UNIVERSITY OF CALIFORNIA, IRVINE

Nitrogen Containing Secondary Organic Aerosols: Experiments and Air Quality Simulations

DISSEPTION

submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in Chemistry

by

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2020
DEDICATION

A mi familia. To my family.
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ABSTRACT OF THE DISSERTATION

Nitrogen Containing Secondary Organic Aerosols: Experiments and Air Quality Simulations

By

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Doctor of Philosophy in Chemistry

University of California, Irvine, 2020

Professor Sergey Nizkorodov, Chair

Secondary organic aerosol (SOA) is a large fraction of particulate matter (PM) worldwide and remains a large source of uncertainty in global models that aim to predict the radiative forcing contribution of PM. The properties of SOA are susceptible to change during transport in the atmosphere in response to different environmental conditions, such as sunlight, temperature, relative humidity (RH), and interaction with other atmospheric species. My research investigated the effects on the physical properties and chemical composition of SOA resulting from the exposure of SOA to common environmental species, such as ammonia, amines, and water vapor mixing ratios.

My first project examined the effect of RH on the chemical composition of SOA formed from low-NOx toluene oxidation. We found that the particle mass loading decreased by nearly an order of magnitude when RH increased from < 2 to 75–90 % for low-NOx toluene SOA, but this effect was much smaller for high-NOx toluene SOA. Mass spectrometry revealed a significant reduction in the fraction of oligomers present in the SOA generated at 75 % RH compared to SOA generated under dry conditions in the low-NOx toluene SOA. The observed
increase in the oligomer fraction and particle mass loading under dry conditions were attributed to the enhancement of condensation reactions which produce water and oligomers from smaller compounds in low-NO$_x$ toluene SOA. These results indicate the mass yield of toluene SOA in the atmosphere depends on NO$_x$ concentrations and RH.

Another focus of my research was to explore the reactive uptake of reduced nitrogen compounds by SOA. Currently, *inorganic* nitrogen contribution to PM is represented in air quality models, but the contribution of nitrogen *organic* compounds (NOC) to PM is missing. We found that the reactive uptake of NH$_3$ or dimethylamine (DMA) by low-NOx SOA (toluene, cedrene, or limonene) did not change SOA particle mass but did change particle composition and color due to the formation of NOC. Air quality model simulations showed that inclusion of this new chemistry significantly reduces gas-phase NH$_3$ and can therefore affect particle pH and reduce the formation of inorganic PM.

An additional study exploring the formation of NOC in SOA consisted of generating SOA from a N-containing biogenic precursor (indole). This study found that indole oxidation by OH, O$_3$ or NO$_3$ efficiently produces brown SOA. Overall, this PhD work highlights the effects that RH can have on SOA formation, as well as the novel chemistry and important properties of NOC in the atmospheric environment.
CHAPTER 1

Introduction

1.1 Atmospheric aerosols

The term “aerosol” refers to a mixture of solids or liquids suspended in a gas by Brownian motion that prevents sedimentation to the ground. Aerosols are ubiquitous in the atmosphere and have far reaching effects at the local, regional, and global scales. The phrase “particulate matter”, which is often used interchangeably with aerosols, refers to only the solid or liquid (i.e., the particle) component of the aerosol. Particulate matter (PM) is of great interest to study because it has been shown to impact public health (Poschl and Shiraiwa, 2015), visibility, and Earth’s climate (Ravishankara et al., 2015; Schneidemesser et al., 2015).

When it comes to exploring the relationship between PM and adverse health effects, it is useful to characterize PM by size, because inhaled particles of different size deposit in different sections of the respiratory system. PM$_{10}$ refers to PM with a diameter of 10 µm or less; PM$_{2.5}$ includes PM with a diameter of 2.5 µm or less. For perspective, the width of a human hair ranges from ~50-100 µm (Wei et al., 2005; Wolfram, 2003). Both PM sizes are currently regulated in the US by the Environmental Protection Agency, which sets the National Ambient Air Quality Standards for PM and five other criteria air pollutants known to adversely affect human health and the environment. When inhaled, PM$_{10}$ can make its way down into the larynx, however smaller PM$_{2.5}$ can travel further into the lungs (Finlayson-Pitts and Pitts, 2000; Yeh et al., 1996). One of the earlier studies that drew attention to the toxicity of PM looked at correlations between increased mortality and pollution in six different cities in the US consisting of Portage, WI, Topeka, KA, Watertown, MS, St. Louis, MI,
Harriman, TN, and Steubenville, OH (Dockery et al., 1993). The study found that air pollutants, specifically PM$_{2.5}$ and sulfates, were strongly correlated with increased mortality. Currently, air pollution regulations for PM are based on particle size and mass concentration, however there is increasing discussion of whether these parameters (as opposed to chemical composition, particle number, and surface area) are the best measures of PM toxicity.

PM can measurably impact the radiative forcing (RF) on the Earth’s climate and can also decrease visibility (IPCC, 2013). Most particles are weakly-absorbing and strongly-scattering, thus contributing to a net cooling effect on climate (i.e., negative RF), but a subset of particles are strongly light-absorbing in the ultraviolet and visible range of the solar spectrum effectively contributing to a warming effect on climate (i.e., positive RF). In a report published by the Intergovernmental Panel on Climate Change (IPCC), the net RF of natural and anthropogenic atmospheric species were quantified relative to the RF in the year 1750 (IPCC, 2013). Greenhouse gases such as CO$_2$, CH$_4$, and halocarbons clearly contribute a net positive RF. On the other hand, the net effect of aerosols and their precursors on climate is less understood with a net RF value spanning both the negative and positive ranges (-0.77-0.23 W m$^{-2}$), due to the large error bars associated with these estimates (IPCC, 2013; Bellouin et al., 2019).

In terms of chemical composition, aerosols can be broadly classified into inorganic and organic. Inorganic aerosols primarily consist of ammonium nitrate and ammonium sulfate salts formed in the atmosphere from through acid/base chemistry (Eqns. 1.1-1.3)

$$\text{NH}_3(g) + \text{H}_2\text{SO}_4(g) \rightleftharpoons \text{NH}_4\text{HSO}_4(s)$$  \hspace{1cm} (1.1)
Organic aerosols are further classified by the mechanism of their formation into primary and secondary. Primary organic aerosols (POA) and primary inorganic aerosols (PIA) are directly emitted into the atmosphere from their sources such as biomass burning, wind-driven suspension of soil and dust, sea-spray, volcanic eruptions, and biological species. Secondary inorganic aerosols (SIA) are formed by reactions 1.1-1.3 and the relative contribution of nitrate and sulphate varies by location (Pilinis and Seinfeld, 1987; Tang et al., 2004). Secondary organic aerosols (SOA) are formed in the atmosphere when volatile organic compounds (VOCs) are oxidized by OH, O₃, NO₃ into less volatile compounds and undergo gas to particle conversion. Unlike SIA that have only a few chemical components, the resulting SOA are chemically complex, are less understood relative to inorganic aerosol, and are the focus of the research discussed throughout this thesis.

This dissertation focuses on three under-investigated aspects of SOA chemistry: the effect of relative humidity on the chemical composition of SOA, the effect of ammonia and amines on the chemical composition of SOA, with emphasis on the formation of nitrogen containing compounds, and the chemistry of SOA from unexplored VOC precursors such as indole. The relevant background for each topic and the motivations for the experiments are described in detail at the beginning of corresponding chapters. A brief summary of the chapter goals are described below.

1.2 Effect of relative humidity on SOA properties
The majority of laboratory-based SOA experimental studies have been conducted under low relative humidity (RH) conditions, yet water is known to affect both the chemical and physical properties of SOA and it remains critical to understand the extent of these effects. The presence of water can affect the physical properties of SOA such as viscosity, particle size, and particle mass as well as its chemical properties such as particle acidity and molecular composition. The physical and chemical properties of SOA are understandably linked; therefore when water affects one parameter of SOA other parameters are often also affected. For example, water can act as a plasticizer for SOA particles, making them less viscous and thereby indirectly affecting reactive gas uptake, diffusion rates of gases, and the rate of SOA growth (Renbaum-Wolff et al., 2013; Perraud et al., 2012; Shiraiwa and Seinfeld, 2012). Moreover, aerosol liquid water (ALW) has a strong effect on the acidity of particles and therefore affects acid-catalyzed processes occurring in particles (Jang et al., 2002). The effects of the presence and absence of water on SOA can be illustrated at both RH extremes by studying SOA solvated in water to mimic cloud conditions. For example, going from supersaturated conditions to dry conditions has been demonstrated to speed up reactions that lead to the formation of nitrogen- and sulfur-containing light-absorbing compounds (Nguyen et al., 2012). Moreover under supersaturated conditions, aqueous chemistry occurring in cloud and fog droplets promotes the conversion of small water-soluble molecules into nonvolatile products that would not form in the absence of liquid water (Herrmann et al., 2015).

Chapter 2 explores how RH affects the chemical composition of SOA formed from the OH oxidation of toluene. This study also discusses how the chemical composition and volatility
distribution of the SOA compounds influences the amount of SOA formed (mass yield) under low and high RHs.

1.3 Organic nitrogen in SOA

Inorganic nitrogen contribution to PM (Eqns. 1.1-1.3) is well represented in air quality models. Less understood and missing from models is the contribution of nitrogen-containing organic compounds (NOC) to PM. NOC can be highly light-absorbing in the visible range and may therefore contribute a positive RF on climate. Another consequence of NOC formation in SOA is that NOC are less efficient than ammonia at neutralizing acids in particles.

One obvious route for the production of NOC in SOA is via the oxidation of a N-containing VOC. Nitrogen-containing aromatic compounds based on pyrrole, pyridine, imidazole, indole, diazines, purines, etc., have been detected in biomass burning emissions (Laskin et al., 2009). Chapter 3 describes the first experimental study of the SOA generation from indole, a N-containing VOC emitted from plants and animal waste. The study also investigates the light-absorbing properties of the NOC produced in the indole SOA. Furthermore, results are presented from an airshed modeling study that explored the potential contribution of indole SOA to PM$_{2.5}$ mass concentrations at the regional scale.

A second potential pathway for the incorporation of NOC into SOA is through reactions of SOA with NH$_3$ (Eqn. 1.4). Ammonia is predominantly emitted from agriculture (e.g., fertilizer use) and is the most abundant basic gas in the atmosphere.

$$\text{NH}_3(\text{g}) + \text{SOA carbonyl compound(s)} \rightarrow \text{NOC(s)}$$

(1.4)
Previous laboratory experiments have shown that exposure of SOA to NH$_3$ can lead to ‘browning’ of SOA (Mang et al., 2008) by a mechanism involving the reaction of NH$_3$ with carbonyls in the SOA that lead to a loss of one or more water molecules (Aiona et al., 2017; Kampf et al., 2016). This proposed mechanism is similar to the Maillard reaction that is responsible for the browning of certain foods after cooking. Few studies have attempted to quantify the uptake coefficient of NH$_3$ on SOA particles (Liu et al., 2015), a useful parameter for translating laboratory results into modeling studies. Chapter 4 describes our study of NH$_3$ uptake by various SOA, as well as the results from an exploratory modeling study that investigated the potential impact of NH$_3$ uptake by SOA on PM$_{2.5}$ mass concentrations at the regional and continental scale. Lastly, a similar mechanism for the incorporation of NOC into SOA may be through the reactions of SOA with other reduced nitrogen compounds present in the atmosphere, such as amines. Chapter 5 discusses experiments investigating the uptake of dimethylamine by various SOA leading to NOC formation, as well as the dependence of this uptake on RH.
CHAPTER 2

Effect of Relative Humidity on the Formation of Low-NO\textsubscript{x} Toluene Secondary Organic Aerosol

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2.1 Introduction

Secondary organic aerosol (SOA) is an important component of atmospheric particulate matter. It is formed in the atmosphere via the oxidation of volatile organic compounds (VOCs) by common atmospheric oxidants such as O\textsubscript{3}, OH, and NO\textsubscript{3} (Seinfeld and Pandis, 2016). The SOA formation mechanisms depend in a complex way on physical environmental parameters such as solar irradiance, temperature, and relative humidity (RH). They also depend on the type of oxidant, the concentration of VOC precursors, which govern RO\textsubscript{2} concentrations, and NO\textsubscript{x} levels, which determine the fate of the RO\textsubscript{2} radicals. The RH controls the amount of available water in the system and therefore affects processes in which water acts as a reactant, product, or solvent in several ways. Firstly, gaseous water can directly participate in the VOC oxidation reactions. For example, it is well known to react with carbonyl oxide intermediates in the ozonolysis of alkenes (Finlayson-Pitts and Pitts Jr., 2000). Additionally, aerosol liquid water (ALW) present in hygroscopic particles can lead to the hydrolysis of organic compounds and other particle-phase reactions involving or
catalyzed by water (Ervens et al., 2011). ALW also has a strong effect on the acidity of particles and therefore affects acid-catalyzed processes occurring in particles (Jang et al., 2002). Furthermore, water can act as a plasticizer for SOA particles, making them less viscous and thus affecting the rate of their growth (Renbaum-Wolff et al., 2013; Perraud et al., 2012; Shiraiwa and Seinfeld, 2012). Under supersaturated conditions, aqueous chemistry occurring in cloud and fog droplets promotes the conversion of small water-soluble molecules into nonvolatile products that would not form in the absence of liquid water (Herrmann et al., 2015). Finally, dissolved SOA compounds may undergo more efficient photodegradation in water (Bateman et al., 2011; Nguyen et al., 2012; Romonosky et al., 2015, 2017; Zhao et al., 2017) compared to dry particles (Kourtchev et al., 2015).

Chemical composition is an important characteristic of SOA because it may determine the climate- and health-relevant properties of particles. The effect of RH on the chemical composition of particles has been studied for several types of biogenic SOA (Nguyen et al., 2011; Zhang et al., 2011; Riva et al., 2016; Harvey et al., 2016). For example, Nguyen et al. (2011) examined high-NOx isoprene SOA formed under high- and low-RH conditions and found that the high-RH samples contained fewer oligomers than the low-RH samples. Zhang et al. (2011) investigated the effect of RH on the composition of high-NOx isoprene SOA and found that oligoesters present in the SOA were suppressed at higher RH, while the formation of organosulfates was enhanced. Riva et al. (2016) studied the effect of RH on SOA made from oxidized isoprene hydroxyhydroperoxide (ISOPOOH) and found that increasing RH led to an increase in the abundance of some oligomers while decreasing the abundance of other oligomers. Harvey et al. (2016) investigated the effect of RH on 3-hydroxypropanal
ozoneolysis SOA and found that increasing RH resulted in a decrease in SOA yield and a decrease in oligomerization.

The effect of RH on SOA formed from monoaromatic compounds, such as benzene, toluene, \textit{m}-xylene, and 1,3,5-trimethylbenzene (TMB), has been studied. Most of these studies focused on the effect of RH on SOA yield (Edney et al., 2000; Zhou et al., 2011; Cocker III et al., 2001; Kamens et al., 2011; Cao and Jang, 2010; Faust et al., 2017; Liu et al., 2017; Jia and Xu, 2017) and not the chemical composition of SOA particles. The comparison between different experiments is complicated by the fact that some experiments are done in the presence of hygroscopic seed particles, where ALW may be playing a role; others are done with seed particles containing strong acids, which favor acid-catalyzed chemistry, and others without seed particles. For toluene SOA produced in presence of hygroscopic seed particles, the yield is generally found to be larger under high-RH conditions (Zhou et al., 2011; Kamens et al., 2011; Faust et al., 2017; Liu et al., 2017; Jia and Xu, 2017) because additional organic compounds are produced by the aqueous photochemistry of small highly soluble compounds, such as glyoxal, partitioned in ALW. However, Cao and Jang (2010) observed a negative correlation between RH and SOA yield for low-\textit{NO}_x experiments; i.e., lower RH resulted in higher SOA yields.

In the experiments done without seed particles, the acid catalysis and chemistry occurring in ALW do not contribute to the particle growth. However, this does not rule out the possibility that RH may affect the SOA chemical composition and yield by mechanisms other than those mentioned above. Indeed, White et al. (2014) investigated the effect of RH on the composition of toluene SOA produced under high-\textit{NO}_x conditions without seed particles and observed higher toluene SOA yields at elevated RH and higher yields of photooxidation
products. In this work, we studied the composition of low-NO$_x$ toluene SOA formed under dry and humid conditions in the absence of seed particles. We observed a significant negative correlation between RH and low-NO$_x$ SOA from toluene SOA mass loading and a strong RH dependence on SOA molecular composition. We attribute this effect to the more extensive oligomerization of SOA compounds driven by condensation reactions under dry conditions. The reduction in the fraction of oligomeric compounds under humid conditions is predicted to partly counteract the previously observed enhancement in the toluene SOA yield driven by the ALW chemistry in deliquesced inorganic seed particles.

2.2 Experimental Methods

SOA was generated by the photooxidation of toluene in a 5 m$^3$ smog chamber surrounded by a bank of UV-B lights. Before each experiment, the chamber was humidified to the desired RH by flowing purified air through a Nafion humidifier (PermaPure). The temperature ($\pm 1^\circ$C) and RH ($\pm 2\%$ RH) inside the chamber were monitored with a Vaisala HMT330 probe. No seed aerosol was used. Hydrogen peroxide (H$_2$O$_2$) was introduced to the chamber by injecting a measured volume of aqueous H$_2$O$_2$ (30 wt %) into a bulb where it was evaporated and carried into the chamber by a flow of purified air over a period of 30 min. The majority of the experiments were done under low-NO$_x$ conditions with concentrations of NO and NO$_y$ being below the 1 ppb detection limit of the NO$_y$ analyzer (Thermo Scientific 42i-Y). In the high-NO$_x$ experiments, gaseous NO (1000 ppm in N$_2$; Praxair) was added to achieve a total NO concentration of 300 ppb. Toluene (Fisher Scientific; ACS grade) was introduced into the chamber by evaporating a measured volume of liquid toluene into a stream of air over a period of 5 min, which resulted in a toluene mixing ratio of either 300 or 1000 ppb. Following
the addition of gaseous reactants into the chamber, the UV lamps were turned on, photolyzing the \( \text{H}_2\text{O}_2 \) and resulting in a steady-state OH concentration of \( 1 \times 10^6 \text{ molec cm}^{-3} \) (determined in a separate experiment from the rate loss of a VOC in the presence of OH). These high concentrations of toluene were chosen in order to produce a sufficient amount of SOA to collect for offline analysis. Throughout each experiment, particle concentrations were monitored with a scanning mobility particle sizer equipped with a condensation particle counter (SMPS model 3080; CPC model 3775; TSI Inc.). We used an effective SOA particle density of \( 1.4 \text{ g cm}^{-3} \) to convert the SMPS measurements into particle mass concentration (Sato et al., 2007; Ng et al., 2007). The concentration of toluene in the chamber was tracked with a proton-transfer reaction time-of-flight mass spectrometer (PTR-ToF-MS; Ionicon 8000). The observed decrease in the toluene concentration (typically \( \sim 40\% \)) was the same under low- and high-RH conditions.

SOA samples were collected onto Teflon filters for offline analysis by nanospray desorption electrospray ionization–high-resolution mass spectrometry (nano-DESI–HRMS). The filters were sealed and frozen immediately after the sample collection to avoid decomposition of less stable compounds, as observed for example by Krapf et al. (2016). The SOA filter samples were brought to room temperature and immediately analyzed in both positive and negative ion modes using an LTQ Orbitrap mass spectrometer (Thermo Corp.) with a resolving power of \( 10^5 \) at \( \text{m}\text{z} \) 400 equipped with a custom-built nano-DESI source (Roach et al., 2010a, b). The advantage of nano-DESI is in minimizing the time in which the sample is exposed to the solvent, thus minimizing solvolysis reactions. Mass spectra of the solvent and blank filters were recorded as controls. Mass spectra of the samples with the highest signal-to-noise ratio were clustered together, and the \( \text{m}\text{z} \) axis was calibrated internally with respect to known
SOA products. The solvent and impurity peaks were discarded. The peaks were assigned formulas, \( \text{C}_c\text{H}_h\text{O}_o\text{N}_n\text{Na}^{+0−1} \) or \( \text{C}_c\text{H}_h\text{O}_o\text{N}^{−n} \), constrained by valence rules (Kind and Fiehn, 2007) and elemental ratios (\( c, h, o, \) and \( n \) refer to the number of corresponding atoms in the ion). The resulting ion formulas were converted into formulas of the corresponding neutral species. All data reported below refer to the formula and molecular weights of the neutral species.

