and Technology (NIST) collects different and large amounts of diesel PM. The samples are commercially available standard reference materials (SRM). Diesel engine PM SRM has been resuspended into aerosol and extracted for in vivo and vitro studies (Lippmann & Chen, 2009). But resuspended particles may not replicate freshly emitted particle size and number distribution. Furthermore (as of September 2010), there is no available NIST ship engine PM SRM. Only recently have PM ship studies gained either on-board or aircraft measurement access (Agrawal et al., 2008; Murphy et al., 2009). Health related studies will benefit from an alternative method to access ship source PM.

Useful health information can be obtained from laboratory-generated particles (Brown et al., 2001; Dick et al., 2003; Gwinn & Vallyathan, 2006; Oberdorster, 2000; Oberdorster et al., 2005; Pinkerton, 2002). Particle concentration, size, hygroscopicity, morphology, transition metal, organic and elemental carbon, and composition adversely affect health (Albritton & Greenbaum, 1998; Blanchard & Willeke, 1984; Broday &
Georgopoulos, 2001; Ferin et al., 1990; Lighty et al., 2000; Pinkerton, 2002; Varghese & Gangamma, 2006). In this study we will synthesize ship-related particles and characterize their above-mentioned specific health related properties.

Particles emitted from ship diesel engines are mainly composed of organic carbon, sulfate, and ash. Nickel and vanadium are the major components of ash and are formed by burning low-grade fuel oils (Lyyränen et al., 1999). Recently, Murphy et al. (2009) performed simultaneous on-board and airborne measurements of particles emitted from a modern container ship. They observed low elemental carbon to organic carbon emission ratios (EC/OC ~ 0.04) and report particles in two size ranges, 5 to 8 nm and 30 to 100 nm. The 5 – 8 nm nanoparticles dominated the total number concentration. Transmission electron microscope (TEM) data showed that these nanoparticles were composed of vanadium, nickel and sulfur. The 30 – 100 nm particle range also contained vanadium, sulfur and nickel components but showed a greater presence of organic carbon. In this study, we synthesized 5 – 8 nm ash with similar physical and chemical characteristics as particles reported by Murphy et al. (2009).

5 – 8 nm particles can be synthesized by the spray flame pyrolysis method (Pratsinis, 2006). The flame provides an environment for liquid phase particle precursor to completely evaporate and nucleate to form nanoparticles. Particles are then formed in the post flame region where temperature cools down. We use heavy fuel oil (HFO) as the liquid phase particle precursor and apply spray flame pyrolysis with a lab-scale oxy-hydrogen flame burner to generate ash particles. A chemical equilibrium model compares and predicts nickel and vanadium compounds from combustion conditions.
Health-related PM characteristics, (e.g., size, hygroscopicity, morphology and composition) of the synthesized particles are compared to data reported in published works. The unique oxy-hydrogen flame burner has two distinct qualities. When heated the burner facilitates the flow of highly viscous HFO in the capillary tube and eliminates elemental carbon formation and contamination. To our knowledge, this is the first time ship ash PM has been aptly synthesized on a laboratory scale.

2. Experimental

2.1. Setup

Particles were synthesized using an oxy-hydrogen flame burner as shown in Figure 1. The apparatus consists of three co-axial stainless steel tubes. The inner diameters and outer diameters of each tube are 0.5 and 0.73, 1.1 and 1.5, 1.8 and 12.7 mm, respectively. The innermost tube is positioned 0.5 mm higher than the other two tubes to form a nozzle on the tip of the burner. The burner is an enhanced design of the Mueller et al (2003) and Guo and Kennedy (2007) burners. The new burner has a turbulent oxy-hydrogen flame. The co-axial oxygen flow provides a wider range of flame heights. The oxy-hydrogen flame is also higher in temperature compared to that of the Mueller et al (2003). Various solvents can be used to dissolve particle precursors in the oxy-hydrogen flame burner. For example, HFO is more easily sprayed into the new configuration compared to the Mueller et al (2003) design. Oxygen flow and flame height are also more easily controlled than Guo and Kennedy (2007). The current burner has simple structure and better scalability. Flame conditions such as temperature, flame height, gas velocity and residence time can be varied in wider range compared to other
designs. The above features provide versatility and flexibility in flame synthesis conditions. This makes the burner an ideal tool as a standard or a reference aerosol generator. An invent disclosure was filed for this burner (Jung et al., 2009) and for more detail see our forthcoming paper (Zheng et al.).