### 2.3 Results and Discussion

The mass spectra of a low-RH sample (< 2 % RH) and a high-RH sample (75 % RH) are shown in Fig. 2.1 plotted as a function of the molecular weight of the neutral compounds. The mass spectra obtained in the positive and negative ion modes represent the SOA compounds ionizable in these modes and are not expected to be identical (Walser et al., 2008). The low-\( \text{NO}_x \) mass spectrum shown in Fig. 2.1 is qualitatively similar to the low-\( \text{NO}_x \) mass spectrum of toluene SOA discussed in a previous study in which it was prepared in a different smog chamber but analyzed by the same nano-DESI instrument (Lin et al., 2015).

As shown in Fig. 2.1, the increase in RH resulted in a visible reduction in the overall peak abundance for both ion modes due to the fact that the high-RH sample had a much lower particle mass during the SOA generation (see below), and thus there was less material on the substrate. There was also a reduction in the number of observed peaks. For example, the positive mode mass spectrum in Fig. 2.1 contains 665 peaks at low RH but only 285 peaks at high RH; the corresponding peak numbers are 276 and 90 for the negative ion mode. Despite this reduction in peak abundance and number, the major observed peaks in the mass spectra remained the same. Table 2.1 lists the five most abundant peaks for both the low- and high-
RH samples observed in the positive and negative modes. The fact that the major peaks are similar between the low- and high-RH samples suggests that the major products are produced by a similar mechanism that is not too sensitive to RH. It is of course still possible that the distribution of different structural isomers within each peak could be affected by humidity, but the nano-DESI method used here would be blind to this effect because it cannot separate isobaric isomers.

![Mass Spectra](image)

**Figure 2.1.** High-resolution mass spectra obtained in negative ion mode (a) and positive ion mode (b). The red upward-pointing mass spectra represent the low-NOₓ SOA sample made under low RH (< 2%) and the blue inverted mass spectra represent the low-NOₓ SOA sample made under high RH (75%).
Table 2.1. The five most abundant compounds observed in the low- and high-RH low-NO\textsubscript{x} toluene SOA samples. In positive ion mode, the most abundant species differed by one compound in the low- and high-RH experiments, and hence the table contains six formulas. In negative ion mode, the same five most abundant peaks were observed at the low and high RH.

<table>
<thead>
<tr>
<th>Nominal mass</th>
<th>Formula</th>
<th>Positive ion mode</th>
<th>Low RH</th>
<th>High RH</th>
<th>Normalized peak abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>174</td>
<td>C\textsubscript{7}H\textsubscript{10}O\textsubscript{5}</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>192</td>
<td>C\textsubscript{7}H\textsubscript{12}O\textsubscript{6}</td>
<td>0.74</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>330</td>
<td>C\textsubscript{14}H\textsubscript{18}O\textsubscript{9}</td>
<td>0.64</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>314</td>
<td>C\textsubscript{14}H\textsubscript{18}O\textsubscript{8}</td>
<td>0.45</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>C\textsubscript{12}H\textsubscript{16}O\textsubscript{8}</td>
<td>0.43</td>
<td>0.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>332</td>
<td>C\textsubscript{14}H\textsubscript{20}O\textsubscript{9}</td>
<td>0.17</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nominal mass</th>
<th>Formula</th>
<th>Negative ion mode</th>
<th>Low RH</th>
<th>High RH</th>
<th>Normalized peak abundance</th>
</tr>
</thead>
<tbody>
<tr>
<td>156</td>
<td>C\textsubscript{7}H\textsubscript{8}O\textsubscript{4}</td>
<td>1</td>
<td>1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>172</td>
<td>C\textsubscript{7}H\textsubscript{8}O\textsubscript{5}</td>
<td>0.71</td>
<td>0.86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>174</td>
<td>C\textsubscript{7}H\textsubscript{10}O\textsubscript{5}</td>
<td>0.43</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>C\textsubscript{7}H\textsubscript{10}O\textsubscript{6}</td>
<td>0.40</td>
<td>0.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>114</td>
<td>C\textsubscript{5}H\textsubscript{6}O\textsubscript{3}</td>
<td>0.38</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

While the major oxidation products were similar at low and high RH, the less abundant products were much more strongly affected by RH. Specifically, the abundances of some high-molecular-weight compounds were visibly reduced at high RH (Fig. 2.1), suggesting that either the gas-phase oligomer formation is suppressed by water vapor or the particle-phase oligomer formation is suppressed by ALW. (An alternative explanation is that oligomers hydrolyze after partitioning into the particle, but the amount of ALW in the particles might be too small to sustain efficient hydrolysis.) To better quantify this effect, Fig. 2.2 shows the combined peak abundances as a function of the number of carbon atoms ($n_{C}$) in each molecule. Monomer compounds containing $n_{C} = 7$ and dimer compounds with $n_{C} = 14$ clearly dominate the distribution. In fact, the combined abundance of dimers ($n_{C} = 14$) represents the highest peak in the distribution in the positive ion mode. Many larger compounds with $n_{C}$ up to 32 also appear in the mass spectrum, and these minor compounds are the ones most affected by RH.
Figure 2.2. Combined abundance of all peaks as a function of the number of carbon atoms in negative mode (a) and positive mode (b). The data for the low-RH sample are shown in red and the data for the high-RH sample are shown in blue. The samples were prepared under low-NO_x conditions.

When comparing the low-RH sample to the high-RH sample, there is a significant decrease in combined peak abundance for molecules with $n_C > 7$ under high-RH conditions (except for the $n_C = 14$ dimers). Because these higher-molecular-weight oligomers tend to have lower volatility (Li et al., 2016), they play an important role in the formation and growth of aerosol particles. With the lower fraction of oligomers produced under high-RH conditions, the population of the oxidation products becomes more volatile on average, which should result in a lower SOA yield.
To better illustrate the possible effect of RH on the yield of condensable oxidation products, the volatility distributions were estimated for the low-NOx toluene SOA compounds using the “molecular corridor” approach (Li et al., 2016; Shiraiwa et al., 2014). This parameterization was developed specifically for atmospheric organic compounds containing oxygen, nitrogen, and sulfur (Li et al., 2016), and it makes it possible to estimate the pure compound vapor pressure, $C_0$, from the elemental composition derived from high-resolution mass spectra (Lin et al., 2016; Romonosky et al., 2017). $C_0$ is related to the more commonly used effective saturation mass concentration, $C^* = \gamma \times C_0$, where $\gamma$ is the activity coefficient (Pankow, 1994). $C_0$ becomes equal to $C^*$ under the assumption of an ideal thermodynamic mixing. The $C_0$ values were calculated for each compound observed in the positive and negative ion mode mass spectra. Note that the molecular corridor approach only predicts $C_0$ (i.e., for pure compound); it does not attempt to predict $C^*$, so there is no need to assume a value for the activity coefficient. The values were binned in equally spaced bins of the base-10 logarithm of $C_0$ as is commonly done in the volatility basis set (VBS; Donahue et al., 2006). The contribution of each compound to its volatility bin was taken to be proportional to its relative abundance in the mass spectrum. A previous study looking at the ESI detection of standards in an SOA mixture demonstrated that while their ion intensities were suppressed to a different extent in the mixture (as opposed to in a pure solvent), the ion intensities remained proportional to the mass concentration of the individual compounds in the complex mixture (Nguyen et al., 2013). This is a considerable approximation because even for a series of carboxylic acids the ESI detection sensitivities can vary by several orders of magnitude within the same sample (Bateman et al., 2012). However, this approximation may
still be useful for comparing distributions for the same types of SOA produced and analyzed under the same experimental conditions (Romonosky et al., 2017).

Figure 2.3 shows the resulting distribution of the SOA compounds by volatility. Under typical ambient conditions, compounds with \( C_0 \) above \( \sim 10 \mu g \text{ m}^{-3} \), i.e., the ones falling above the \( \log (C_0) = 1 \) bin, should exist primarily in the gaseous phase. Some of these more volatile compounds were detected in the negative ion mode. They may correspond to carboxylic acids that adsorbed to the filter during sampling or were trapped in the SOA. Less volatile compounds were preferentially observed in the positive ion mode. In both positive and negative ion modes, the compounds falling in the lower volatility bins were visibly suppressed at high RH. For example, the high-RH to low-RH ratio of the combined peak abundances for the compounds falling below \( \log (C_0) = 1 \) is 0.3 in the positive ion mode and 0.05 in the negative ion mode.
In order to investigate whether the decrease in oligomers affects the SOA mass loading, we carried out additional experiments in which the particle mass concentration was tracked with the SMPS at different RH. The SMPS data were corrected for particle wall-loss effects assuming an effective first-order rate constant for the loss of mass concentration of $9.3 \times 10^{-4} \text{ min}^{-1}$, which was measured in a separate experiment (the rate constant was assumed to be independent of particle size). The SMPS experiments were performed under both low-$\text{NO}_x$ and high-$\text{NO}_x$ conditions. A summary of these experiments is presented in...
Table 2.2. Representative examples of the wall-loss-corrected particle mass concentration as a function of photooxidation reaction time are shown in Fig. 2.4 for both the low-NO$_x$ and the high-NO$_x$ toluene SOA systems.

![Figure 2.4](image)

**Figure 2.4.** Examples of particle mass concentration measurements by SMPS (corrected for wall loss) as a function of photooxidation time under low-NO$_x$ (a) and high-NO$_x$ (b) conditions. Under high-NO$_x$ conditions, there was a small difference in the maximum mass concentration achieved under < 2, 40, and 75 % RH (less than a factor of 2), but under low-NO$_x$ conditions the difference was substantially larger. For the low-NO$_x$ system, the wall-loss-corrected particle mass concentration decreased by a factor of 8 over the range of RHs studied. The effect was reproducible as essentially the same mass concentration was observed in experiments repeated on different days under the same initial conditions.
Combining the measured particle mass concentrations with the toluene concentration measurements from PTR-ToF-MS makes it possible to estimate the apparent SOA yields, which are listed in the last column of Table 2.2. Under high-NO_x conditions, the yield decreased from ∼27 to ∼19 % as RH increased from < 2 to 77 %. Under low-NO_x conditions, the yields dropped from 15 to 2 % for the same change in RH. We note that the previously reported SOA yields from toluene SOA formed in the presence of ammonium sulfate seed aerosol displayed the opposite trend, with the yield being higher (∼30 %) under low-NO_x conditions and lower under high-NO_x conditions (∼19 %; Ng et al., 2007). Hildebrandt et al. (2009) noted that the yields in the toluene SOA system are highly sensitive to the oxidation conditions, including the type of UV lights used in photooxidation and the seed aerosol concentration. Furthermore, the wall-loss effects are especially prominent in the toluene SOA system (Zhang et al., 2014). We attribute the difference in the absolute values of yields between our experiments and experiments by Ng et al. (2007) to the difference in the experimental design, likely due to the lack of seed particles in our experiment and lower OH-oxidation rate of toluene.
Table 2.2. Summary of SMPS experiments. The uncertainties included in this table are based on 1 standard deviation in the data for repeated experiments.

<table>
<thead>
<tr>
<th>Initial RH</th>
<th>No. of experiments</th>
<th>NO₂ ppm</th>
<th>Toluene ppm</th>
<th>H₂O₂ ppm</th>
<th>SOA from SMPS μg m⁻³</th>
<th>Wall-loss-corrected SOA μg m⁻³</th>
<th>SOA yield (%)</th>
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</thead>
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<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low NOₓ – high toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 2</td>
<td>4</td>
<td>–</td>
<td>1.0</td>
<td>2.0</td>
<td>180 ± 20</td>
<td>210 ± 20</td>
<td>15 ± 2</td>
</tr>
<tr>
<td>20 ± 3</td>
<td>2</td>
<td>–</td>
<td>1.0</td>
<td>2.0</td>
<td>76 ± 4</td>
<td>87 ± 6</td>
<td>6.2 ± 0.5</td>
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<tr>
<td>43</td>
<td>1</td>
<td>–</td>
<td>1.0</td>
<td>2.0</td>
<td>74</td>
<td>84</td>
<td>5.9</td>
</tr>
<tr>
<td>76 ± 1</td>
<td>4</td>
<td>–</td>
<td>1.0</td>
<td>2.0</td>
<td>27 ± 7</td>
<td>28 ± 7</td>
<td>2.0 ± 0.5</td>
</tr>
<tr>
<td>89 ± 1</td>
<td>2</td>
<td>–</td>
<td>1.0</td>
<td>2.0</td>
<td>25 ± 8</td>
<td>26 ± 9</td>
<td>1.9 ± 0.6</td>
</tr>
<tr>
<td>Low NOₓ – lower toluene</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 2</td>
<td>1</td>
<td>–</td>
<td>0.3</td>
<td>0.6</td>
<td>23</td>
<td>27</td>
<td>5.5</td>
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<tr>
<td>75</td>
<td>1</td>
<td>–</td>
<td>0.3</td>
<td>0.6</td>
<td>8</td>
<td>9</td>
<td>2.2</td>
</tr>
<tr>
<td>High NOₓ – high toluene</td>
<td></td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>&lt; 2</td>
<td>1</td>
<td>0.3</td>
<td>1.0</td>
<td>2.0</td>
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<td>390</td>
<td>27</td>
</tr>
<tr>
<td>43</td>
<td>1</td>
<td>0.3</td>
<td>1.0</td>
<td>2.0</td>
<td>210</td>
<td>260</td>
<td>18</td>
</tr>
<tr>
<td>77</td>
<td>1</td>
<td>0.3</td>
<td>1.0</td>
<td>2.0</td>
<td>230</td>
<td>270</td>
<td>19</td>
</tr>
</tbody>
</table>

The differences between the low- and high-RH systems cannot be explained by the hygroscopic growth of particles at elevated RH. Throughout the experiment, the SMPS sampled air directly from the chamber. Each experiment lasted many hours, which allowed the sheath flow in the SMPS to approach the RH of the chamber air. Therefore, the particles sized by the SMPS contained some ALW and would appear larger than their dry size. If the organic mass in particles did not change at different RH levels, we would have observed an increase as opposed to a decrease in the measured particle mass concentration. With a typical hygroscopic growth factor (the ratio of particle diameters in humidified and dry air) for SOA of 1.1 at 85 % RH (Varutbangkul et al., 2006), the increase in the apparent mass concentration would have been by a factor of about 1.3. Instead, the mass concentration decreased by almost a factor of 8 at higher RHs. The strong dependence of the low-NOₓ toluene SOA mass loading on RH is therefore not an artifact of the SMPS measurements.
We cannot rule out the possibility that the mass loading of SOA was affected by the enhanced wall loss of more water-soluble compounds under high-RH conditions. Indeed, the chamber wall effects are expected to be stronger for the slowly reacting toluene compared to monoterpenes that are oxidized much faster (Pierce et al., 2008). Furthermore, in the absence of seed particles, toluene SOA aerosol growth takes longer, making the wall-loss effects larger (Kroll et al., 2007; Zhang et al., 2014). It is conceivable that the products of the low-NO\textsubscript{x} oxidation of toluene are more water soluble than the products of the high-NO\textsubscript{x} oxidation of toluene. This would result in a stronger effect of RH on the mass loading of low-NO\textsubscript{x} SOA because these products would be more efficiently absorbed by the wetted chamber walls. Distinguishing the wall-loss effects from the effect of water on the distribution of oligomers would require more careful chamber measurements of SOA yields over a broad range of concentrations and in the presence of seed aerosol (to suppress the wall-loss effects).

A possible chemical explanation for the observed RH effect is that there are chemical reactions in the system that directly involve water and change the chemical composition of the particles, thereby affecting their growth rate. Previous studies have shown that RH can affect the composition and potential yield of SOA by altering the fraction of low-volatility oligomers in SOA. Increased RH could suppress the oligomerization occurring by condensation reactions (i.e., reactions between monomers that produce water as a by-product) by shifting the reaction equilibrium toward the monomers as discussed in Nguyen et al. (2011). Conversely, increased RH could promote the hydrolysis of oligomers after they are produced in the gas phase and partition into wet particles. As pointed out above, the latter mechanism is less likely due to the low ALW content of the organic particles.
To investigate the mechanism, we examined the frequency of occurrence of mass differences (corresponding to molecular fragments) between the peaks in the high-resolution mass spectra. Table 2.3 lists the most common mass differences in all four mass spectra.

**Table 2.3. Most common mass differences in the high-resolution mass spectra of low-NO<sub>x</sub> toluene SOA (in the order of decreasing frequency of occurrence).**

<table>
<thead>
<tr>
<th>Positive ion mode</th>
<th>Negative ion mode</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low RH</strong></td>
<td><strong>High RH</strong></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>O</td>
</tr>
<tr>
<td>C</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>O</td>
<td>C</td>
</tr>
<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CO</td>
</tr>
</tbody>
</table>

The most frequently observed mass difference in the low-RH sample was C<sub>2</sub>H<sub>2</sub>O, and its frequency of occurrence dropped in the high-RH sample. It is possible that C<sub>2</sub>H<sub>2</sub>O results from the oligomerization chemistry of glycolaldehyde (C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>), which can react by an aldol condensation mechanism with compounds containing a carbonyl group (Scheme 2.1). Glycolaldehyde has been observed previously in the oxidation of toluene (White et al., 2014; Yu et al., 1997), likely as an oxidation product of methylglyoxal. The mass difference corresponding to H<sub>2</sub>O was not amongst the most common and therefore not listed in Table 2.3; however, it became more prevalent in the high-RH sample, consistent with hydration reactions. Anhydrides, commonly found in toluene SOA (Bloss et al., 2005; Forstner et al., 1997; Sato et al., 2007), may undergo hydrolysis, which adds an H<sub>2</sub>O unit to the formula.
Scheme 2.1. An aldol condensation reaction involving glycolaldehyde that results in the addition of C$_2$H$_2$O to the formula of the aldehyde co-reactant.

We additionally tested whether oligomeric compounds occurring in low-RH toluene SOA can be produced by either simple addition or condensation of monomer compounds occurring in high-RH toluene SOA. If simple addition is responsible for the oligomerization, we would expect to see peaks in the low-RH mass spectrum with molecular weights equal to the sum of two peaks from the high-RH mass spectrum. If condensation is responsible for the oligomerization, we would expect to see peaks in the low-RH mass spectrum with molecular weights equal to the sum of two peaks from the high-RH mass spectrum minus the mass of water (the same relationship would hold in reverse for oligomers undergoing hydrolysis in the particle). In positive ion mode, the fraction of peaks that could be matched by the addition reactions was 69 %, while the fraction of peaks matched by the condensation reactions was 83 %. These numbers were 62 and 69 %, respectively, for negative ion mode. This suggests that condensation reactions (that remove water) are more likely to be responsible for the enhanced oligomer formation under dry conditions. This conclusion is similar to the one reached in the study of the effect of RH on oligomerization in high-NO$_x$ isoprene SOA (Nguyen et al., 2011).
2.4 Conclusions

This study demonstrates that the composition of low-NOx toluene SOA depends on RH when it is produced in smog chamber experiments without seed particles. Oligomers produced by condensation reactions were observed in higher concentrations in the mass spectra of toluene SOA produced under low RH and were suppressed under high RH conditions. Additionally, the mass loading of low-NOx toluene SOA was reduced under high RH conditions. The plausible reason for the suppression of SOA mass loading at high RH is the change in the SOA chemical composition that favors lower molecular weight, more volatile compounds. The reduction of dimers and trimers in the high RH samples suggests that low-volatility oligomers are not forming in toluene SOA under low-NOx conditions, which means particle growth is suppressed and mass loading is reduced.