For this study, H\(_2\) (99.5%, Praxair) was introduced through the innermost and intermediate tubes. O\(_2\) (99.5%, Praxair) was introduced between the intermediate and outermost tubes. Flow rates of H\(_2\) and O\(_2\) were controlled by mass flow controllers (647C and 1179A, MKS Instruments Inc., MA). An oxy-hydrogen flame was formed at the tip of the burner. A H\(_2\) flow rate of 5 Lpm and O\(_2\) flow rate of 2.5 Lpm were used in this synthesis. HFO (taken directly from the ship fuel tank same as Murphy et al. 2009 used) was first fed through the innermost tube with a syringe pump (EW-74900-00, Cole Parmer) to precisely control the feed rate. At the tip of the burner, HFO was dispersed into micrometer droplets via H\(_2\) shear flow. The liquid droplets then underwent a series of physical and chemical processes-evaporation, combustion and nucleation-to form solid particles.

Chemical and physical properties of HFO are shown in Table 1. It is extremely difficult to pump and disperse highly viscous HFO at room temperature. In real-world ship engine operations, the HFO is heated up to about 100 °C to facilitate pumping and nebulization. In the current experiment, we also heated the HFO to elevated temperatures. A plastic syringe was replaced with a heat resistant stainless steel syringe (780813, KD Scientific). The syringe and oxy-hydrogen flame burner were connected by a 25 cm long stainless steel tube (outer diameter 6.4 mm). A fiberglass yarn insulated flexible heating
tape (4550T131, McMaster-Carr) was wrapped around the syringe and the connecting tube to sustain temperatures higher than room temperature. A K-type thermocouple (not shown in the figure) was attached on the surface of the connecting stainless steel tube at a position close to the burner. The K-type thermocouple measured the heating temperature. The 25 cm stainless steel connecting tube provided a long enough residence time for the HFO to be heated up and reduce viscosity. A temperature controller (PM6C1CA, Watlow) controlled heating temperatures. To avoid damage, the contact surface between the stainless steel syringe and plastic syringe pump was cooled by compressed air. Particles were synthesized at HFO feeding rates of 5 and 15 ml/h and heating temperatures of 60 and 100 °C.

2.2. Sampling and characterizing

An L shape stainless steel sampling tube (3.2 mm inner-diameter (ID), 6.4 mm outer diameter (OD) with one end facing down was placed 6 cm above the oxy-hydrogen flame tip. The other end was connected to an ejector pump (Air-Vac, TD110H). Synthesized particles were drawn into the ejector pump and diluted. Filter samples were taken for offline chemical analysis. Particles were also analyzed with online instruments. A Scanning Mobility Particle Sizer (SMPS) measured synthesized particle size and number distribution. The SMPS was composed of a neutralizer, a Differential Mobility Analyzer (DMA, TSI model 3080) and a Condensation Particle Counter (CPC, TSI model 3776).

The cloud condensation nuclei (CCN) behavior of synthesized particles was characterized by a TSI 3080 SMPS (DMA 3080, CPC 3772) and a Cloud Condensation
Nuclei Counter (CCNC) (Droplet Measurement Technology). Particles are size selected by the DMA and then the monodisperse aerosol stream is split. Particles of a given size are counted by the CPC and exposed to a prescribed amount of water vapor, or supersaturation, \( s \), in the CCNC instrument. Particles whose critical \( s \) exceeds that of the instrument, form droplets. The droplet number or CCN concentration is counted by an optical particle counter in the instrument (Roberts and Nenes, 2005). For this study the instrument \( s \) ranged from 0.18\% to 0.94± 0.03\%.

A handheld electrostatic precipitator (ESP) (Miller et al., 2010) was used to collect particles onto a 200 mesh copper TEM grid (3420C, SPI) for morphology characterization. A 47 mm diameter preweighed 2 \( \mu \)m pore size PTFE Teflon filter (Pall Gelman) was mounted on a filter holder to collect particles for PM mass and ions analysis. The volumetric flow rate passing through the filter was maintained at 20 Lpm using a critical orifice (McMaster-Carr, 3962T44) and a vacuum pump. Sampling time was 30 minutes. Particles were also collected on a preconditioned 47 mm diameter quartz filter (Pall, 2500 QAT-UP) for EC/OC analysis.