In previous studies on the effect of RH on SOA yield from toluene in the presence of hygroscopic seed (Zhou et al., 2011; Kamens et al., 2011; Faust et al., 2017; Liu et al., 2017; Jia and Xu, 2017), an opposite effect was observed in which the SOA yield increased at high RH. This was attributed to the aqueous partitioning and subsequent reactions in ALW of smaller photooxidation products, such as glyoxal (Faust et al., 2017). Our results suggest that the increase in the SOA yield due to the ALW-supported chemistry is at least partly counteracted by the lower yield of oligomers under high-RH conditions. While it is not straightforward to compare experiments done with and without seed aerosol in different smog chambers, the ALW-supported chemistry enhancement of the yield appears to be a more important effect.

It is conceivable that the effect of RH on the SOA yield is a common feature of all low-NOx aromatic SOA, all of which should contain aldehyde compounds capable of oligomerization
by condensation reactions. If this is the case, the production of SOA from naturally emitted aromatic compounds (indole, benzyl acetate, benzaldehyde, etc.), which exist in low-NO\textsubscript{x} environments, would be strongly modulated by the ambient relative humidity. This definitively warrants further investigation.
CHAPTER 3

SECONDARY ORGANIC AEROSOL FROM INDOLE OXIDATION

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3.1 Introduction

Atmospheric particulate matter (PM) absorbs and scatters solar radiation and is responsible for diminished visibility in urban areas and for global changes in climate. A key component of PM is secondary organic aerosol (SOA). While air quality model prediction capabilities have improved in recent years, disagreements between SOA predictions and measurements remain (Couvidat et al., 2013; Heald et al., 2005; Hodzic et al., 2010; Jiang et al., 2012; Volkamer et al., 2006). Discrepancies may result from incorrect or incomplete parameterizations of mechanisms for known SOA precursors, as well as from unaccounted precursors of SOA. Atmospheric researchers have investigated in detail the SOA generated from oxidation of basic anthropogenic and biogenic volatile organic compounds (VOCs), such as isoprene, monoterpenes, saturated hydrocarbons, and aromatic hydrocarbons. Much less is known about SOA from nitrogen-containing VOCs, even though such VOCs are also common in the atmospheric environment and can potentially provide significant additional pathways for SOA formation. For example, photooxidation of amines could serve as a
possible SOA source (Atkinson et al., 1987; Price et al., 2014; Silva et al., 2008; Tuazon et al., 1984; Tuazon et al., 1994).

Heterocyclic nitrogen-containing aromatic compounds based on pyrrole, pyridine, imidazole, indole, diazines, purines, etc., have been detected in biomass burning emissions (Laskin et al., 2009). Such compounds can also be emitted by vegetation, for example, indole is produced by wide variety of plants (Cardoza et al., 2003; De Boer et al., 2004; Gols et al., 1999; McCall et al., 1993; Turlings et al., 1990; Zhuang et al., 2012). Indole is emitted in response to physical or herbivore-induced stress (Erb et al., 2015; Frey et al., 2004; Misztal et al., 2015; Niinemets et al., 2013; Schmelz et al., 2003; Turlings et al., 2004) and during flowering events (Gentner et al., 2014). Once emitted, indole performs critical roles in plant ecology, for example, in attracting pollinators (Zito et al., 2015). For decades, indole and its derivatives (Fig. 3.1) have been utilized in agriculture, dyes, perfumes, and pharmaceutical applications. One of the better-known derivatives of indole is indigo dye (also known as indigotin), which is used to dye jeans to their characteristic deep blue color.
Figure 3.1. Chemical structures, common names, molecular formulas, and nominal molecular weights for indole and its oxidized derivatives discussed in this work.

Studies of maize plants under stress revealed that indole acts as an aerial priming agent, released before terpenoids (Erb et al., 2015; Schmelz et al., 2003). For example, Schmelz et al. (2003) examined insect induced volatile emissions in Zea Mays seedlings and demonstrated direct positive relationships between jasmonic acid levels and both sesquiterpene and indole volatile emissions. Additionally, they showed that indole can reach maximal emission levels during nocturnal herbivory and concluded that indole could
function as an early morning signal for parasitoids and predators searching for insect hosts and prey. Niinemets et al. (2013) found evidence that quantitative relationships exist between the severity of biotic stress and induced volatile emissions, in addition to the previously demonstrated dose-response relationships for abiotic stresses. Erb et al. (2015) showed that herbivore induced indole emissions in maize plants precede the release of mono-, homo-, and sesquiterpenes, supporting the conclusion that indole is involved in the airborne priming of terpenoids. Different plant stress mechanisms typically elicit release of the same ubiquitous stress volatile, such as indole, and more stress-specific mono- and sesquiterpene blends (Erb et al., 2015; Gentner et al., 2014; Niinemets et al., 2013; Schmelz et al., 2003).

Emissions of indole have also been well correlated with monoterpenic emissions during flowering events (Gentner et al., 2014). In the San Joaquin Valley, an agricultural region in California, indole was measured at 4.72-17.74 µg m⁻³, which was comparable to or greater than β-myrcene concentrations, the dominant monoterperne in this study (Gentner et al., 2014). The authors stressed the need for future laboratory and modeling studies on the SOA formation potential of indole and other novel compounds identified in their study. A later study by Misztal et al. (2015) used a combination of laboratory experiments, ambient measurements, and emissions modeling to show that plants emit a wide variety of benzenoid compounds (including indole) to the atmosphere at substantial rates, and that current VOC inventories underestimate biogenic benzenoid emissions. They concluded that emissions of benzenoids from plants are likely to increase in the future due to changes in the global environment and stressed that atmospheric chemistry models should account for this potentially important precursor of SOA.
An additional source of indole is the microbial processing of L-tryptophan in the intestine or feces of livestock animals (Le et al., 2005). In concentrated animal feeding operations (CAFOs), indole is primarily emitted from animal waste (Yuan et al., 2017) and can contribute significantly to the malodors in cattle feedyards and swine facilities (Feilberg et al., 2010; Wright et al., 2005). Indole has been measured in cattle facilities or during the land application of cattle manure, with emission rates of 0.002 – 9.41 µg m⁻² min⁻¹ (Parker, 2008; Woodbury et al., 2015; Cai et al., 2015) and concentrations of 2.4 – 32.6 µg m⁻³ (0.5 - 6.8 ppb; Parker, 2008). The range of emission rates and concentrations of indole detected in swine facilities or during the land application of swine slurry were 0.13-2.67 µg m⁻² min⁻¹ (Le et al., 2005; Cai et al., 2015; Parker et al., 2013; Bongiorno et al., 2004) and 0.07-500 µg m⁻³ (0.01 - 100 ppb; Hobbs et al., 1997; Zahn et al., 2001; Jo et al., 2015; Osaka et al., 2018), respectively. Emissions of indole from animal husbandry were not included in this study but should be considered when modeling areas with active animal husbandry facilities.

Despite the importance of indole in the atmospheric environment, few studies exist on the mechanism of its photooxidation. Gas-phase oxidation of indole by OH, O₃, and NO₃ was previously studied by Atkinson et al. (1995). They found that indole reacts with OH and NO₃ at collision-limited rates, with rate constants of 1.5×10⁻¹⁰ cm³ molec⁻¹ s⁻¹ and 1.3×10⁻¹⁰ cm³ molec⁻¹ s⁻¹, respectively. The rate for the reaction of indole with O₃ (rate constant of 5×10⁻¹⁷ cm³ molec⁻¹ s⁻¹) and the rate of direct photolysis were found to be too low to compete with the OH and NO₃ reactions. Atkinson et al. (1995) observed 2-formylformanilide (Fig. 3.1) as the major primary product of oxidation of indole by both O₃ and OH. Oxidation of indole was also studied by Iddon et al. (1971) in γ-irradiated aqueous solutions, where oxidation by OH was the dominant reaction mechanism. The reaction produced 3-oxoindole, indoxyl red,
indirubin, indigo dye, and eventually resulted in a trimer of 3-oxoindole and two indole molecules as the major products.

Previously, the formation of SOA from indole has not been investigated. One of the motivations for investigating indole SOA is that it may possess unusual optical properties. Many of the indole-derived products are brightly colored and have distinctive absorption bands in visible spectrum. If these products are formed during atmospheric oxidation of indole and partition into aerosol particles, they could contribute to the pool of organic light-absorbing species. Such organic compounds that absorb radiation strongly in the near-UV and visible spectral ranges are collectively known as “brown carbon” in the atmospheric literature (Andreae and Gelencser, 2006; Laskin et al., 2015). Examples include secondary aerosols generated by photooxidation of polycyclic aromatic compounds and primary aerosols produced by biomass burning. The chemical composition of the aerosol depends on the source. For example, nitroaromatic compounds are known to be major chromophores in biomass burning aerosols produced by flaming combustion, while humic-like substances are emitted from smoldering fires. It is important to characterize known sources of light-absorbing aerosols and to account for missing sources in order to better predict the effect of aerosols on global temperatures.

This chapter describes a series of experiments and model simulations on the formation of SOA via the oxidation of indole by OH, O₃, and NO₃. The molecular composition of indole SOA and the effect of relative humidity on its optical properties were explored using smog-chamber and flow reactor experiments. These results were incorporated into an airshed model with detailed SOA chemistry to estimate the effect of indole on the total SOA and on the light-absorbing components of SOA. The model predicted that indole can measurably
contribute to SOA loading even in urban environments, where anthropogenic emissions dominate over biogenic ones, such as the South Coast Air Basin of California (SoCAB). Furthermore, we showed that indole SOA contains unique strongly-absorbing compounds and can contribute to decreased visibility, especially under plant-stressed conditions or during flowering events.

3.2 Experimental Methods

3.2.1 Smog Chamber Experiments

SOA was generated in a 5 m³ Teflon chamber at different levels of relative humidity (RH <2, 25, 50%; measured by a Vaisala HMT333 probe). No inorganic seed aerosol was used to avoid interference with off-line mass-spectrometric analysis of SOA. Indole (99% purity, Sigma-Aldrich) was dissolved in methanol (LC-MS grade, 99.9% purity, Honeywell) and was evaporated into the chamber to obtain an initial mixing ratio of 200 parts per billion by volume (ppbv), which is equivalent to 960 μg m⁻³. While 200 ppb of indole was used in most experiments to collect sufficient mass for analysis, several experiments were done at lower mixing ratios (50 ppbv and 100 ppbv) to test the dependence of indole SOA optical properties on the starting indole mixing ratios. The injector and inlet lines were heated to 70°C to minimize losses of indole on the injector surfaces. At room temperature, the reported vapor pressure of indole is 0.012 mmHg (Das et al., 1993), which is equivalent to ~ 16 parts per million by volume (ppmv). Therefore, most of the injected indole should have remained in the gas phase although some of it could remain adsorbed to the injection line and chamber wall surfaces, contributing to the variability in the SOA yield (the concentration of indole in the chamber was observed to decline even without reaction, consistent with first order loss
on the chamber walls, Figure 3.2). In the ozonolysis experiments, O₃ was introduced to achieve a mixing ratio of 1 ppmv. In the nitrate radical experiments, NO₃ was generated in the chamber by introducing O₃ and NO in a small excess of the 2:1 ratio (500 ppbv O₃ and 200 NO ppbv). In the photooxidation experiments, hydrogen peroxide was introduced into the chamber by evaporation of a 30 wt% solution of H₂O₂ in water (Fisher Scientific) into a flow of clean air to achieve an initial mixing ratio of 2 ppmv. UV-B lamps were turned on to initiate the photooxidation, which led to an [OH] of ~1.4×10⁶ molec cm⁻³ (see below). The content of the chamber was mixed with a fan for 10 min following the injection. In some of the photooxidation experiments, complete mixing was achieved only after the lamps were turned on as evidenced by the measured indole concentrations continuing to increase in the initial photooxidation period. Although mixing was not fast, it was faster than the timescale of the reaction, so it should not have affected the SOA mass yield calculations.

The OH concentration was estimated from the rate of loss of indole (measured using the $^{13}$C isotopic ion of protonated indole observed at $m/z$ 119 a proton-transfer-reaction time-of-flight mass spectrometer) shown in Figure 3.2. The slope translates into [OH] ~1.4×10⁶ molec cm⁻³. The shaded region denotes the time when the chamber lamps were on.
**Figure 3.2:** Decay of the $^{13}$C isotopic ion of protonated indole as a function of time used to estimate the OH concentration in the chamber. Data range used for fit was from 45-180 minutes.

Throughout the experiment, size and number concentration of particles were monitored with a scanning mobility particle sizer (SMPS; TSI 3936) equipped with a condensation particle counter (CPC; TSI 3775). A proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS; Ionicon model 8000) monitored the decay of indole, as well as the formation of volatile photooxidation products. The PTR-ToF-MS had a resolving power of $m/Δm \sim 5 \times 10^3$ and was operated with the following settings: drift tube temperature of 60 °C, drift tube voltage of 600 V, field strength of $\sim 135$ Td, and inlet flow of 0.2 SLM. The chemical composition of the SOA particles was probed with a Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS) operated in both the V-mode (provides higher signal, but lower resolution) and W-mode (provides less signal, but higher resolution) ion flight paths. The ToF-AMS data were analyzed using SQUIRREL 1.62A software with PIKA 1.22A. When the SOA particles reached a peak concentration in the chamber, the polydispersed particles were
collected on one Teflon filter (47 mm diameter, Millipore FGLP04700) at 20 L min\(^{-1}\) for 2-3 hours. One filter was collected per each chamber run; therefore, each replicate sample was collected from a separate experiment run under the same conditions. The amount of the collected SOA material on each filter was estimated from SMPS data assuming 100% collection efficiency by the filters and SOA density of 1.4 g cm\(^{-3}\). The density of indole SOA is unknown, but the adopted value of 1.4 g cm\(^{-3}\) is similar to the reported range of densities of 1.47–1.55 g cm\(^{-3}\) for SOA prepared from another bicyclic aromatic compound, naphthalene (Chan et al., 2009; Chen et al., 2016). In addition, densities of known indole oxidation products, for example isatin (1.47 g cm\(^{-3}\)), anthranilic acid (1.40 g cm\(^{-3}\)), indigo dye (1.20 g cm\(^{-3}\)), isatoic anhydride (1.52 g cm\(^{-3}\)), and 3-oxindole (1.20 g cm\(^{-3}\)), range from 1.2 to 1.5 g cm\(^{-3}\), suggesting that 1.4 g cm\(^{-3}\) should be a reasonable guess for indole SOA. For comparison, the mass of collected SOA material on each filter was also determined by weighing using a microbalance (Sartorius ME5F, +/- 0.001 mg). When comparing the SOA mass calculated from SMPS to the weighed mass, the weighed mass was often higher, as can be seen in Figure 3.3. Possible reasons for this discrepancy in mass include that the SMPS does not work well at high concentrations, SMPS was not recently calibrated, and/or incorrect particle density assumed. Unfortunately, the experiments of indole photooxidation carried out at low RH and used in the SOA yield calculations were done early in the study and relied solely on SMPS estimations for the collected mass. In all other experiments, the mass was determined by weighing rather than SMPS measurements.
Figure 3.3. Plot comparing the mass of SOA material collected as determined from SMPS calculations (y-axis) and weighing (x-axis). The dashed line has a slope of 1, which denotes agreement between the two measurements.

The SOA yield in the early indole+OH SOA experiments was calculated from Eq. (3.1).

\[ Yield = \frac{\Delta SOA}{\Delta VOC} \]  

The increase in the mass concentration of particles, \( \Delta SOA \), was obtained from SMPS measurements (since we began weighing in later experiments) and corrected for the particle wall loss. The change in the mass concentration of indole, \( \Delta VOC \), was equated to the initial indole concentration because PTR-ToF-MS measurements suggested complete removal of
indole during the photooxidation. The wall loss correction was done by assuming a first-order particle size independent loss of particle mass concentration ($PM$)

$$\frac{dPM}{dt} = \text{Source}(t) - \text{Loss}(t) = \text{Source}(t) - k_w \times PM$$  \hspace{1cm} (3.2)

where the $\text{Source}(t)$ and $\text{Loss}(t)$ are time dependent production and removal rates for the particles. The effective first-order rate constant $k_w = 0.00090 \text{ min}^{-1}$ was determined in a separate experiment in which indole SOA was produced, the lamps were turned off, and mass concentration of SOA was followed with the SMPS for 10 hours without collecting SOA on filters. In the experiment used to calculate $k_w$, the RH in the chamber was low. At higher RHs, greater wall loss would be expected (Huang et al., 2018). Using the known $k_w$, we could determine $\text{Source}(t)$ from the actual measured PM concentration in every experiment.

$$\text{Source}(t) = \frac{dPM}{dt} + k_w \times PM$$  \hspace{1cm} (3.3)

The corrected PM concentration (i.e. the hypothetical PM concentration that would be achieved if the wall loss was absent) was calculated from:

$$PM_{\text{corrected}}(t) = PM(t = 0) + \int_0^t \text{Source}(t) dt$$  \hspace{1cm} (3.4)

The integration of data was carried out numerically in Excel.

After collecting SOA on a filter, the color of the filter depended on the oxidant and amount of SOA collected, and could be brown, yellow-green, or even black in appearance. Examples of filter photographs are given in Fig. 3.4.
One half of the filter sample was extracted in methanol (LC-MS grade, 99.9% purity, Honeywell) and shaken vigorously on a shaker for five minutes. The filter color changed from the initial brown or yellow-green to white suggesting most of the light-absorbing compounds were extracted. More quantitative extraction efficiency tests, in which the same filter was extracted multiple times, suggested that the initial extraction removed >95% of the filter material (see Fig. 3.5). The SOA methanol extract was analyzed by UV-Vis spectrophotometry in a dual beam spectrophotometer (Shimadzu UV-2450), with pure methanol used as reference.
Figure 3.5. UV-Vis absorption spectra for sample of indole + O₃ SOA at 25% RH extracted multiple times. The solution obtained from the first extraction saturated the detector. Therefore, the solution was diluted by a factor of 10, and the absorption values were multiplied by 10 to generate the effective absorbance shown as the dotted trace. Across the UV-Vis spectrum, the absorbance of extraction 1 was 20-30 times higher than that of extraction 2, suggesting that the first extraction extracted >95% of the soluble material.

The wavelength-dependent mass absorption coefficient (MAC) was calculated for indole SOA from the base-10 absorbance, $A_{10}$, of an SOA extract, the path length, $b$ (cm), and the solution mass concentration, $C_{mass}$ (g cm$^{-3}$):

$$MAC (\lambda) = \frac{A^{solution}_{10} (\lambda) \times \ln (10)}{b \times C_{mass}}$$

(3.5)

The main uncertainty in the calculated MAC values comes from the uncertainty of the mass concentration, which arises from uncertainties in the SMPS measurement of aerosol mass
concentration (Fig. 3.3), filter collection efficiency, and solvent extraction efficiency. We estimate that MAC values should be accurate within a factor of 2 (Romonosky et al., 2015a). The imaginary part of the refractive index, $k$, which describes the absorptive properties the particle material was calculated from MAC values using equation 3.6. As discussed earlier, the indole SOA density, $\rho$, was assumed to be 1.4 g cm$^{-3}$.

$$k (\lambda) = \frac{MAC (\lambda) \times \rho \times \lambda}{4\pi}$$  (3.6)

The second half of the filter was used for direct analysis in real-time mass spectrometry (DART-MS) measurements. The filter half was extracted in the same way with acetonitrile (LC-MS grade, 99.9 % purity, Honeywell). Assuming a complete extraction of the SOA material, the mass concentration of 0.03–0.22 mg mL$^{-1}$ was much lower than the solubility of 19 mg mL$^{-1}$ reported for isatin in acetonitrile (Liu et al., 2014). (We elected to use different solvents for UV–vis and DART-MS because methanol afforded measurements deeper in the UV region and acetonitrile gave cleaner background spectra in DART-MS.) Aliquots from the acetonitrile SOA extracts were transferred onto a clean stainless-steel mesh, dried in air, and manually inserted between the DART ion source and mass spectrometer inlet. The DART-MS consisted of a Xevo TQS quadrupole mass spectrometer (Waters) equipped with a commercial DART ion source (Ion-Sense, DART SVP with Vapur® Interface). It was operated with the following settings: 350 V grid electron voltage, 3.1 L min$^{-1}$ He gas flow, 350°C He gas temperature, and 70°C source temperature. The samples were analyzed with DART-MS in both positive and negative ion modes. Background spectra from the pure solvent were also collected and subtracted from the DART mass spectra.
Additional sample filters were analyzed via nanospray desorption electrospray ionization high-resolution mass spectrometry (nano-DESI-HRMS) and high-performance liquid chromatography, coupled to photodiode array spectrophotometry and high-resolution mass spectrometry (HPLC-PDA-HRMS). The former method provides a spectrum of the entire mixture without prior separation; it is useful for providing an overview of the types of compounds present in SOA. The latter method is suited for advanced detection of individual light-absorbing components in SOA (Lin et al., 2015a, b; Lin et al., 2016). Both methods employ an LTQ-Orbitrap mass spectrometer (Thermo Corp.) with a resolving power of $10^5$ at $m/z$ 400, sufficient for unambiguous characterization of SOA constituents.

For the HPLC-PDA-HRMS measurements, one-quarter of the filter was extracted using 350 μL acetonitrile (CH$_3$CN, gradient grade, ≥ 99.9 % purity) and the change in filter color from colored to white suggested that most light-absorbing compounds were extracted into the solution. Separation of the SOA extract was achieved with a Scherzo SM-C18 column (Imtakt USA). The gradient elution protocol included a 3 min hold at 10 % of CH$_3$CN, a 45 min linear gradient to 90 % CH$_3$CN, a 16 min hold at this level, a 1 min return to 10 % CH$_3$CN, and another hold until the total scan time of 90 min. The column was maintained at 25°C and the sample injection volume was 8 μL. The UV–vis spectrum was measured using the PDA detector over the wavelength range of 250 to 700 nm. The ESI settings were positive ionization mode, +4.5 kV spray potential, 35 units of sheath gas flow, 10 units of auxiliary gas flow, and 8 units of sweep gas flow.

The HRMS data analysis was performed by methods summarized by Romonosky et al. (2015b). Briefly, the mass spectra were clustered together, the $m/z$ axis was calibrated internally with respect to expected products of photooxidation, and the peaks were assigned
to formulas $C_cH_hO_oN_nNa^{+\text{0-}1}$ or $C_cH_hO_oN_n^{-}$ constrained by valence rules and typical elemental ratios ($c$, $h$, $o$, $n$ refer to the number of corresponding atoms in the ion). These were then converted to formulas of the corresponding neutral species, obtained by removing Na or H from the observed positive ion formulas or adding H to the negative ion formulas. The HPLC-PDA-HRMS analysis was done as described in Lin et al. (2015b, 2016).

### 3.2.2 Oxidation Flow Reactor Experiments

Oxidation flow reactor experiments were conducted by Professor Yinon Rudich and Dr. Qunafu He in order to obtain more information regarding the optical properties of indole SOA particles. SOA was generated in three different oxidation flow tube reactors (OFRs) without seed aerosol to simulate indole oxidation initiated by OH radical, O$_3$, and NO$_3$ radical. These experiments were done by our collaborators in the Weizmann Institute of Science. Pure indole (99% purity, Sigma-Aldrich) was placed in a bubbler and was introduced into the OFRs by a gentle N$_2$ flow to obtain an initial mixing ratio of 200 ppbv. SOA generation through OH oxidation of indole was done in a potential aerosol mass (PAM) OFR. A total flow of 4.2 L min$^{-1}$ of N$_2$ and 0.3 L min$^{-1}$ O$_2$ at RH of 36–38% was used in the PAM with a corresponding residence time of 184 s. The OH concentration was varied by changing the UV light intensity. To simulate SOA formation in the presence of NOx, 1%, 2%, and 4% N$_2$O were added to the PAM chamber as NO$_x$ source (Lambe et al., 2017), with corresponding NO$_x$ concentration of 133, 669, and 2425 ppbv (Model T200, Teledyne, USA). The OH exposures were regulated to $\sim 4.2\times10^{11}$ molecules cm$^{-3}$ s which were determined by measuring the decay of the SO$_2$ (Model 49i, Thermo Fisher Scientific, USA). Due to the limitation of the lamp power, the OH exposures were controlled to $\sim 3.1\times10^{11}$ molecules cm$^{-3}$ s for experiments conducted with 4.0% N$_2$O. SOA generation from ozonolysis of indole under dry conditions
was performed in a glass OFR (20 L in volume) with an initial O$_3$ concentration of 20 ppm. High O$_3$ concentration was used due to the short residence time of the glass reactor (~20 minutes at the total flow of 1.0 L min$^{-1}$). To simulate NO$_3$ oxidation of indole, N$_2$O$_5$ synthesized from NO$_2$ reaction with ozone was used as the source of NO$_3$ radical. NO$_3$ radical was produced by thermal decomposition of N$_2$O$_5$ which was carried out by pure nitrogen from a N$_2$O$_5$ crystal cold trap. SOA production was achieved in a glass OFR (OFR, L: 70 cm, ID: 7 cm) where we mixed the N$_2$O$_5$ (~ 1 ppm) and other gases. Particles were produced by homogeneous nucleation and condensation following NO$_3$ oxidation. The relative humidity in the OFR was set to <5%, 25%, 51%, and 76% to examine how the RH affects the aerosol optical properties. For all of the experiments, particle size distribution was monitored by the SMPS and an HR-ToF-AMS operated alternatively in V mode and W mode was employed to probe the chemical composition of the generated aerosols.

Assuming that the SOA particles are spherical and non-porous, the particle effective density was calculated by comparing the aerodynamic diameter (obtained from the aerosol aerodynamic classifier, AAC) and the mobility diameter (measured by SMPS). The particle effective density ($\rho_{\text{eff}} = \frac{d_{\text{Aero}}}{d_{\text{m}}} \rho_0$), which is the aerodynamic diameter ($d_{\text{Aero}}$) divided by the mobility diameter ($d_{\text{m}}$), was obtained from optical measurements. The average of the measured effective densities (1.21 g/cm$^3$; see Table 3.1) was used as an independent approach (from the method described in section 3.2.1) to calculate $k$. 
Table 3.1. Particle effective density measured by AAC and SMPS. The standard deviation (STD) corresponds to one sigma.

<table>
<thead>
<tr>
<th>Oxidation type</th>
<th>RH</th>
<th>N₂O</th>
<th>Effective Density g/cm³</th>
<th>STD g/cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH oxidation</td>
<td>38.2</td>
<td>0%</td>
<td>1.33</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>37.1</td>
<td>1%</td>
<td>1.15</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>37.6</td>
<td>2%</td>
<td>1.17</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>37.6</td>
<td>4%</td>
<td>1.31</td>
<td>0.01</td>
</tr>
<tr>
<td>NO₃ oxidation</td>
<td>&lt;5%</td>
<td>0%</td>
<td>1.29</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>21%</td>
<td>0%</td>
<td>1.13</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>51%</td>
<td>0%</td>
<td>1.24</td>
<td>0.03</td>
</tr>
<tr>
<td></td>
<td>76%</td>
<td>0%</td>
<td>1.18</td>
<td>0.06</td>
</tr>
<tr>
<td>O₃ oxidation</td>
<td>&lt;5%</td>
<td>0%</td>
<td>1.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The complex refractive index of the aerosols can be retrieved by measuring the extinction cross section of several different sizes of particles and followed by fitting a theoretical Mie curve to the measured extinction cross sections at each specific wavelength (Riziq et al., 2007; Lang-Yona et al., 2009; Washenfelder et al., 2013). To measure the optical cross section of the size-selected particles, aerosol from the OFR was sampled, passed through a VOCs denuder and a drier, size selected with an AAC, and directed into the broadband cavity-enhanced spectrometer (BBCES) system (two broadband channels which span the 360–390 and 385–425 nm spectral regions) while counted by the CPC. Notably, another BBCES system which spans the wavelength range of 315–345 and 380-700 nm was employed for measuring light extinction of particle from O₃ oxidation of indole.

3.3 Modeling Methods

Air quality simulations were performed by Professor Donald Dabdub and Dr. Jeremy Horne to complement laboratory experiments and to assess the formation of indole SOA from photooxidation in a coastal urban area. The University of California, Irvine, and California Institute of Technology (UCI-CIT) regional airshed model with a state-of-the-art chemical
mechanism and aerosol modules was used in this study. The model domain utilized 4970 computational cells (five vertical layers with 994 cells per layer) with a 5 km × 5 km horizontal grid size and encompassed the SoCAB, including the Pacific Ocean on the western side, heavily populated urban areas around Los Angeles, and locations with a high density of plant life such as the Angeles National Forest on the eastern side. The model included spatially and temporally resolved emissions and typical meteorological conditions for this region. The emission inventory used in this study was based on the 2012 Air Quality Management Plan (AQMP) provided by the South Coast Air Quality Management District (SCAQMD, 2013). Boundary and initial conditions were based on historical values. Simulations were performed for a 3-day summer episode. Two days of model spin-up time were used to reduce the influence of initial conditions and allow sufficient time for newly added emissions to drive changes in air quality. Results shown below are for the third day of the simulations.

The UCI-CIT model utilizes an expanded version of the Caltech atmospheric chemical mechanism (CACM; Dawson et al., 2016; Griffin et al., 2002a, b, 2005) and has been used in numerous other studies to simulate air quality in the SoCAB (Carreras-Sospedra et al., 2006; Carreras-Sospedra et al., 2010; Chang et al., 2010; Nguyen and Dabdub, 2002). The CACM includes a comprehensive treatment of SOA known as the Model to Predict the Multiphase Partitioning of Organics (MPMPO) (Griffin et al., 2003, 2005). MPMPO is a fully coupled aqueous–organic equilibrium-partitioning-based model and is used to calculate gas–particle conversion of secondary organic species. The SIMPOL1 group-contribution method of Pankow and Asher (2008) was used to calculate vapor pressures of SOA species for use in MPMPO. Activity in both the aqueous and organic phases was determined using the UNIFAC
model of Hansen et al. (1991). Henry's law constants were calculated according to the group contribution method of Suzuki et al. (1992). Several studies have used the UCI-CIT model to investigate SOA formation, dynamics, reactivity, and partitioning phase preference in the SoCAB (Carreras-Sospedra et al., 2005; Chang et al., 2010; Cohan et al., 2013; Dawson et al., 2016; Griffin et al., 2002b; Vutukuru et al., 2006). For a more detailed description of recent model developments incorporated into the UCI-CIT model and its SOA modules, the reader is referred to Dawson et al. (2016).

For the present study, the chemical mechanism was modified from the base case version to include species and processes shown in Fig. 3.6. Two new gas-phase species were added: indole and one representative oxidation product, indigo dye. Because of the high mass yield of indole SOA, with most of the products ending up in the particle phase, any reasonable indole oxidation product with a low vapor pressure would be suitable. We elected to use indigo dye (C_{16}H_{10}O_{2}N_{2}) because it is a very common derivative of indole and because its formula was reasonably close to the average formula of SOA compounds determined from nano-DESI (C_{15}H_{11}O_{3}N_{2}). One new gas-phase reaction was added, which forms gas-phase indigo dye via oxidation of gas-phase indole by hydroxyl radical. Lastly, indigo dye was also added to the model as a new SOA species. Gas-phase indigo dye was assumed to partition into the aerosol phase based on its calculated vapor pressure and Henry's law constant. We did not experimentally determine the viscosity of indole SOA, therefore this partitioning does not take into account indole SOA viscosity. After the modifications described here, the model contained a total of 202 gas-phase species, 607 gas-phase reactions, and 18 SOA species. Each SOA species was sorted into eight distinct size bins based on particle diameter, up to a maximum of 10 \mu m. The activity coefficient of indigo dye was assumed to be 1.
Because gas-phase indole was not included in the base case emissions inventory, its emission rate was estimated based on available literature data. As discussed in the introduction section, emissions of indole have been shown to be well correlated to emissions of monoterpenes in a variety of plant species (Erb et al., 2015; Gentner et al., 2014; Niinemets et al., 2013). However, most existing data were obtained from controlled laboratory experiments and emissions of indole at the regional scale are not well constrained. In this work, emissions of gas-phase indole were added to the base case emissions inventory by using a ratio to “BIOL”, an existing gas-phase species in the emission inventory. BIOL is representative of lumped biogenic monoterpenes and contains spatially and temporally resolved emissions in the base case inventory. Therefore, the spatiotemporal distribution of indole emissions follows that of BIOL, with the magnitude of the emissions set to a given percentage of BIOL emissions. Please note that no emissions of indole derived from agriculture and animal husbandry activities were added in the model. In addition, no direct emissions of gas-phase indigo dye were added to the model. Because of the uncertainty and episodic nature of gas-phase indole emissions, simulations were performed with a range of
possible emission factors to determine the sensitivity of indole SOA formation to gas-phase indole emissions.

Five scenarios were considered for model calculations. The first scenario had zero emissions of gas-phase indole. This scenario will be referred to as the “base case” and serve as the reference scenario to which the other scenarios are compared to determine changes in air quality. The second, third, and fourth scenarios had emissions of gas-phase indole set to 5, 10, and 25 % of BIOL emissions, referred herein as “low”, “medium”, and “high” emissions, respectively. When averaged over the entire simulation domain, the corresponding average emission factors for indole were 0.25, 0.51, and 1.27 μg m⁻² h⁻¹, respectively. A comparable emission factor of 0.6 μg m⁻² h⁻¹ for indole was used in a previous study of Misztal et al. (2015), in which indole emissions under average stress conditions were incorporated in the MEGAN 2.1 biogenic VOC emissions model to estimate total global emissions. Therefore, the medium emission scenario considered in this study should be representative of the emissions of indole under average stress conditions, while the high emission scenario is more likely to represent episodic emission events such as those during springtime flowering or herbivore infestation.

The focus of this modeling work was to study the formation of SOA from the photooxidation of indole by OH, in order to complement the experimental data reported in this work. While the SOA formation from oxidation of indole by NO₃ was not experimentally studied prior to the modeling, the reaction of indole with NO₃ is fast and may provide an additional source of indole SOA. The fifth and final scenario explored the potential impact of including an additional oxidation pathway for gas-phase indole via reaction with NO₃. This scenario corresponds to the high emission scenario with one new gas-phase reaction included in the
model in addition to those described previously. For this new reaction, it is assumed that
gas-phase indole reacts with NO₃ to produce indigo dye, the same representative oxidation
product assumed for the reaction of gas-phase indole with hydroxyl radical. A rate constant
of 1.3 × 10⁻¹⁰ cm⁻³ molec⁻¹ s⁻¹ was used following Atkinson et al. (1995). No other changes
were made to the model or its inputs in this scenario.

3.4 Experimental results

The initial focus of this research was to explore the formation and composition of SOA
produced from indole photooxidation, and therefore this SOA system is discussed in more
detail throughout this chapter than the other two, i.e., indole produced via O₃ and NO₃
oxidation. Indole oxidation by OH is likely to be the dominant oxidation pathway of indole
in the SoCAB during the daytime due to the high rate constant (on the order of 10⁻¹⁰ cm⁻³
molec⁻¹ s⁻¹) of this reaction. These initial experiments resulted in SOA that was highly
absorbing in the UV-Vis spectrum, and therefore follow up experiments focused on further
exploring the optical properties of indole+OH SOA, indole+NO₃ SOA, and indole+O₃ SOA.

3.4.1 Gas-phase oxidation products of indole + OH SOA

The PTR-ToF mass spectrum of indole before photooxidation (Figure 3.7) was dominated by
the protonated indole at m/z 118.067 (the m/z values cited in the text correspond to the
measured m/z values; the corresponding exact m/z values are listed in Table 3.2). After
photooxidation, a few other prominent peaks appeared.
Figures 3.8 and 3.9 show the time-dependence profiles of several peaks of interest detected by PTR-ToF-MS during the photooxidation of indole, and Table 3.2 contains their proposed assignments. Peaks at \( m/z \) 120.072, 131.062, and 132.050 (Figure 3.9) appeared simultaneously with indole injection, suggesting that the indole sample contained small amounts (<2%) of indoline, diazanaphthalene, and 3-oxyindole impurities, respectively, which may have contributed to SOA formation. From the ions that first appeared and then were consumed during photooxidation (Figure 3.8), the one at \( m/z \) 122.061 had the largest peak abundance. It corresponds to protonated 2-formylformanilide [M+H]\(^+\) ion (Figure 3.1), a major gas-phase product of indole oxidation by OH (Atkinson et al., 1995). Another significant product was detected at \( m/z \) 148.041 and was tentatively assigned to the [M+H]\(^+\) ion from isatin (Figure 3.1). Isatin also was observed as an abundant peak in both DART(+) and nano-DESI(+) mass spectra, suggesting that it can partition between the gas and particle phases. Smaller peaks produced and then consumed in photooxidation included indoxyl,
benzonitrile, and phenylamine. A few peaks at smaller $m/z$ grew during the photooxidation including cyanic acid, acetaldehyde, acetone, and acetic acid.

Figure 3.8: Time-dependent signals of ions that were produced and then removed. Shaded region denotes the time when the chamber lamps were on. The top panel shows data on the log scale and the bottom panel shows data on the linear scale.