TEM analysis was performed at the Central Facility for Advanced Microscopy and Microanalysis (CFAMM) at UCR. TEM grid was mounted on a FEI double-tilt low background sample holder and examined at accelerating voltages of 200 and 300 kV in a FEI CM300 transmission electron microscope, equipped with an EDAX Genesis Energy Dispersive X-ray Spectrometer (EDS) fitted with Si(Li) detector. EDS analyses of the chemical composition of the particles collected on TEM grid was performed at 200 kV at tilt angle of 25° towards the detector. Loaded Teflon filter was weighed for net weight
gain by a microbalance (Cahn C-35). Sulfate ions were extracted from the filter by HPLC grade water and isopropyl alcohol and analyzed using an ion chromatograph (Dionex DX-120). EC/OC content was obtained by analyzing loaded quartz filter with a Sunset Laboratory (Forest Grove) Thermal/Optical Carbon Aerosol Analyzer.

3. Results and Discussions

3.1. Particle Size

Effects of heating temperature and HFO feeding rate on particle size distribution were investigated. Heating temperature was varied from 60 to 100°C to simulate temperatures during ship engine operation. Two HFO feeding rates were studied, 5 and 15 ml/h. H₂ and O₂ flow rates were fixed at 2.5 and 5 Lpm in all cases.

Figure 2 shows high heating temperature and low feeding rate conditions lead to lower particle precursor concentration and result in smaller particle sizes. The volumetric feed rate was kept constant and as the heating temperature increased, the mass feeding rate decreased accordingly. Therefore the amount of vapors available to readily form particles was reduced.

A quenching ring (5 cm OD), as described in Teleki et al. (2009), was used to further reduce the laboratory-generated particle size to comparable ship emitted PM sizes (Jiang, 2008). The quenching device was made of a stainless steel tube (6.4 mm OD). 8 holes of 1 mm diameter were drilled inside the quenching ring so that the exiting gas formed a 10° angle with the radial direction of the quenching ring and a 20° angle with horizontal surface. The distance between the burner tip and quenching ring was set at 6 cm. N₂ gas at a gauge pressure of 2 bar and flow rate of 20 Lpm was supplied to the
quenching ring and introduced into the flame zone with a 20° angle pointing downstream of the flame. Heating temperature was set at 60 °C and feeding rate was 5 ml/h. A NanoDMA (3085, TSI) measured particle size distributions with the quenching ring. Rapid cooling and dilution by N₂ slowed down the collision and sintering growth of particles and reduced particle diameter (Jiang et al., 2007). Figure 2 shows that the mode particle diameter of synthesized ash was reduced to 11 nm, close to observed in-situ metal particle size range (Murphy, et al., 2009).

3.2 Morphology

A TEM image of laboratory-generated particles is shown in figure 3a. These particles were collected at HFO feeding rate of 15 ml/h and heating temperature of 60 °C. In the TEM image, the majority of the particles are between 20 to 30 nm. The images are consistent with the size distribution measured by the SMPS (figure 2). A TEM image of particles sampled in the stack of a main engine on ocean-going ship is also shown in figure 3b. TEM particles are sampled as in as Murphy et al. (2009). Figures 3a and 3b show that synthesized particles have similar morphology to particles emitted from ship. The synthesized particles are slightly larger in diameter (mode of 11 nm versus 5.8 nm). By varying synthesis conditions and adding a quenching ring, smaller particles that better represent actual ship emitted particles may be achieved (figure 2). EDS analysis of synthesized particles showed sulfur and vanadium peaks similar to actual ship emitted particles (Murphy, et al., 2009).

3.3 Chemical Composition
Results of EC/OC and anion analysis are shown in table 2. About 60% of total PM mass was OC and no EC was present on the filter. Ash content was obtained by subtracting EC and OC mass from the total PM mass. The absence of EC and OC to ash ratio measured in our study was very similar to those of Murphy et al. (2009) for ship PM measured onboard (Table 3). The spray flame used generated a much smaller fraction of particulate sulfate compared to real ship PM. This is likely due to the absence of a long exhaust pipe in the laboratory test. Gaseous SO$_2$ can convert to SO$_3$ and H$_2$SO$_4$ given sufficient residence times; most of synthesized sulfur emission was in the form of SO$_2$.

3.4 Chemical Equilibrium Calculation

A chemical equilibrium calculation is a useful tool to understand the possible combustion products of metal containing fuels (Abdul-Khalek et al., 1998; Jang et al., 2007). The calculations were applied to a low-speed 2-stroke main engine and our lab-scale oxy-hydrogen flame to predict equilibrium concentrations of vanadium and nickel containing compounds. The National Aeronautics and Space Administration (NASA) computer program Chemical Equilibrium with Applications (CEA, version 2) (Gordon & McBride, 1994) with Java graphical user interface was used. A thermodynamic input file including vanadium, nickel, and sulfur properties was used (Linak et al., 2000; Linak et al., 2004). The chemical equilibrium model confirmed that the real-world ship diesel engine and synthesized flame burner combustion processes produced the same vanadium, nickel and sulfur PM products as detailed in the following sections.

3.4.1. 2-stroke engine
For the 2-stroke main engine, 1 and 100 bar operating conditions were used. The chemical composition of HFO in table 1 was used for predictions. The equivalence ratio of combustion was calculated as 0.6 from Man B&W Diesel Report (ManDiesel, 2004). At 1 bar, all vanadium and nickel compounds, mostly VO$_2$ and Ni, were in the gas phase for combustion temperatures above ~ 1700 °C (figure 4a and 4b). Liquid phase V$_2$O$_5$(L) was predicted at intermediate temperatures (between 600 to 1400 °C ). The liquid phase was converted to solid phase V$_2$O$_5$(S) at lower temperature ranges (500 to 700 °C). Gas phase Ni(OH)$_2$ dominated nickel compounds between 1300 to 1700 °C. At intermediate temperatures (700 to 1100 °C), solid phase NiSO$_4$(S) and NiFe$_2$O$_4$(S) became dominant. As temperatures decreased, solid sulfate compounds were dominant. VOSO$_4$(S) and NiSO$_4$(S) were formed below 600 °C and 700 °C, respectively. At 100 bar, NiSO$_4$(S) and VOSO$_4$(S) solidified at higher temperatures (200 to 300 °C; figure 4c and 4d). The chemical equilibrium model predicted two major differences in the 1) presence of solid phase V$_2$O$_5$(S) at 1 bar between 500 and 800 °C and 2) in the dominance of gas phase Ni(OH)$_2$ at 100 bar above 1300 °C.

3.4.2. Oxy-hydrogen flame

Input parameters for the chemical equilibrium prediction of oxy-hydrogen flame are shown in table 3. It is assumed that particles are formed in the post flame region where the equivalence ratio is low (in other words, oxygen rich) and temperature cools down (Guo & Kennedy, 2007). This assumption is supported by the observed particle size reduction from the adoption of the quenching ring in the post flame region (figure 2). Temperature of the current oxy-hydrogen flame was calculated for different equivalence
ratios. All predicted flame temperatures were greater than 1400 °C. This result also supports assumptions of particle formation in the post flame region. Oxygen flow rate of 3.5 Lpm was used for calculation instead of the experimental value 2.5 Lpm to simulate ship diesel engine conditions and have an equivalence ratio of 0.6 as described previously. As can be seen in figure 5a and 5b, changes of nickel and vanadium compounds for oxy-hydrogen flame have similar trends as the 1 bar case for the ocean going ship 2-stroke diesel engine. This supports that the lab-scale oxy-hydrogen burner is a useful device to generate the same type (or at least similar) particles to ship emitted particles. This study confirms the formation of vanadium and sulfur compounds during both real engine combustion and oxy-hydrogen flame combustion.

3.5. Hygroscopicity

CCN experiments characterized and compared the hygroscopicity of laboratory-generated particles to those described in Murphy et al. (2009). CCN measurements were conducted for flame conditions at 15 ml/h and 60 °C. The amount of water vapor, the supersaturation in the instrument ranged from 0.18 to 0.94%. At low supersaturations ($s < 0.8\%$) a small fraction of nuclei (<10% of particles with size > 100nm) formed droplets above the size of the optical particle counter detection limit (0.75µm). This was expected, as the majority of particles from the flame study were very small insoluble metals. At $s = 0.94 \pm 0.03\%$, the particle critical diameter was ~90 nm; above this size 70% of the total particle concentration became active and formed droplets. For the same CCNC instrument conditions ($s = 0.94\%$) calibration ($\text{NH}_4\text{SO}_4$) particles activated above 29 nm. The HFO particles formed by flame pyrolysis are thus much less hygroscopic
than soluble inorganic species. It is noted that the condensation of gasses was minimized and the potential soluble particulate contributions from sulfates were significantly reduced in this study. However, VOSO$_4$(S), formed below 600 °C did not enhance CCN activity. Despite the reduction in sulfate containing compounds, these CCN results are consistent with Murphy et al. 2009 who also show low CCN activity and very low hygroscopicity for real-world ship PM emissions.