Segments of the sampling line for PTR-ToF-MS were not heated, and the time dependence the observed in Figs. 3.8 and 3.9 may be complicated by the adsorption equilibria on the
sampling tube surfaces. For example in Fig. 3.8, the unusual time dependence for $m/z$ 150.055 (yellow trace) and $m/z$ 148.041 (green trace) was reproducible, and likely resulted from delayed passage of these compounds through the sampling lines. However, the time dependence makes it possible to sort observed compounds into ones produced by the UV radiation from the chamber lamps, and ones that are less affected (or not affected at all) by the UV radiation. This particular plot shows compounds that clearly went up when the UV lamps were on; their removal at later time is from secondary photooxidation or photolysis.
Figure 3.9: Time-dependent signals of ions that were removed during photooxidation. Shaded region denotes the time when the chamber lamps were on. The top panel shows data on the log scale and the bottom panel shows data on the linear scale. Indoline and diazanaphthalene were likely present in the indole sample to begin with, as impurities.
Table 3.2. Summary of assigned PTR-ToF-MS peaks

<table>
<thead>
<tr>
<th>Calibrated m/z</th>
<th>Exact m/z</th>
<th>Ion Formula</th>
<th>Neutral Formula</th>
<th>Possible Assignment</th>
<th>Behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>44.014</td>
<td>44.0131</td>
<td>CH₂NO⁺</td>
<td>HOCN</td>
<td>cyanic acid</td>
<td>produced</td>
</tr>
<tr>
<td>45.034</td>
<td>45.0335</td>
<td>C₂H₂O⁺</td>
<td>C₂H₂O</td>
<td>acetaldehyde</td>
<td>produced</td>
</tr>
<tr>
<td>46.029</td>
<td>46.0287</td>
<td>CH₃NO⁺</td>
<td>CH₂NO</td>
<td>nitrosomethane</td>
<td>produced</td>
</tr>
<tr>
<td>47.014</td>
<td>47.0128</td>
<td>CH₃O₂⁺</td>
<td>HCOOH</td>
<td>formic acid</td>
<td>produced</td>
</tr>
<tr>
<td>59.050</td>
<td>59.0491</td>
<td>C₃H₂O⁺</td>
<td>C₃H₂O</td>
<td>acetone</td>
<td>produced</td>
</tr>
<tr>
<td>61.029</td>
<td>61.0284</td>
<td>C₂H₃O⁺⁺</td>
<td>C₂H₃O₂</td>
<td>acetic acid</td>
<td>produced</td>
</tr>
<tr>
<td>90.950</td>
<td>90.9477</td>
<td>FeO₂H₃⁺⁺</td>
<td>H₂O·FeO</td>
<td>produced in ion source</td>
<td></td>
</tr>
<tr>
<td>94.067</td>
<td>94.0651</td>
<td>C₆H₇N⁺⁺</td>
<td>C₆H₇N</td>
<td>phenylamine (aniline)</td>
<td>produced then removed</td>
</tr>
<tr>
<td>98.026</td>
<td>98.0237</td>
<td>C₂H₃NO₂⁺⁺</td>
<td>C₂H₃NO₂</td>
<td>maleimide</td>
<td>produced</td>
</tr>
<tr>
<td>99.008</td>
<td>99.0077</td>
<td>C₄H₄O⁺⁺</td>
<td>C₄H₄O</td>
<td>maleic anhydride</td>
<td>produced</td>
</tr>
<tr>
<td>104.050</td>
<td>104.0495</td>
<td>C₆H₆N⁺⁺</td>
<td>C₆H₆CN</td>
<td>benzonitrile</td>
<td>produced then removed</td>
</tr>
<tr>
<td>118.067</td>
<td>118.0651</td>
<td>C₆H₇N⁺⁺</td>
<td>C₆H₇N</td>
<td>indole</td>
<td>removed</td>
</tr>
<tr>
<td>120.072</td>
<td>120.0808</td>
<td>C₈H₁₀N⁺⁺</td>
<td>C₈H₁₀N</td>
<td>indoline (impurity)</td>
<td>removed</td>
</tr>
<tr>
<td>122.061</td>
<td>122.0600</td>
<td>C₈H₇NO⁺⁺</td>
<td>C₈H₇NO</td>
<td>2-formylformanilide</td>
<td>produced then removed</td>
</tr>
<tr>
<td>131.062</td>
<td>131.0604</td>
<td>C₈H₇N₂⁺⁺</td>
<td>C₈H₇N₂</td>
<td>diazanaphthalene (impurity)</td>
<td>removed</td>
</tr>
<tr>
<td>132.050</td>
<td>132.0444</td>
<td>C₈H₇NO⁺⁺</td>
<td>C₈H₇NO</td>
<td>3-oxyindole</td>
<td>removed</td>
</tr>
<tr>
<td>134.061</td>
<td>134.0600</td>
<td>C₈H₇NO⁺⁺</td>
<td>C₈H₇NO</td>
<td>indoxyl</td>
<td>produced then removed</td>
</tr>
<tr>
<td>148.041</td>
<td>148.0393</td>
<td>C₈H₇NO₂⁺⁺</td>
<td>C₈H₇NO₂</td>
<td>isatin</td>
<td>produced then removed</td>
</tr>
<tr>
<td>150.055</td>
<td>150.0550</td>
<td>C₈H₇NO₃⁺⁺</td>
<td>C₈H₇NO₃</td>
<td>3-oxy-2-hydroxy-indole</td>
<td>produced then removed</td>
</tr>
</tbody>
</table>

3.4.2 Yield of indole + OH SOA

Figure 3.10 illustrates the time dependence of mass concentrations of indole and particulate matter in a typical chamber experiment. The particles had a geometric mean diameter of approximately 0.3 µm when the filter collection started. The terminal wall-loss corrected mass concentration of particles (Fig. 3.10) was higher than the initial concentration of indole, suggesting that the SOA yield, defined by Eq. (3.1), was high. A high SOA yield suggests that most of the oxidation products of indole end up in the particle phase, indicating that indole is an effective precursor for SOA.
Figure 3.10. The mass concentration of indole (solid trace), the mass concentration of particles (open circles), and the wall loss-loss-corrected mass concentration of particles (solid circles) over time. Indole was not yet fully mixed in the chamber by the time photooxidation started at t=0, resulting in an apparent initial rise in the measured indole concentration.

For five experiments repeated under the same conditions on separate days, the SOA yields calculated from Eq. (3.1) were 1.21, 1.10, 0.86, 1.77, and 1.46 with an average of 1.3 ± 0.3. We normally obtain much more reproducible yields for more volatile precursors, such as monoterpenes; it is not clear why the yield of indole SOA is so variable. Indole oxidation products could be lost to the walls reducing the apparent yield and contributing to its scatter. However, this effect is probably minor given that the apparent yield is quite high. The yield is higher than that for SOA formed from another bicyclic aromatic compound, naphthalene, which has a reported yield range of 0.04-0.73 under low-NOx conditions (Chan et al., 2009; Chen et al., 2016). The high yield suggests that the major fraction of indole oxidation products ends up in the particle phase at the concentrations used in this work. The yield of 1.3 would require that, on average, at least two oxygen atoms should add to the indole during
oxidation (C₈H₇N → C₈H₇NO₂.₂), which is quite reasonable and qualitatively consistent with mass spectrometric observations.

3.4.3 Composition of indole + OH SOA

We used two offline MS methods (DART and nano-DESI) and both negative (-) and positive (+) ion modes to characterize the SOA composition to detect a broader range of compounds than possible with a single method. Figure 3.11 shows the DART and nano-DESI mass spectra of indole SOA in both positive and negative modes. The high resolving power of nano-DESI-HRMS afforded unambiguous formula assignments for all peaks up to m/z 500, and the molecular weights (MWs) of the neutral compounds could be determined from the corresponding ion formulas. About half of the ions observed in nano-DESI (+) mass spectra were [M+Na]+ adducts, and the remaining compounds were protonated ions, [M+H]+. The DART mass spectra were acquired on a triple quadrupole mass spectrometer with only unity mass resolution. As a result, only the nominal m/z values for the observed peaks could be determined. It was assumed that the dominant mechanism of ionization was protonation ([M+H]+ ions formed; nominal MW = nominal m/z – 1) in the positive ion mode and deprotonation ([M-H]⁻ ions formed; nominal MW = nominal m/z + 1) in the negative ion mode (Nah et al., 2013). For ease of comparison, all the mass spectra were plotted as function of the exact mass of the corresponding neutral compounds.
Figure 3.11. Nano-DESI and DART mass spectra of indole photooxidation SOA plotted as a function of the molecular weights of the neutral compounds. The nano-DESI mass spectra contain only peaks assignable to specific formulas, while DART mass spectra contain all observed peaks. The five most abundant peaks in each mass spectrum are indicated with letters: (a) 248Da, C_{15}H_{10}O_{2}N_{2}, tryptanthrin; (b) 250Da, C_{15}H_{10}O_{2}N_{2}, tryptanthrin; (c) 262 Da, C_{16}H_{10}O_{2}N_{2}, indirubin and/or indigo dye; (d) 264 Da, C_{16}H_{12}O_{2}N_{2}, dihydro indigo dye; (e) 266 Da, C_{15}H_{10}O_{2}N_{2}; (f) 147Da, C_{8}H_{5}O_{2}N, isatin; (g) 252Da, C_{15}H_{12}O_{2}N_{2}; (h) 280Da, C_{16}H_{12}O_{2}N_{2}; (i) 282Da, C_{16}H_{12}O_{2}N_{2}; (j) 121Da, C_{9}H_{7}O_{2}N, 2-formylformanilide; (k) 162 Da, C_{8}H_{5}O_{2}N_{2}; (l) 163 Da, C_{8}H_{5}O_{3}N_{2}, isatoic anhydride; (m) 165 Da, C_{8}H_{7}O_{2}N.

For a given ion mode, the DART and nano-DESI mass spectra were qualitatively similar, although nano-DESI appeared to favor larger, more oxidized compounds compared to DART. Both DART and nano-DESI mass spectra showed a clear separation into distinct clusters of peaks corresponding to monomer, dimer, trimer, and tetramer oxidation products.
given ion mode, the major monomer peaks were the same in DART and nano-DESI strongly suggesting that they correspond to more abundant indole oxidation products (as opposed to minor SOA compounds that happened to have unusually high ionization efficiencies). There was also good correspondence between the major dimer peaks recorded in DART and nano-DESI. In the nano-DESI mass spectra, the peak abundances in the negative ion mode spectra were shifted towards higher molecular weights compared to the positive ion mode mass spectra. The preferential negative ion formation from more oxidized compounds was previously observed in ESI mass spectra of limonene SOA (Walser et al., 2008). Although we cannot assign formulas to the DART-MS peaks, it is evident from Figure 5 that this ionization method also favors larger, and presumably more oxidized, compounds in the negative ion mode. For example, carboxylic acids are more readily observed in the negative ion mode DART mass spectra (Nah et al., 2013).

Table 3.3 lists the most abundant peaks observed in the monomer and dimer ranges of nano-DESI-HRMS and DART-MS spectra, as well as additional smaller peaks for the specific compounds discussed in this paper. Isatin (C₈H₅O₂N, MW = 147 Da) was the single dominant peak in the monomer range observed in both nano-DESI(+) and DART(+); it was also detected in the negative ion mode mass spectra. Isatoic anhydride (C₈H₅O₃N; MW = 163 Da) was the second most abundant monomeric peak in all four mass spectra, but much lower abundance. Other abundant monomeric products included 3-oxyindole (C₈H₅ON; MW = 131 Da) and 2-formylformanilide (C₇H₇ON; MW = 121 Da). Of the compounds shown in Figure 1, tryptanthrin (C₁₅H₁₀O₂N₂; MW = 250 Da), indirubin (C₁₆H₁₀O₂N₂; MW = 262 Da), indigo dye (C₁₆H₁₀O₂N₂; MW = 262 Da), and dihydro indigo dye (C₁₆H₁₂O₂N₂; MW = 264 Da) were the most abundant dimer peaks. Meanwhile, indoxyl red (C₁₆H₁₀ON₂; MW = 246 Da) was
detected with lower but appreciable abundances in nano-DESI(-) and in both DART mass spectra. The prominent dimer compounds listed in Table 3.3 contained additional oxygen atoms compared to indoxyl red, indirubin, indigo dye, and dihydro indigo dye, and could be formed by further oxidation of these compounds.

### Table 3.3. Monomer and dimer peaks with the largest peak abundance observed in DART-MS and nano-DESI-HRMS spectra for indole photooxidation SOA. Selected peaks corresponding to the compounds shown in Figure 3.1 are also included. Proposed assignments are based on the formulas from nano-DESI-HRMS. Peak abundances are normalized with respect to the most abundant peak in each spectrum.

<table>
<thead>
<tr>
<th>Nominal Mass</th>
<th>Formula</th>
<th>Ionization by H+ or Na+ in nano-DESI (+)</th>
<th>Peak Abundance by nano-DESI-HRMS(+) (%)</th>
<th>Peak Abundance by nano-DESI-HRMS(-) (%)</th>
<th>Peak Abundance by DART-MS(+) (%)</th>
<th>Peak Abundance by DART-MS(-) (%)</th>
<th>Tentative Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomers</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<td>121</td>
<td>C7H4ON</td>
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<td>11</td>
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<td>20</td>
<td>2-formylformanilide</td>
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<tr>
<td>130</td>
<td>-</td>
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<td>-</td>
<td>-</td>
<td>7.7</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
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<td>C8H4ON</td>
<td>H+</td>
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<td>-</td>
<td>9.0</td>
<td>0.10</td>
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<td>H+</td>
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<td>0.65</td>
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<td>34</td>
<td>23</td>
<td>isatin</td>
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<td>-</td>
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<tr>
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<td>-</td>
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<td>8.9</td>
<td>45</td>
<td>14</td>
<td>indirubin, indigo dye</td>
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<td>12</td>
<td>dihydro indigo dye</td>
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<tr>
<td>266</td>
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<td>4.9, 21</td>
<td>8.9</td>
<td>45</td>
<td>14</td>
<td></td>
</tr>
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<tr>
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<td>8.7</td>
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</tr>
<tr>
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<td>C16H12O2N</td>
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<td>0.18, 5.6</td>
<td>4.3</td>
<td>2.0</td>
<td>7.4</td>
<td></td>
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</tbody>
</table>
Figure 3.12 shows the distribution of the number of C atoms in the indole SOA compounds, as detected by nano-DESI-HRMS (for each group of compounds with the same number of C atoms, the abundances in the positive and negative ion mode mass spectra were added together). Most of the observed compounds contained 8, 16, or 24 C atoms, corresponding to the monomer, dimer, and trimer derivatives of indole. Peaks with 7 and 15 carbon atoms were also prominent, suggesting an important role of the primary C7 oxidation product 2-formylformanilide in the formation of low volatility species. Minor peaks containing other C-numbers were also present suggesting further fragmentation of the primary oxidation products. The average formula for all observed SOA compounds was C15H11O3N2.

![Graph showing distribution of C atoms](image)

**Figure 3.12.** Distribution of the number of C atoms in the indole photooxidation SOA compounds detected in both positive and negative ion modes by nano-DESI-HRMS.

Figure 3.13 shows the distribution of the N/C ratios in indole SOA compounds. Many of the compounds had the same N/C ratio as indole (N/C = 1/8) indicating the oxidation and oligomerization reactions conserved both N and C atoms in many of the products. Loss and
gain of C atoms should result in a small increase and decrease in the N/C ratio, respectively. Some products had a slightly larger ratio consistent with a loss of C atoms (e.g., N/C = 1/7 and 2/15), whereas few products gained extra C atoms. One product with a relatively large abundance, $C_{12}H_{14}O_4$, had no N atoms left in it. Moreover, there were several $C_{8-9}H_{h}O_{o}N_{2}$ products, which gained an additional N atom. The mechanism of photooxidation is clearly complex involving a large number of secondary reactions. The full mechanism of indole photooxidation cannot be obtained from this data set. In the discussion that follows (section 3.4.6), the focus will be on the mechanism of formation of light-absorbing products.

![Figure 3.13: The N/C ratio of indole SOA compounds. The thick horizontal line corresponds to the N/C ratio in indole.](image)

3.4.4 Optical properties of indole SOA

Chemical composition data showed that dimers are present in indole photooxidation SOA (Fig. 3.12). Additionally HPLC-PDA-HRMS (Table 3.4) showed that dimers contribute significantly to the absorption of indole SOA. Dimer formation may be artificially increased
by higher starting indole concentrations. To test for the possible precursor concentration effects on the absorption of SOA samples, indole+NO$_3$ SOA was prepared under different starting indole mixing ratios. As shown in Figure 3.14, Indole+NO$_3$ SOA absorption did not significantly depend on the indole mixing ratios (50-200 ppb) explored in this study, therefore 200 ppb of indole was used in the remaining experiments in order to collect sufficient mass for offline analysis. The lack of sensitivity of the spectra to the indole concentration suggests that the dimers, which are responsible for the 600 nm band, are produced by particle-phase chemistry as opposed to gas-phase chemistry.

![Image](image.png)

**Figure 3.14.** Wavelength-dependent MAC of indole + NO$_3$ SOA for different starting concentrations of indole.

Figure 3.15 shows the MAC values measured for an extract of indole + OH SOA in methanol. MAC values reached ~2 m$^2$/g at $\lambda = 300$ nm. At $\lambda = 400$-700 nm, the MAC values ranged from
These high MAC values are comparable to values of strongly absorbing SOA derived from naphthalene or methylpyrroles (Romosnky et al., 2015), as well as to MAC values of biomass burning organic aerosol (Sun et al., 2007). The wavelength dependence of MAC deviates from the power law commonly observed for brown carbon, e.g., see reviews of Laskin et al. (2015) and Moise et al. (2015), and has a reproducible broad band at ~350 nm, possibly due to the well-known derivatives of indole: indirubin, indigo dye, and indoxyl red, which have characteristic absorption bands at this wavelength. For the wavelength range of 300-600 nm, the absorption Angstrom exponent was ~6, comparable to the value of ~5 reported for brown carbon from biomass burning (Kirchstetter et al., 2012).

**Figure 3.15.** Wavelength-dependent mass absorption coefficient (MAC) of indole+OH SOA prepared under dry conditions. The inset shows the log-log version of the same data used to determine the absorption Angstrom exponent (fitted from 300 to 600 nm) and photographs of the indole SOA collected on a filter and extracted in methanol.
Figure 3.16 shows the wavelength dependent ($\lambda = 220\text{-}700$ nm) MAC of indole SOA samples prepared under the different oxidation conditions and relative humidities. The MAC spectra for indole SOA prepared under all conditions have characteristic features of brown carbon, with strong absorption in the UV and weaker absorption over the visible range. However, there are striking differences between the spectra. For example, the peak at 350 nm due to nitroindole (see Section 3.4.5) is highly prominent for the indole+NO$_3$ SOA. It also observable in the indole+OH+NO$_x$ SOA but it is missing for the indole+O$_3$ and indole+OH SOA systems. Another striking difference is the significant abundance of the indigo dye, recognized by its characteristic absorption band at 600 nm, in the indole + NO$_3$ SOA when prepared under low or 25% RH. The indigo dye peak is the largest under dry conditions but becomes much smaller at 50% RH. While much smaller, this peak at 600 nm is also observable in the indole+O$_3$ SOA at low RH and 25% RH traces, and also goes away at 50% RH.
Figure 3.16. Wavelength-dependent mass absorption coefficient (MAC) of a) indole + OH SOA, b) indole + OH + NO\textsubscript{x} SOA, c) indole + O\textsubscript{3} SOA, and d) indole + NO\textsubscript{3} SOA generated at different RH.

The MAC values (Fig. 3.16) were used to calculate the extinction coefficient, $k$, (Figs. 3.17-3.19 a) and were compared to the $k$ values obtained through broadband cavity enhanced spectroscopy (BBCES) (Figs. 3.17-3.19 b). Overall, the $k$ values obtained from the two independent methods were within the same order of magnitude suggesting good agreement between the two methods, and had the best agreement for the indole SOA prepared from photooxidation. Indole+OH SOA had higher $k$ values at higher RH (Fig. 3.17a) and in the presence of NO\textsubscript{x} (Fig. 3.17b). Moreover, the indole+OH+NO\textsubscript{x} SOA had a stronger wavelength dependence compared to the SOA prepared under low NO\textsubscript{x} conditions. The dependence of the extinction coefficient for indole+O\textsubscript{3} SOA on RH (Fig. 3.18a) had the same trend as the photooxidation samples; increasing $k$ values with increasing RH.
Figure 3.17. a) $k$ values calculated from MAC of indole + OH SOA prepared in a chamber under low and high NO$_x$ conditions. Measured b) $k$ and c) $n$ for indole SOA generated in an OFR under low and increasing NO$_x$ conditions.
Figure 3.18. a) $k$ values calculated from MAC of indole + O$_3$ SOA prepared in a chamber under different RH (<2, 25 or 50%). Measured b) $k$ and c) $n$ for indole + O$_3$ SOA generated in a glass OFR under dry conditions. The pink and green traces were collected using the BBCES in the 315-345 nm and 380-700 nm channels, respectively.
Figure 3.19. a) $k$ values calculated from MAC of indole + NO$_3$ SOA prepared in a chamber under different RH (≤2, 25 or 50%). Measured b) $k$ and c) $n$ for indole + NO$_3$ SOA generated in a glass OFR reactor at various RH (0, 25, 51, 76%). The dotted and solid traces were collected using the BBCES in the 360-390 nm and 385-425 nm channels, respectively.

Unlike SOA prepared by photooxidation or ozonolysis, $k$ values for indole+NO$_3$ SOA did not have a monotonic dependence on RH (Figs. 3.19-3.20). Instead, the $k$ values for indole+NO$_3$ SOA were highest for SOA prepared under low RH, then decreased at 25% RH, and subsequently increased at 50% RH, a trend captured by both methods (Fig. 3.19a-b).

When the $k$ values at 400 nm reported in Fig. 3.19b were replotted as a function of RH (Fig. 3.20), we observed that going from low to 25% RH resulted in a decrease in the $k$ value by
approximately half. Increasing the RH again by increments of ~25% led to modest increases in the k value.

**Figure 3.20.** Measured k for indole + NO₃ SOA generated in a glass OFR reactor at various RH (0, 25, 51, 76%). (Same data from Fig. 3.19b)

Based on AMS data, chemical families that showed a similar RH dependence were the CₓHᵧO and CₓHᵧOₓ families (Fig. 3.21), with the most prominent ion fragments consisting of CO⁺ and CO₂⁺ (Fig. 3.22). On the other hand, families like NO⁺ and CₓHᵧ⁺ followed the opposite RH dependence as the k values, with prominent ion fragment including NO⁺, NO₂⁺, and C₁-C₆ compounds (Fig. 3.23). It is possible that fragments which follow the same trend as k values do with respect to RH contribute to the absorption of the particles. However, more data are needed in order to investigate the mechanisms responsible for this absorption and the role of RH in these reactions. A future set of experiments could be done via HPLC-PDA-HRMS for indole+NO₃ SOA generated at different RH (as opposed to just one measurement at a single RH, Section 3.4.5) in order to investigate what happens to the chromophoric compounds in the SOA as a function of RH.
Figure 3.21. Indole + NO₃ SOA: AMS Families vs RH

Figure 3.22. AMS families that followed the same trend with RH as k vs RH. Individual ion fragments signals are shown for indole+NO₃ SOA generated under <5% RH (a), 25% RH (b), 51% RH (c), and 76% RH (d). The ion signal has been normalized such that the total ion signal for all assigned peaks in an average mass spectrum is 1.
Figure 3.23. Examples of AMS families that followed opposite trend with RH to k vs RH. Individual ion fragments signals are shown for indole+NO$_3$ SOA generated under <5% RH (a), 25% RH (b), 51% RH (c), and 76% RH (d). The ion signal has been normalized such that the total ion signal for all assigned peaks in an average mass spectrum is 1.

3.4.5 Chromophores in indole SOA

Figure 3.24 shows the HPLC-PDA chromatogram of an indole+OH SOA sample demonstrating its components with strong light-absorbing properties near-UV and visible spectral ranges (above 300 nm). To identify specific chromophores from the HPLC-PDA-HRMS data, the methods described by Lin et al. (2015b, 2016) were followed. High-resolution mass spectra were examined to identify $m/z$ values that appear at the retention times associated with the peaks in the HPLC chromatograms. The PDA absorption spectra associated with these retention times were then compared with possible candidates constrained by their molecular formula determined from the mass spectra.
Figure 3.24. HPLC-PDA chromatogram of indole photooxidation SOA. The absorbance is plotted as a function of both retention time and wavelength. Peaks are labelled by their PDA retention time followed by their proposed assignment. Bold-faced assignments are specific isomers that are discussed further in the text. Note the reference line for dihydro indigo points to a small peak between two larger peaks that obscure it in this projection.

Figure 3.25 shows a comparison of the absorption spectra for the key peaks in the HPLC-PDA chromatogram with absorption spectra of selected compounds reported in the literature. The match is excellent in terms of the absorption peak maxima: 280, 310, 334, 392 nm for tryptanthrin; 240, 283, 335, 610 nm for indigo dye; 242, 290, 365, 540 nm for indirubin; and 217, 273, 350, 520 nm for indoxyl red. The shapes of the spectra do not match perfectly because the chromophores are not fully separated by the HPLC column (Fig. 3.24) and may co-elute with additional minor compounds. Likely, more than one chromophore contributed to the absorbance at any given retention time. However, the power of the method is clear, as illustrated, for example, by the separation of the structural isomers indigo dye and indirubin (Fig. 3.24).
The HPLC-PDA chromatograph for the indole+O₃ and indole+NO₃ SOA samples is shown in Figure 3.26 and a list of the individual chromophores along with proposed structures based on elemental formulas obtained from the HRMS analysis and reference spectra from the literature are listed in Table 3.4. Altogether 28 individual compounds were identified, which included 6 monomers, 20 dimers, and 2 trimers. Monomeric compounds are especially relevant as the dimers and trimers are much less likely to form under realistic concentrations in the atmosphere. Three chromophores (tryptanthrin, indigo dye, and indirubin) were observed in all three SOA types, and an additional seven of the chromophores were shared by two SOA types. The chromophore indigo dye, while not
unique to the indole+NO$_3$ SOA, contributed to the prominent peak at 600 nm in the indole+NO$_3$ SOA absorbance spectrum.

![Indole + NO$_3$ SOA chromatogram](image)

**Figure 3.26.** HPLC-PDA chromatogram of indole ozonolysis SOA sample (top panel) and indole + NO$_3$ SOA sample (bottom panel) generated at low RH. The absorbance is plotted as a function of both retention time and wavelength. Peaks are labelled by their proposed assignment. See table 3.4 for more details.

**Table 3.4.** Proposed chromophores from indole + NO$_3$ SOA, indole + O$_3$ SOA, and indole + OH SOA generated at low RH.

<table>
<thead>
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<th>Retention time (min)</th>
<th>Molecular weight (amu)</th>
<th>Elemental formula</th>
<th>Tentative structure</th>
<th>UV-Vis Absorption spectrum</th>
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<td>163</td>
<td>C$_8$H$_5$NO$_3$</td>
<td>Isatoic anhydride</td>
<td>X</td>
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<tr>
<td>Retention time (min)</td>
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<td>Elemental formula</td>
<td>Tentative structure</td>
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<td>UV-Vis Absorption spectrum</td>
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<tr>
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<td>Molecular weight (amu)</td>
<td>Elemental formula</td>
<td>Tentative structure</td>
<td>UV-Vis Absorption spectrum</td>
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<td>30.58 (NO&lt;sub&gt;3&lt;/sub&gt;) 30.81 (O&lt;sub&gt;3&lt;/sub&gt;)</td>
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<td>C&lt;sub&gt;13&lt;/sub&gt;H&lt;sub&gt;8&lt;/sub&gt;N&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;2&lt;/sub&gt;</td>
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<td>38.33 (NO₃) 38.45 (O₃)</td>
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<td>![Absorbance Graph]</td>
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<td>278</td>
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3.4.6 Proposed mechanisms for the production of chromophores in indole+OH SOA

The precursors to indoxyl red and indigo dye, dihydro indoxyl red and dihydro indigo dye, respectively, were also identified by HPLC-PDA-HRMS analysis, and were observed in nano-DESI mass spectra. This observation supports a mechanism similar to the aqueous-phase indole oxidation proposed by Iddon et al. (1971), in which indole first oxidizes to 3-oxindole, then to dihydro indigo dye or dihydro indoxyl red, then finally to indigo dye and indoxyl red (Figure 3.27a). We note that the mechanism by Iddon et al. (1971) was developed for the aqueous oxidation of indole. While our experiments were performed under dry conditions, it is conceivable that similar oligomerization processes can occur in the gas phase and/or in the organic particle phase. For example, Healy et al. (2012) observed efficient dimerization of naphthoxy radicals in the gas phase leading to rapid formation of SOA following photolysis of 1-nitronaphthalene. The dimerization of oxindole to dihydro indigo dye, as well as other oligomerization processes in indole SOA, could follow a mechanism similar to the one described by Healy et al. (2012).

Several products were assigned based on previous observations by Novotna et al. (2003), who studied photodegradation of indigo dye in dichloromethane solution. They proposed the mechanism shown in Figure 3.27b to explain the production of tryptanthrin and anthranilic acid from ambient indigo dye oxidation. In this mechanism, hydroxyl radicals attack the carbonyl carbon atoms of isatin ultimately opening the 5-membered N-heterocyclic ring to yield anthranilic acid. Although anthranilic acid does not show up in Figure 3.24 because it is not a chromophoric species, it was detected by nano-DESI-HRMS. As shown in Figure 3.27b, anthranilic acid can react with another molecule of isatin to produce tryptanthrin. This mechanism is relevant to indole photooxidation SOA, because
isatin can be produced not only from the oxidation of indigo dye but also directly from indole, through the intermediacy of 3-oxindole (Figure 3.27a). Moreover, Novotna and colleagues suggested that isatoic anhydride should also be formed from indigo dye oxidation. A compound with this formula had large abundance in both HPLC-PDA-HRMS (Figure 3.24) and nano-DESI-HRMS and DART-MS (Figure 3.11, Table 3.3). Combined with the evidence that tryptanthrin is a major secondary chromophore, this could be a significant pathway to brown carbon formation in the oxidation of indole.

We emphasize that the mechanism outlined in Figure 3.27 is tentative and is based on the limited information from our experiments and previous experimental data from the literature. Multiple unresolved questions remain. For example, formation of tryptanthrin was very slow in experiments by Novotna et al. (2003), and it is not at clear how this compound could form in just a few hours of photooxidation in the chamber. Furthermore, it is not clear which processes occur in the gaseous phase versus the particle phase. Although indeterminable from the current experiments, at least some of the dimer formation pathways described in Figure 3.27 likely occur in the particle phase.
Figure 3.27. Tentative mechanism for the formation of observed chromophores in the photooxidation of indole. (a) Processes leading to indigo dye and indoxyl red based on Iddon et al. (1971). (b) Processes leading to tryptanthrin based on Novotna et al. (2003). “Ox” denotes an oxidation step.
3.5 Modeling Results

The spatiotemporal distribution of indole+OH SOA is likely controlled by a combination of: (i) the spatiotemporal distribution of gas-phase indole and its emissions sources, (ii) the availability of hydroxyl radical for gas-phase oxidation chemistry and (iii) meteorological conditions in the region, including temperature, humidity, and wind direction. Once emitted, indole reacts with hydroxyl radical to form gas-phase indigo dye. Gas phase indigo dye can then partition into the aerosol phase to form indole SOA. The presence of a sea breeze in the SoCAB results in a prevailing wind direction of north-northeast, transporting pollutants inland during the daytime hours. As a result, peak concentrations of indole+OH SOA should be located further inland than peak concentrations of gas-phase indole and occur in areas that are already burdened with poor air quality.

Figure 3.28 shows the spatial distribution of 24-hour average gas-phase indole concentrations in the SoCAB for the low, medium, and high emissions scenarios considered in this study. The amount of indole+OH SOA formed in the model, and thus the impact of indole on the total predicted SOA concentrations, depends strongly on the emissions of gas-phase indole. In the high emissions scenario, hourly gas-phase indole concentrations peaked at 0.3 ppbv, with the highest concentrations occurring in the early morning hours before sunrise (Fig. 3.31). For comparison, during a field measurement campaign in the San Joaquin Valley of California, Gentner et al. (2014) reported gas-phase indole concentrations of about 1-3 ppbv in ambient air during a springtime flowering event. Measured concentrations of indole were slightly higher during the late night and early morning hours than during the daytime, consistent with the model results obtained in this study. Gentner et al. (2014) also
showed that flowering was a major biogenic emissions event, causing emissions of many compounds to increase by several factors to over an order of magnitude. Therefore, episodic emissions of indole in rural areas are likely to be significantly greater than the emissions used in this study. Based on the high SOA yield from gas-phase indole found in the indole+OH SOA experiments, we propose that biogenic emissions events such as springtime flowering may degrade local air quality.

Figure 3.28. The 24-hour average gas-phase indole concentrations. The indole mixing ratios in ppbv are shown in the low emission scenario (a), medium emissions scenario (b), and high emission scenario (c).

Figure 3.29 a shows 24-hour average SOA concentrations in the base case model simulation, and Figures 3.29 b-d show the additional SOA resulting from indole photooxidation in the three emissions scenarios. The highest SOA concentrations occurred directly east of Riverside where a combination of biogenic and anthropogenic precursors accumulated during days one and two and into day three. The 24-hour average indole+OH SOA
concentrations peaked at about 0.13 µg/m³ in the high emissions scenario (Figure 3.29d). The highest concentrations of indole+OH SOA occurred north of Los Angeles and Riverside.

To put this number in perspective, aerosol with mass concentration of 0.1 µg/m³ and MAC of 0.5 m²/g will have an absorption coefficient of 0.05 Mm⁻¹ (we neglect the particle size effects in this estimation). Thompson et al. (2012) reported an absorption coefficient of 4 Mm⁻¹ at 532 nm during the 2010 CalNex campaign in Pasadena, California, with the absorption being dominated by black carbon. The average absorption coefficients reported for “average urban USA” and “average remote USA” by Horvath et al. (1993) were 22 Mm⁻¹ and 0.7 Mm⁻¹, respectively. While the absorption by indole+OH SOA is unlikely to compete with that by black carbon in urban areas, it may contribute to the aerosol absorption in more remote areas, where the black carbon concentrations are smaller.

Figure 3.29. Twenty-four-hour average concentrations (µg m⁻³) of (a) total SOA in the base case and additional SOA resulting from indole photooxidation in (b) the low emission scenario, (c) the medium emission scenario, and (d) the high emission scenario.
SOA concentrations averaged over the entire domain are shown in Figure 3.30 for the first four modeled scenarios. The averaged SOA concentrations were computed by averaging the concentration of total SOA in all computations cells in the domain. Therefore, changes in the averaged SOA concentrations are representative of the overall impact on total SOA concentrations for the entire basin. In the high emissions scenario, the averaged SOA concentrations increased by about 4-13%, indicating that indole+OH SOA can contribute significantly to total organic aerosol concentrations. While base case SOA concentrations peaked during the early morning and late-night hours when metrological conditions were favorable, the largest changes in SOA concentrations occurred during the late morning and afternoon hours. The formation of gas-phase indigo dye and indole+OH SOA depends on the availability of the hydroxyl radical, which reaches peak concentrations during daylight hours when photochemistry is active. Therefore, increased production of hydroxyl radical during the daytime accelerates the oxidation of gas-phase indole, ultimately resulting in increased formation of indole+OH SOA. Increases in total SOA are due mostly to the formation of indole+OH SOA, with only small changes in the concentration of other SOA species.
Figure 3.30. Domain-wide average SOA concentrations in the base case (black line, left axis) and the relative increase in domain-wide average SOA concentrations (right axis) driven by the oxidation of indole by OH in the (a) low emission scenario, (b) medium emission scenario, and (c) high emission scenario. Figure 3.32 additionally shows the effect of inclusion of the indole + NO$_3$ reaction on the model.

Figures 3.31 and 3.32 suggest that the oxidation of indole via reaction with NO$_3$ may also be an important pathway to indole SOA formation during the late night and early morning hours when photochemistry is inactive. When the oxidation of indole via reaction with NO$_3$ is included in the fifth modeled scenario, gas-phase indole concentrations are lower (Fig. 3.31) and indole SOA concentrations are higher (Fig. 3.32) than in the fourth scenario. The differences are most pronounced during the late night and early morning hours due to the different diurnal profiles of OH and NO$_3$; OH concentrations peak during the daytime hours when photochemistry is active, whereas NO$_3$ concentrations peak at night. Thus, the relative increase in total SOA concentrations due to indole SOA shows less temporal variability.
throughout the day when the reaction of gas-phase indole with NO$_3$ is included in the model, but peak indole SOA concentrations remain essentially unchanged.

**Figure 3.31.** Gas-phase indole concentrations. The indole mixing ratios in ppbv are shown for the low emissions scenario (a), medium emissions scenario (b), and high emissions scenario (c). In addition, trace (c2) shows mixing ratios in the high emissions scenario with indole oxidation via reaction with NO$_3$ included in the model. Domain wide average concentrations are shown in the top panel and domain maximum concentrations are shown in the bottom panel.
Figure 3.32. Domain wide average SOA concentrations. The base case mass concentration of SOA is shown in black line referenced to the left axis. Also shown is the percent increase in the domain wide average SOA concentrations (right axis) due to indole SOA in the high emissions scenario (c), and high emissions scenario with indole oxidation via reaction with NO$_3$ included in the model (c2). The daytime concentrations are not significantly affected by NO$_3$ but the nighttime concentrations increase.

The amount of indole SOA formed in each scenario was found to be directly proportional to the emissions of gas-phase indole. In the low emissions scenario, gas-phase indole and indole SOA concentrations were about factor of five lower than those seen in the high emissions scenario, with 24-hour average indole SOA concentrations peaking at about 0.025 µg/m$^3$. Similarly, relative increases in the averaged SOA concentrations ranged from 1-3% in the low emissions scenario. In the medium emissions scenario, 24-hour average indole SOA concentrations reached about 0.05 µg/m$^3$, causing total SOA concentrations to increase by 2-6%. In all three emissions scenarios, the spatial distribution of indole SOA remained essentially the same, with peak concentrations occurring in the northeast portion of the basin, an area already burdened with poor air quality.
3.6 Conclusions

This work demonstrates that indole is an effective precursor to SOA. At the concentrations used in this chamber study, the majority of indole photooxidation products ended up in the particle phase, with an effective SOA yield of $\sim 1.3 \pm 0.3$. SOA generated from either OH, O$_3$, or NO$_3$ oxidation was found to be strongly light-absorbing, with MAC values ranging from $\sim 1$ to 0.02 m$^2$/g across the visible spectrum and approaching those of strongly-absorbing brown carbon from biomass burning. The high MAC values were due to various products of indole oxidation, including well-known chromophoric compounds such as isatin, tryptanthrin, indirubin, indoxyl red, and indigo dye which were identified by their molecular formulas and characteristic peaks in their absorption spectra. These observations suggest that N-heterocyclic compounds may be important contributors to secondary brown carbon. Moreover UV-Vis experiments of bulk indole SOA samples and BBCES experiments of indole SOA particles both showed that the absorption properties of indole SOA are sensitive to relative humidity. More experiments are necessary to better understand the role of water in indole oxidation reactions in order to better inform modelers of the absorptive properties of indole SOA in various RH environments.

Contribution of indole to SOA formation can potentially result in reduced visibility, particularly in regions where plants are exposed to biotic and abiotic stresses. When combining the experimental MAC values with peak SOA concentrations predicted in the model, the estimated maximum absorption coefficient is 0.05 Mm$^{-1}$ due to indole+OH SOA. This is smaller than the values typically reported for SoCAB but comparable to values reported in more remote areas. Thus, despite its large MAC, indole+OH SOA is not likely to contribute to particle absorption in urban areas, where anthropogenic black carbon
dominates the aerosol absorption. However, the situation could be different in remote areas, where black carbon does not contribute to aerosol absorption, and indole emissions are higher.

The UCI-CIT regional airshed model showed significant potential for indole SOA formation driven by the oxidation of indole by OH. Simulations indicate that the oxidation of indole via reaction with NO$_3$ may also be an important SOA formation pathway during the late night and early morning hours when photochemistry is inactive. While the mass loading of indole SOA in the SoCAB was relatively low in all scenarios, it represents a previously unconsidered source of SOA in air quality models, which have been improved in recent years, but still tend to disagree with measured SOA concentrations (Couvidat et al., 2013; Heald et al., 2005; Hodzic et al., 2010; Jiang et al., 2012; Volkamer et al., 2006). Indole SOA can interact with other aerosol-phase species, causing indirect changes in the concentration of total SOA. Such interactions were not considered in this study because an activity coefficient of unity was used for indole SOA in the model simulations. Rural or agricultural regions with significant biomass burning or a high density of plant life likely have much higher emissions of gas-phase indole than the SoCAB. For example, field measurement studies (Gentner et al., 2014) reported ambient indole concentrations up to an order of magnitude greater than the peak modeled concentrations employed in this study, indicating a significant potential for indole SOA formation in rural areas. Furthermore, future climate change is likely to increase gas-phase indole emissions through environmental and physical stress factors such as drought, elevated temperatures, increased CO$_2$ and O$_3$ concentrations, and enhanced herbivore feeding (Yuan et al., 2009). Therefore, indole represents a potentially important source of biogenic SOA that should be included in regional and global models.
CHAPTER 4

Ammonia Uptake by Secondary Organic Aerosol

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4.1 Background

As the most abundant basic gas in the atmosphere (Behera et al., 2013), gaseous ammonia (NH₃) has long been considered responsible for controlling the eutrophication and acidification of ecosystems (Erisman et al., 2008; Sheppard et al., 2011; Sutton et al., 1993). More recently, studies also demonstrated the importance of NH₃ in the formation of airborne fine particulate matter (PM₂.₅) (Vayenas et al., 2005; Wang et al., 2013; West et al., 1999). Through reactions with acidic species, NH₃ is converted into ammonium salts, such as ammonium nitrate and ammonium sulfate, which constitute an important fraction of total PM₂.₅ mass (Behera and Sharma, 2010). Fine particulate matter consists of approximately 25–50% inorganic compounds and 40–65% organic compounds on a mass basis (Gray et al., 1986; Zhang et al., 2000). Gaseous NH₃ is a precursor to inorganic aerosols and can be the limiting reactant in their formation (Wang et al., 2013; Lelieveld et al., 2015). These aerosols
have been proven to affect human health (Lelieveld et al., 2015; Pope III et al., 2002), visibility (Ye et al., 2011), and the atmospheric radiative balance (Park et al., 2014; Xu and Penner, 2012).