4. Conclusions

Alternative particles of ash PM emitted from ships were generated in the lab using an oxy-hydrogen spray flame burner. With the aid of a quenching ring, at heating temperature of 60 °C and feeding rate of 5 ml/h, laboratory-generated particles have a peak size of 11 nm, close to that of real ship emitted ash particles. Sulfur and vanadium signals were observed in both laboratory-generated and real ship emitted particles. The absence of elemental carbon in laboratory-generated particles is comparable to the nano mode (e.g. 5 to 8 nm) ship emitted particles. Chemical equilibrium calculations showed that flame synthesis condition can predict the same particle product as that of ship diesel engine. Both laboratory-generated and ship emitted particles are not hygroscopic and are not very CCN active. The consistency in PM characteristics (size, morphology, hygroscopicity, composition) of synthesized ash particles to ship diesel engine ash particles will significantly affect the feasibility of ship-related PM health studies.
5. References


### 6. Tables

Table B.1 Selected Properties of HFO.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 15 °C (g/ml)</td>
<td>0.99</td>
</tr>
<tr>
<td>Viscosity at 40 °C (mm$^2$/s)</td>
<td>743.4</td>
</tr>
<tr>
<td>Viscosity at 100 °C (mm$^2$/s)</td>
<td>31.78</td>
</tr>
<tr>
<td>Carbon (wt %)</td>
<td>85.87</td>
</tr>
<tr>
<td>Hydrogen (wt %)</td>
<td>9.63</td>
</tr>
<tr>
<td>Oxygen (wt %)</td>
<td>1.64</td>
</tr>
<tr>
<td>Nitrogen (wt %)</td>
<td>0.46</td>
</tr>
<tr>
<td>Ash (wt %)</td>
<td>0.072</td>
</tr>
<tr>
<td>Sulfur (wt %)</td>
<td>2.03</td>
</tr>
<tr>
<td>Vanadium (mg/kg)</td>
<td>178</td>
</tr>
<tr>
<td>Nickel (mg/kg)</td>
<td>58</td>
</tr>
<tr>
<td>Iron (mg/kg)</td>
<td>19</td>
</tr>
</tbody>
</table>
Table B.2 EC/OC and anion offline filter analysis.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>PM (µg)</td>
<td>55.6</td>
</tr>
<tr>
<td>OC (µg)</td>
<td>34.1</td>
</tr>
<tr>
<td>EC (µg)</td>
<td>0</td>
</tr>
<tr>
<td>Ash (µg)</td>
<td>21.5*</td>
</tr>
<tr>
<td>$\text{H}_2\text{SO}_4\cdot 6.5\text{H}_2\text{O}$ (µg)</td>
<td>0.00032</td>
</tr>
</tbody>
</table>

* Ash content was obtained by subtracting EC and OC mass from the total PM mass.
Table B.3 Input parameters for oxy-hydrogen flame chemical equilibrium predictions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ flow rate (Lpm)</td>
<td>5</td>
</tr>
<tr>
<td>O₂ flow rate (Lpm)</td>
<td>3.5</td>
</tr>
<tr>
<td>HFO feeding rate (ml/h)</td>
<td>15</td>
</tr>
</tbody>
</table>
7. Figures

Figure B.1 Schematic of experimental setup.

A: Heavy fuel oil (HFO)
B: H₂
C: O₂
D: Passage for C
E: Passage for B

compressed air  vent to analyzing instruments

ejector pump

mass flow controller

O₂

H₂
cooling air

heating tape

syringe
Figure B.2 Particle size distributions measured by the SMPS and the NanoDMA at different HFO flow rates and heating temperatures. The SMPS measured size distributions of particles formed without a quenching ring. The NanoDMA measured size distributions of particles formed with a quenching ring. A lognormal fit was applied to NanoDMA data.
Figure B.3 TEM images of (a) synthesized particles for feeding rate of 15 ml/h and heating temperature of 60 °C; (b) particles collected from the exhaust stack of an ocean going vessel when a main engine was in operation.
Figure B.4 Equilibrium mass fractions in engine combustion condition: (a) vanadium compounds at 1 bar condition, (b) nickel compounds at 1 bar, (c) vanadium compounds at 100 bar condition, and (d) nickel compounds at 100 bar condition.
Figure B.5 Equilibrium mass fractions for synthesizing combustion condition: (a) vanadium compounds, and (b) nickel compounds.