In the South Coast Air Basin of California (SoCAB), a large fraction of total PM$_{2.5}$ mass is comprised of ammonium sulfate (NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$) and ammonium nitrate (NH$_4$NO$_3$) (Kim et al., 2010), produced by the reaction of NH$_3$ with sulfuric acid (H$_2$SO$_4$) and nitric acid (HNO$_3$), respectively. In the SoCAB, the largest NH$_3$ emission sources are agricultural activities (e.g., dairy facilities) and automobiles (Nowak et al., 2012), whereas HNO$_3$ and H$_2$SO$_4$ come from the oxidation of NO$_x$ and SO$_2$ from various combustion sources. The total automobile and agricultural NH$_3$ emissions are estimated as similar in magnitude (Nowak et al., 2012). However, the spatial concentration and high emissions of dairy facilities cause downwind NH$_3$ mixing ratios to be about an order of magnitude greater than those from vehicle emission sources (Nowak et al., 2012). These concentrated NH$_3$ plumes can be transported from their source region and react with inorganic acids to form ammonium salts. The high concentration of NH$_3$ in these plumes drives all of the H$_2$SO$_4$ and most of the HNO$_3$ into the particle phase, causing high concentrations of inorganic PM$_{2.5}$ in the eastern part of the SoCAB (Hughes et al., 2002; Neuman et al., 2003; Nowak et al., 2012).

In the US, the largest NH$_3$ emission source is agricultural activity (∼85% of total US NH$_3$ emissions) (Pinder et al., 2004, 2006), largely from animal waste and commercial fertilizer application, such as the intensive farming in California’s Central Valley (Jovan and McCune, 2005) and industrialized hog farms in central North Carolina (Aneja et al., 2000; McCulloch et al., 1998). Ammonia-rich plumes from those areas drive most of the nitric acid into the particle phase, resulting in high PM$_{2.5}$ concentrations in those regions (Baek and Aneja, 2004;
Neuman et al., 2003). The equilibrium of this reaction is sensitive to relative humidity and temperature, with lower temperatures and higher humidity favoring the formation of the particle phase (Stelson et al., 1979; Stelson and Seinfeld 1982).

Over the past two decades atmospheric NH₃ has increased and is expected to continue increasing as a result of global warming, increasing agricultural activity, and intensifying fertilizer use due to a growing population (Amann et al., 2013; Galloway et al., 2008; Warner et al., 2017).

The conversion of inorganic gases into ammonium, nitrate, and sulfate particles is well understood (Seinfeld and Pandis, 2016). However, significant uncertainty remains regarding reactions between gaseous NH₃ and organic compounds found in secondary organic aerosols (SOA). Ammonia has been shown to react with certain carbonyl compounds found in SOA (Hawkins et al., 2016; Laskin et al., 2015). These reactions convert NH₃ into heterocyclic nitrogen-containing organic compounds (NOC) that remain in particles. The neglect of this process may result in an incorrect prediction of the distribution of organics in PM, and at the same time, over-prediction of gas-phase NH₃, and therefore inorganic PM concentrations, in models. NOC have also been observed in ambient particles in California (O’Brien et al., 2013a, 2013b) and in China (Wang et al., 2010), with evidence for NH₃ playing a key role in their formation. For example, O’Brien et al. (2013b) analyzed the molecular composition of aerosol samples collected during CalNex 2010 in Bakersfield, California and concluded that NOC, which accounted for more than 40% of the observed organic compounds, were produced via reactions between NH₃ and carbonyl groups converting them into imines. Similarly, O’Brien et al. (2013a) compared the composition of field-collected and laboratory-generated SOA and found that some of the NOC observed in Bakersfield were likely formed
through reactions of products of oxidation of diesel fuel emissions with gas-phase NH₃, potentially driven by high concentrations of gaseous NH₃ in the area. Their conclusions were supported by photochemical chamber experiments, where the addition of gaseous NH₃ to SOA generated from diesel fuel oxidation was necessary to produce many of the compounds observed in Bakersfield, and improved overlap between laboratory-generated and observed compounds. It is likely that similar reactions occur in the Los Angeles basin, particularly in areas downwind of strong NH₃ emissions sources with high NH₃ concentrations. In addition, a browning effect on SOA under NH₃ exposure was observed by Updyke et al. (2012), indicating the production of light-absorbing products. These processes are not included in current air quality models, which could lead to overestimation of gaseous NH₃ concentrations and thus inorganic aerosol concentration. Additionally, the neglect of these processes may also result in underestimation of organics aerosol, especially species related to acid-catalyzed reactions (Lin et al., 2013), and an incorrect prediction of aerosol particle acidity.

In 2015, Liu et al. reported for the first time chemical uptake coefficients for NH₃ onto SOA particles measured by direct observation of NOC by an aerosol mass spectrometer. The initial reactive uptake coefficients were on the order of 10⁻² to 10⁻³, dropping to 10⁻⁵ after six hours of reaction. Several other studies demonstrated chemical reactions between NH₃ and various types of SOA but have not quantified the uptake coefficients, rate constants, or equilibrium constants that could be used in models (Bones et al., 2010; Laskin et al., 2010; Updyke et al., 2012). The maximal yield of NOC in reactions between NH₃ and SOA has not been quantified, but there are indications that the yield is modest, on the order of a few percent (Laskin et al., 2014).
In this study, experiments were performed to explore the effect of NH$_3$ on SOA mass loading and composition in order to better constrain the maximal possible fraction of NOC in SOA after long-term exposure to NH$_3$. Moreover, a surface reaction between NH$_3$ and SOA particles was implemented into the University of California, Irvine – California Institute of Technology (UCI-CIT) model based on the NH$_3$ uptake coefficients onto SOA reported by Liu et al. (2015) to estimate the impact of this process on NH$_3$ and PM$_{2.5}$ concentrations in the SoCAB region. Similarly, a first-order loss rate for NH$_3$ onto SOA was implemented into the Community Multiscale Air Quality (CMAQ) model in order to explore the impact of this uptake on air quality in the continental United States. In order to also investigate the seasonal impact on this process for the continental US, simulations were conducted for both winter and summer. Air quality simulations for both the SoCAB and continental US regions were conducted using a range of uptake coefficients to determine the sensitivity of NH$_3$ removal to the magnitude of the uptake coefficient. This study represents the first attempt to quantify the potential importance of including NH$_3$ + SOA chemistry in air quality models and presents the initial findings of implementing a simplified uptake mechanism into a high-resolution air quality model. Although there are limitations to the simplified mechanism implemented into the model, it provides a modeling framework and methodology that can be refined and applied in future studies to better characterize and simulate interactions between NH$_3$ and organic particles.

4.2 Experimental Methods

In order to confirm NOC formation in SOA + NH$_3$ reactions and establish an upper limit on the fraction of SOA compounds that can be converted to NOC, we performed several smog chamber experiments. A biogenic (limonene) or an anthropogenic (toluene, n-hexadecane)
VOC was oxidized in a 5 m³ Teflon chamber to generate SOA under low-NOx conditions. We deliberately used low-NOx conditions (even for anthropogenic VOCs) to avoid interference between NOC formed during the oxidation and NOC resulting from the reactive uptake of NH₃ onto SOA particles. No inorganic seed aerosol was used to avoid interference with mass-spectrometric analysis of SOA. Relative humidity (RH) in the chamber was achieved by flowing purified air through a Nafion humidifier. The relative humidity (±2% RH) and temperature (±1°C) were monitored with a Vaisala HMT330 probe. The RH was <2% for most experiments. However, in addition to generating toluene SOA at low RH, a set of experiments were also performed at ~50% RH due to the known high viscosity of toluene SOA at low RH. Limonene (97%, Sigma Aldrich) was introduced to the chamber to reach a mixing ratio of 500 ppb. Subsequently, 1 part per million by volume (ppm) of O₃ was introduced into the chamber, and gases in the chamber were mixed with a fan for 10 minutes. The fan was turned off after that to slow down particle wall loss. Anthropogenic SOA was produced from photooxidation of 1 ppm toluene (99.8%, Fisher Scientific) or 500 ppb n-hexadecane (99%, Sigma-Aldrich). In these photooxidation experiments, evaporated aqueous hydrogen peroxide (30 wt %, Fisher Scientific) was injected into the chamber by evaporation into a flow of clean air to achieve an initial mixing ratio of 2 ppm. After mixing with a fan for 10 minutes, UV-B lamps were turned on to initiate the photooxidation. After the particle mass concentration of SOA reached a peak value, a measured volume of gas mixture containing NH₃ (1000 ppm NH₃ in N₂, Airgas) was introduced into the chamber. The target mixing ratio of NH₃ in the chamber was supposed to be 500 ppb, however, due to losses in the inlet lines and chamber walls the actual mixing ratio of NH₃ was around 200 ppb as verified with an Ecotech 9842 NH₃/NOx analyzer (which uses an external converter
to convert NH₃ to NO and then measures NO via chemiluminescence). Particle volume concentration was monitored with a scanning mobility particle sizer (SMPS; TSI 3936) equipped with a condensed particle counter (CPC; TSI 3775). The chemical composition of SOA particles was probed online with a Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS). The ToF-AMS data were analyzed using PIKA 1.16I with SQUIRREL 1.57I software. The polydisperse particles were collected on a Teflon filter (47 mm diameter, Millipore FGLP04700) at 20 L min⁻¹ for 3 hours and prepared for composition analysis via direct analysis in real time mass spectrometry (DART-MS). The sample was extracted by placing the filter face down in a petri dish containing 3 mL of acetonitrile (LC-MS grade, 99.9% purity, Honeywell) and placed in a shaker for 5 minutes. Aliquots from the acetonitrile SOA extracts were transferred onto a clean stainless-steel mesh, dried in air and manually inserted between the DART ion source and mass spectrometer inlet. The DART-MS consisted of a Xevo TQS quadrupole mass spectrometer (Waters) equipped with a commercial DART ion source (Ion-Sense, DART SVP with Vapur® Interface). It was operated with the following settings: -350 V grid electron voltage, 3.1 L/min He gas flow, 350°C He gas temperature, and 70°C source temperature. The samples were analyzed with DART-MS in both positive and negative ion modes. Background spectra from the pure solvent were also collected and subtracted from the DART mass spectra.

Additional experiments were performed in which SOA particles were collected and then exposed to NH₃ vapor. The Teflon filter containing the collected particles was cut in half. Each filter half was placed in a small petri dish and was allowed to float on the surface of a liquid in a larger petri dish. One of the larger petri dishes contained nanopure water and another contained a 0.1 M ammonium sulfate (>99%, EMD) solution. Each larger petri dish
was covered separately and stored in the dark. The filter was never in direct contact with liquid, but it was exposed to the vapors above the liquid. The estimated mixing ratio of gaseous ammonia above 0.1 M ammonium sulfate solution is about 300 ppb according to AIM-II model [Clegg et al., 1998]. In the case of limonene SOA, the filter that was aged over the ammonium sulfate solution became visibly brown, in agreement with previous experiments conducted in our group [Laskin et al., 2010]. After two days of aging, the samples were extracted in acetonitrile and analyzed with DART-MS as described above.

In a typical DART ionization, a proton is either added (positive mode) or subtracted (negative mode) leading to largely unfragmented molecular ions of with an m/z of [M+H]^+ or [M-H]^- ions, respectively. We expected the SOA compounds which were not exposed to NH₃ to consist of only C, H, and O atoms (CHO compounds). The CHO compounds have even nominal molecular weights and appear in the DART mass spectra at odd nominal m/z values. After the exposure, we expected some of the CHO compounds to be converted into molecules having one nitrogen atom. The resulting CHON compounds would have odd nominal molecular weights and appear at even m/z values. Our (crude) way of testing for the occurrence of the \( \text{CHO} + \text{NH}_3 \rightarrow \text{CHON} \) reaction was to compare the combined abundances of all even peaks and odd peaks before and after the exposure to ammonia. Specifically, the average nitrogen fraction \( f_N \) of nitrogen-containing organic compounds (NOC) in the SOA sample exposed to NH₃ was estimated with the following equations:

\[
\begin{align*}
    f_N &= \frac{1}{\sigma} \left( \text{Ratio}_{\text{NH}_3} - \text{Ratio}_{\text{control}} \right) \quad (4.1) \\
    \text{Ratio} &= \frac{\sum_{\text{even}i} t_i}{\sum_{\text{odd}i} t_i} \quad (4.2)
\end{align*}
\]
The variable “σ” accounts for the different ionization probability of CHON compounds (typically higher in the positive ion mode mass spectra) relative to that of CHO compounds. In the absence of better information, the average detection sensitivity for CHO and CHON was assumed to be equal (σ = 1). We note that this is a highly approximate treatment, and therefore, the fractional amount of nitrogen obtained from these equations should be treated as an order-of-magnitude estimate.

4.3 Modeling Methods

4.3.1 Modeling Methods for the South Coast Air Basin of California (SoCAB)

Modeling was performed to assess the potential impact of this chemistry on the formation of particulate matter at the regional and continental scales. All of the modeling simulations reported in this chapter were carried out by Professor Donald Dabdub, Dr. Jeremy Horne, and Dr. Shupeng Zhu. The UCI-CIT regional airshed model was used for the air quality simulations. The modeling domain covered the SoCAB, which contains Orange County and portions of Riverside, Los Angeles, San Bernardino, and Ventura counties. It utilized 994 computational cells, each with an area of 5 km × 5 km. The unique modeling domain encompassed a variety of landscapes, including seaside communities, urban and suburban areas, and agricultural activity centered around Chino. Numerous studies have used the UCI-CIT model to simulate air quality in the SoCAB (Nguyen and Dabdub, 2002; Carreras-Sospedra et al., 2006, 2010; Chang et al., 2010; Horne and Dabdub, 2017; Montoya-Aguilera et al., 2017). The model’s chemical mechanism is based on the Caltech Atmospheric Chemical Mechanism (CACM) (Griffin et al., 2002a, 2002b, 2005), expanded to include additional SOA precursors (Dawson and Griffin, 2016). The 3-day episode August 27–29 was chosen for the
air quality simulations, using meteorological conditions that typically occur in the region during the summertime and for which the model has been previously evaluated (Nguyen and Dabdub, 2002; Carreras-Sospedra et al., 2006, 2010; Chang et al., 2010), with 2008 emissions. The model’s spatially and temporally resolved emissions were derived from the South Coast Air Quality Management District’s 2012 Air Quality Management Plan (SCAQMD, 2013). A previous study conducted with the UCI-CIT model indicated that model-predicted NH$_3$ concentrations were similar to those measured in Chino during a field study (Perraud et al., 2015), supporting the accurate representation of NH$_3$ emissions in the model. Initial conditions and boundary conditions were based on values typical to the region. All results presented in this study were from the final simulation day using the emissions described above.

To explore the potential impact of the heterogeneous uptake of NH$_3$ by SOA on air quality, a parameterization of the removal of gaseous NH$_3$ by SOA compounds was implemented into the UCI-CIT model as follows. First, the total concentration of SOA in each of the eight size bins ($C_{\text{mass}_1}$, $C_{\text{mass}_2}$, ..., $C_{\text{mass}_8}$) was calculated. Next, assuming spherical particles with a density of 1.2 g/cm$^3$, the area of SOA particles per volume of air was computed for each size bin ($C_{\text{area}_1}$, $C_{\text{area}_2}$, ..., $C_{\text{area}_8}$) from the mass concentration of SOA in each bin ($C_{\text{mass}_1}$, $C_{\text{mass}_2}$, ..., $C_{\text{mass}_8}$) and the representative (average) diameter of particles in that bin ($d_{p1}$, $d_{p2}$, ..., $d_{p8}$).

$$C_{\text{area}_i} = \frac{C_{\text{mass}_i}}{\rho} \times \frac{6}{d_{pi}}$$

(4.3)
The total available area of SOA particles per volume of air was then determined by summing the combined area of SOA particles in each of the eight size bins.

\[ C_{area} = \sum_{i=1}^{8} area_i \]  

(4.4)

The area calculated by this approach is an approximation for the surface area presented by the SOA compounds because the actual particles contain inorganic species and have complex non-spherical morphologies. Finally, using an average speed of NH₃ molecules of \(6.1 \times 10^2\) m/s \((v_{NH3})\) at 298 K, the first-order loss rate constant, \(k\), was calculated as

\[ k = \gamma \times \frac{v_{NH3} \times C_{area}}{4} \]  

(4.5)

where \(\gamma\) is the reactive uptake coefficient for NH₃. The above calculations were performed separately for each model grid cell at every time step to determine the effective first order rate constant in that cell at that time. The loss rate for NH₃ was then determined from the first-order rate constant and the gas-phase NH₃ concentration in that cell at that time, with one limitation. The loss rate for NH₃ was limited by the yield of NOC observed in previous studies (Laskin et al., 2014) and estimated in this work. Specifically, we assumed that the yield of NOC from reactions between NH₃ and SOA compounds cannot exceed 10%. Therefore, the maximum amount of NH₃ that could be taken up by SOA in each model grid cell at each time step was 0.1 mole of NH₃ per mole of SOA compounds.

Ammonia uptake coefficients (\(\gamma\) values) were obtained from Liu et al. (2015), who studied particulate NOC formation after SOA formed from OH oxidation of m-xylene and ozonolysis of α-pinene were exposed to NH₃. They showed that NOC compounds can be formed reasonably quickly via the uptake of NH₃ by SOA and reported uptake coefficients for NH₃
onto SOA ranging from $10^{-5}$ to $10^{-2}$, with an average value of $4.0 \times 10^{-3}$. Here, simulations were performed with a variety of $\gamma$ values as reported by Liu et al. (2015) to determine the sensitivity of NH$_3$ removal to changes in the uptake coefficient. Figure 4.1 illustrates our modeling approach in which NH$_3$ (g) is in equilibrium with inorganic salts in PM$_{2.5}$ but may now also be irreversibly uptaken by organic aerosols and converted to NOC.

**Figure 4.1.** The modeling approach for the reactive uptake of ammonia by secondary organic aerosol. In addition to the equilibrium between ammonia and inorganic aerosol, the irreversible conversion of ammonia into NOC was added to the model, with its rate controlled by reactive uptake coefficient, $\gamma$. Since NOC is less basic than ammonia, formation of NOC reduces the amount of inorganic salts, as well as affects the particle pH.

In total, five scenarios were considered: (a) reference case with no NH$_3$ uptake, (b) NH$_3$ uptake with $\gamma = 10^{-2}$, (c) NH$_3$ uptake with $\gamma = 10^{-3}$, (d) NH$_3$ uptake with $\gamma = 10^{-4}$, and (e) NH$_3$ uptake with $\gamma = 10^{-5}$. Results for (b), (c), (d), and (e) were compared to the reference case model simulations in (a), where the removal of NH$_3$ by SOA was not included, to determine the impact on NH$_3$ and PM$_{2.5}$ concentrations. This study assumed that $\gamma$ remained constant in each scenario (i.e., no saturation effects) and therefore each scenario represented an upper limit to the amount of NH$_3$ removed by SOA with the selected uptake coefficient. However, the uptake was programmed to stop once the molar fraction of NOC in SOA
particles reached 0.1, as mentioned above. A sensitivity analysis was performed to determine the influence of this assumption on simulation results. Additional model runs conducted assuming a maximum NOC molar fraction of 0.05 or 0.20 changed domain-averaged NH$_3$ and PM$_{2.5}$ concentrations by < 1% in all scenarios except (b) when the largest uptake coefficient ($10^{-2}$) was utilized. Although the impact on gas-phase NH$_3$ concentrations in this scenario was reduced and increased by about 5% when changing the assumed molar fraction of NOC from 0.10 to 0.05 and from 0.10 to 0.20, respectively, the impact on PM$_{2.5}$ concentrations remained essentially unchanged in both cases. All other model inputs (emissions, meteorology, etc.) were held constant between each scenario. Results presented here were for the final simulation day to provide adequate time for NH$_3$ uptake processes to occur and minimize the influence of initial conditions.

This study assumed that the NOC products of reactions between NH$_3$ and particulate organics remain in the particles and do not cause a significant increase in the mass concentration of particulate organics. In these reactions, carbonyl groups are first converted into primary imines, and further reactions lead to more stable secondary imines and heterocyclic compounds (Laskin et al., 2015). The uptake of NH$_3$ is accompanied by loss of one or several water molecules, and the molecular weight and volatility of the NOC product should not be too different from those of the starting SOA compound. Indeed, experiments by Liu et al. (2015) as well as our experiments show that there is no significant change in the particle mass concentration after exposure of SOA particles to NH$_3$. Furthermore, although reactions between NH$_3$ and organic acids/carbonyls can potentially lead to condensable NOC (Duporté et al., 2017), we assumed that the contribution of these reactions to particle-phase NOC is negligible based on the results of Liu et al. (2015). In Liu et al. (2015), gas-phase
reactions leading to particulate NOC were assumed to be negligible based on (1) the observed anti-correlation between the calculated reactive uptake coefficient and NH₃ concentration, and (2) the exceedingly slow rate of the termolecular reaction between NH₃, acid, and carbonyls required in the gas phase to form particle-phase NOC. Therefore, the chemical uptake of gas-phase NH₃ in the model was assumed to occur only via the surface reaction with SOA particles.

This study also assumed that NOC are less effective than NH₃ in neutralizing inorganic acids. In other words, the formation of nitrates and sulfates of protonated NOC (salts containing an organic cation and inorganic anion) was neglected. If the basicity of NOC were as high as that of NH₃, the conversion of NH₃ into NOC would cause little to no change in PM concentrations. However, NH₃ is a stronger base compared to the stable NOC products it forms: the pKₐ = 4.8 of NH₃ is smaller than pKₐ of secondary imines (pKₐ ∼ 10) and nitrogen containing aromatic compounds (e.g., pyrrole pKₐ = 13.6, pyridine pKₐ = 8.8). Therefore, neglect of NOC salts is a reasonable approximation.

4.3.2 Modeling Methods for the Continental United States

The CMAQ modeling system (Byun and Schere, 2006) is a widely used state-of-the-art chemical transport model. In the United States, it is among the most commonly used air quality models in attainment demonstrations for National Ambient Air Quality Standards for ozone and PM₂.₅ (US EPA, 2007). In our study, eight simulations were conducted using the 2017 release of CMAQ (version 5.2), including one base case simulation for the winter (Jan. 1 - Feb. 27, 2011), one base case simulation for the summer (1 July–30 August 2011), and
three different NH$_3$ uptake scenarios for each period. The carbon bond version 6 (CB6) mechanism (Yarwood et al., 2010) was used for the gas-phase chemistry, which includes 127 species as detailed on the website (Adams, 2017), and the AERO6 module was used for aerosol dynamics, which includes 21 inorganic species and 34 organic species (28 SOA and 6 primary organic species) as detailed on the CMASWIKI website (Pye, 2016). The modeling domain used in this study covers the contiguous US using a 12 km × 12 km horizontal-grid resolution (resulting in 396 ($x$) × 246 ($y$) = 97 416 grid cells) and a 29-layer logarithmic vertical structure (set on a terrain following sigma coordinate, from the surface to 50 hPa) with the depth of the first layer around 26 m. Only the simulation results from the first layer, representative of ground level, were used for the analysis in this study.

The meteorological fields were derived from NCEP FNL (Final) Operational Global Analysis data (NCEP, 2000) using the Weather Research and Forecasting Model (WRF, version 3.7) (Skamarock et al., 2008), with the MODIS land use database (Friedl et al., 2010) and the Yonsei University (YSU) parametrization (Hong et al., 2006) for the planetary boundary layer. The WSM3 scheme (Hong et al., 2004) was used for the microphysics option of WRF, and the Kain–Fritsch convective parametrization (Kain, 2004) was used for cumulus physics. These fields were then processed using version 4.3 of Meteorology–Chemistry Interface Processor (MCIP) (Otte and Pleim, 2010). The initial and boundary conditions were obtained from the Model for Ozone and Related Chemical Tracers (MOZART v2.0) (Horowitz et al., 2003). Emissions were generated based on the 2014 National Emissions Inventory (NEI) (US EPA, 2017a) and processed by the Sparse Matrix Operator Kernel Emission (SMOKE, version 4.5) processor (US EPA, 2017b). Biogenic emissions were obtained from the Biogenic
Emission Inventory System (BEIS) (Pierce and Waldruff, 1991), and emissions from cars, trucks, and motorcycles were calculated with MOBILE6 (US EPA, 2003).

In this study, the AERO6 module in CMAQ was updated to simulate the heterogeneous uptake of NH$_3$ by SOA. AERO6 used the modal representation to simulate aerosol dynamics (Binkowski and Roselle, 2003). The size distribution of the aerosol particles was represented by three log-normal modes: the Aitken mode (size up to approximately 0.1 µm), the accumulation mode (size between 0.1 to 2.5 µm), and the coarse mode (size between 2.5 to 10 µm). The particles were assumed to be internally mixed within each mode. In the AERO6 modal approach, three integral properties of the size distribution were followed for mode $j$: the total particle number concentration $N_j$, the total wet surface area concentration $S_j$, and the total mass concentration $m_{ij}$ of each individual chemical component $i$. In order to calculate the total uptake of NH$_3$ by SOA, one must know the representative wet surface area concentration of SOA ($S_{SOA}$) (SOA hygroscopic growth is not considered in the model), which can be calculated as follows (assuming a uniform density across different chemical components):

$$S_{SOA} = \sum_{j=1}^{x} \left( S_j \sum_{k=1}^{y} \frac{m_{ij}}{m_{kj}} \right)$$  (4.6)

where $y$ is the total number of SOA species in mode $j$, $z$ is the total number of aerosol species in mode $j$, and $x$ is the total number of modes that contain SOA species. Here, $x = 2$ since SOAs only exist in the Aitken mode and the accumulation mode. From $S_{SOA}$ the first-order rate of NH$_3$ uptake was calculated the same as in the UC-CIT model

$$k = \gamma \times \frac{v_{NH_3} \times S_{SOA}}{4}$$  (4.7)
where $\gamma$ is the reactive uptake coefficient for ammonia and $v_{NH3}$ is the average speed of NH$_3$ molecules. The above calculations were performed separately for each grid cell at every time step to obtain the effective first-order rate constant for each individual cell at each time step. The first-order rate constant of NH$_3$ uptake was then multiplied by the gas-phase NH$_3$ concentration to determine the loss rate of NH$_3$ in each cell at each time step.

As in the UCI-CIT modeling approach for the SoCAB region, we assumed that all NH$_3$ taken up by SOA carbonyls led to the formation of NOCs (Laskin et al., 2015). These reactions are expected to lead to the loss of one or more water molecules; because the difference in the molecular weights of water and ammonia is small, we neglected the mass loss of particulate organics directly due to the NH$_3$ uptake in these simulations.

Although, the NH$_3$ uptake process does not directly impact the mass of SOA, the conversion of NH$_3$ into NOCs can affect the SOA mass indirectly due to particle acidity changes. The particle acidity is altered because strongly basic NH$_3$, which is converted into weakly basic NOCs, is no longer available to form inorganic salts of NH$_4^+$. Therefore, as the extent of neutralization of inorganic acids with NH$_3$ is reduced, the particle acidity may increase.

A range of uptake coefficients ($\gamma$) based on the work of Liu et al. (2015) was selected and applied to all SOA species Liu et al. (2015) reported a range of possible uptake coefficients from 10$^{-5}$ to 10$^{-2}$. However, some of our initial modeling tests showed that the use of a 10$^{-2}$ uptake coefficient value would lead to an unrealistic amount of NH$_3$ taken up by SOA, where within a single time step the number of moles of NH$_3$ taken up exceeded 10% of the total moles of SOA in one grid cell, a limit derived from the mass spectrometry experiments in our work. Based on this limit, an uptake coefficient of 10$^{-3}$ was considered a more reasonable
upper limit value for the continental US simulations instead of the $10^{-2}$ upper limit applied in the SoCAB simulations. Therefore for the continental US, four simulations were performed for each period to investigate the sensitivity of NH$_3$ removal to changes in the uptake coefficient: (a) base case with no NH$_3$ uptake, (b) NH$_3$ uptake with $\gamma = 10^{-3}$, (c) NH$_3$ uptake with $\gamma = 10^{-4}$, and (d) NH$_3$ uptake with $\gamma = 10^{-5}$.

Results from each simulation were evaluated by comparing with observations from multiple monitoring networks. Then simulation results for scenario (b)–(d) are compared to the base case results in (a) to determine the impact of different uptake coefficients on different gas- and particle-phase species. The value of $\gamma$ was assumed to remain constant in each scenario (i.e., no saturation or aging effects), which means each scenario represents an upper limit for the amount of NH$_3$ that would be taken up by SOA with the chosen value of the uptake coefficient. No further changes were made to the model or its inputs between each scenario. Results of the first 7 days of each simulations were discarded as a model spin-up period to minimize the effect of initial conditions and allow sufficient time for the NH$_3$ removal process to occur.

**4.4 Experimental Results**

After exposure of SOA to a pulse of NH$_3$ in the chamber, there was no change in the particle mass concentration for any of the three SOA systems (Fig. 4.2). After the experiments, we were able to get an NH$_3$ analyzer, which upon being connected to the chamber showed that most of the injected NH$_3$ was actually quickly removed by the chamber walls making it difficult to quantify the uptake coefficient from the ToF-AMS data. Despite the NH$_3$ wall loss, slow chemical uptake of NH$_3$ was observable in some ToF-AMS data. Specifically, when
limonene/O$_3$ SOA was exposed to NH$_3$, there was a slow increase in the N:C ratio (Fig. 4.3). However, we observed no uptake of NH$_3$ on toluene/OH SOA (Fig. 4.3), despite the fact that efficient uptake was observed by Liu et al. (2015) for related xylene/OH SOA. It is possible that the difference is due to the presence of NO$_x$ in Liu et al. (2015) experiments and absence of NO$_x$ in our experiments; the presence of nitric acid produced by photooxidation of NO$_x$ is likely to promote uptake of NH$_3$ and subsequent acid-catalyzed conversion of NH$_3$ to NOC.
Figure 4.2. Plots showing the particle mass concentration over time under low RH conditions. The time during which NH$_3$ was injected in the chamber is shown by the shaded region. For all three SOA tested: limonene/O$_3$ SOA (top), toluene/OH SOA (middle), and n-hexadecane/OH SOA (bottom) the injection of ammonia did not have an effect on the total particle mass loading.
Figure 4.3. Plots showing the N:C ratio of the particle composition over time for limonene/O₃ SOA and n-hexadecane/OH SOA generated under low RH and toluene/OH SOA generated under 54% RH in the chamber. Ammonia exposure (shaded region) caused a small increase in the N:C ratio in the limonene/O₃ SOA (top). In contrast, after NH₃ exposure, no clear changes in N:C ratio were observed in the toluene/OH SOA (middle) nor n-hexadecane/OH SOA (bottom). Given the known higher viscosity of toluene/OH particles at low RH, toluene/OH was also generated at higher RH (54%) shown here. The H:C and O:C ratios (not shown) remained approximately constant in all three SOA systems over time.
There was an increase in the abundance of even \( m/z \) peaks in the DART mass spectra of the limonene/O\(_3\) SOA particles that were exposed to NH\(_3\) in the chamber (Fig. 4.4). The fraction of NOC (\( f_N = 20\% \)) was estimated from the increases in the relative abundance of the even \( m/z \) peaks in the DART mass spectra based on the procedure described in the methodology section. Liu et al. (2015) reported comparable conversion efficiencies for SOA particles, with 9% of \( \alpha \)-pinene/O\(_3\) SOA compounds and 32% of m-xylene SOA compounds (by mass) being converted to NOC. Prolonged exposure of bulk SOA filter samples to NH\(_3\) led to browning of limonene/O\(_3\) SOA material, as observed in previous experiments (Updyke et al., 2012). The limonene/O\(_3\) bulk SOA sample exposed to NH\(_3\) on a filter had an \( f_N \) value of 11%, lower than that resulting from an exposure of SOA particles to NH\(_3\) in the chamber. These results suggest that NH\(_3\) reacts with SOA more efficiently with suspended particles compared to the bulk SOA sample. It may also be that NH\(_3\) is incorporated more effectively into the SOA as the SOA is forming. The \( f_N \) values for the toluene/OH and hexadecane/OH bulk SOA samples exposed to NH\(_3\) were a factor of two smaller than for limonene/O\(_3\) SOA, with an \( f_N \) of 5% for both samples. This suggests that different types of SOA exhibit different reactivity towards NH\(_3\). The low values of \( f_N \) observed in this work are similar to the results of Laskin et al. (2014), who estimated from IR spectra that less than 5% of SOA carbonyls in SOA filter samples are converted in NOC.
Figure 4.4. DART mass spectra of limonene/O3 SOA samples generated under low RH conditions in the chamber in the absence of NH₃ (black) and in the presence of NH₃ (red). The shaded box in the top panel is magnified in the middle panel. In the bottom panel, the ratio of the peak abundance of the SOA exposed to NH₃ over the peak abundance of SOA not exposed to NH₃ is plotted as a function of m/z. The bottom plot illustrates how presence of NH₃ generally leads to an increase in the abundance of even m/z peaks in the limonene SOA system. The peak abundance at each m/z has been normalized with respect to the sum of total peak abundances in each mass spectrum.
Figure 4.5. DART mass spectra of toluene/OH SOA samples generated under low RH conditions in the chamber in the absence of NH$_3$ (black) and in the presence of NH$_3$ (red). The boxed region in the top panel is magnified in the middle panel. In the bottom panel, the ratio of the peak abundance of the SOA exposed to NH$_3$ over the peak abundance of SOA not exposed to NH$_3$ was plotted as a function of m/z. The bottom plot illustrates how NH$_3$ exposure generally leads to an increase in even m/z peaks in toluene SOA products. The peak abundance at each m/z has been normalized with respect to the sum of total peak abundances in each mass spectrum.
**Figure 4.6.** DART mass spectra of n-hexadecane/OH SOA samples generated under low RH conditions in the chamber, collected onto filters, and then aged in the presence of H$_2$O (black) and NH$_3$ (red). The shaded box in the top panel is magnified in the middle panel. In the bottom panel, the ratio of the peak abundance of the SOA exposed to NH$_3$ over the peak abundance of SOA exposed to H$_2$O was plotted as a function of m/z. The bottom plot illustrates how NH$_3$ exposure generally leads to an increase in even m/z peaks in the n-hexadecane SOA system. The peak abundance at each m/z has been normalized with respect to the sum of total peak abundances in each mass spectrum.

In summary, the experiments described here generally support the assumptions made in the model, specifically, the assumption that on the order of 10% of SOA compounds can be converted to NOC. However, they do not provide additional information on the uptake coefficients relative to the previous study by Liu et al. (2015).
4.5 Model Predictions for the SoCAB

The air quality impacts of including the uptake of NH$_3$ by SOA vary greatly between scenarios depending on the magnitude of the uptake coefficient. Table 4.1 and Fig. 4.7 show the impact of the NH$_3$ + SOA reactions on the domain-averaged hourly NH$_3$ and PM$_{2.5}$ concentrations. When using $\gamma = 10^{-2}$, domain wide average NH$_3$ concentrations decrease by 15–40%, with the greatest percentage decreases (30–40%) occurring between 08:00 h and 17:00 h local time. Because domain wide averages are computed by averaging all cells in the model domain, this indicates that more than one third of all gas-phase NH$_3$ in the basin is removed in this scenario during these times. However, the decrease in NH$_3$ concentrations is highly spatially dependent. In certain areas, such as those with a high concentration of SOA and relatively low (<40 ppb) gas-phase NH$_3$ concentrations in the reference case, hourly NH$_3$ concentrations decrease by over 60%. On the other hand, areas near the coast experience little change in NH$_3$ concentration due to low levels of both gaseous NH$_3$ and SOA in the reference case (see Fig. 4.8 for map of SOA concentrations in the reference case).
Figure 4.7. Domain wide average concentrations of ammonia (NH$_3$, top panel) and PM$_{2.5}$ (bottom panel) in the (a) base case, (b) $\gamma = 10^{-2}$ scenario, (c) $\gamma = 10^{-3}$ scenario, and (d) $\gamma = 10^{-4}$ scenario. Ammonia and PM$_{2.5}$ concentrations change by less than 1% at all hours of the day in the $\gamma = 10^{-5}$ scenario (not shown).

Figure 4.8. 24-hour average concentrations of SOA (μg/m$^3$) in the reference case.
Table 4.1. Domain-averaged (left columns) ammonia concentrations (NH$_3$, ppb) and (right columns) PM$_{2.5}$ mass concentrations (μg/m$^3$) in the reference case shown in (a). Absolute and percent change in concentration versus the reference case shown in (b), (c), and (d) when using (b) $\gamma=10^{-3}$, (c) $\gamma=10^{-4}$, and (d) $\gamma=10^{-5}$. Decreases relative to the reference case are indicated by negative values. Changes in concentration less than the number of significant digits shown are indicated by a double dash (--). Both NH$_3$ and PM$_{2.5}$ concentrations change by less than 1% when using (e) $\gamma=10^{-5}$ (not shown).

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Fig. 4.9 shows the spatially resolved 24-h average NH₃ concentrations in the reference case and the changes induced by the reactive uptake of NH₃. The greatest decreases occur near and downwind of areas with agricultural activity and large quantities of NH₃ emissions. 24-hour average NH₃ concentrations near Chino peak at 250 ppb in the reference case and are reduced by up to 15 ppb in the same area when using γ = 10⁻² (Fig. 4.9b, left column). Although the greatest decreases occur near the strongest emissions sources, NH₃ continues to be removed by SOA as it is transported further inland. As a result, hourly and 24-h average NH₃ concentrations decrease by 15–20 ppb and 5–10 ppb, respectively, for many areas in the northeast portion of the basin. Changes in the concentration of gas-phase NH₃ can affect the formation of inorganic PM due to its rapid reaction with different acids (e.g., nitric acid and
sulfuric acid) to form corresponding salts, which contribute to secondary particle formation and particle growth (Schiferl et al., 2014).

**Figure 4.9.** 24-hour average concentrations of NH$_3$ (ppb) and PM$_{2.5}$ (μg/m$^3$) in the reference case shown in (a). Difference in concentration versus the reference case shown in rows (b), (c), (d), and (e) when using (b) $\gamma = 10^{-2}$, (c) $\gamma = 10^{-3}$, (d) $\gamma = 10^{-4}$, and (e) $\gamma = 10^{-5}$. Concentration decreases relative to the reference case are indicated by negative values.

Table 4.1 shows domain-averaged concentrations of PM$_{2.5}$ in the reference case, as well as the absolute and percent change in concentration for scenarios (b), (c), and (d) versus the
reference case, (a). With the uptake coefficient of $10^{-2}$ used in this scenario, decreases in domain wide average concentrations range from 2% late at night to 11% during midday (Fig. 4.7). In some locations, the impact on hourly PM$_{2.5}$ concentrations is far greater, with decreases up to 35 μg/m$^3$ (60%) in areas northeast of Riverside. A combination of meteorological and geographical features in the SoCAB cause the buildup of pollutants in the downwind (northeastern) portion of the basin. A sea breeze during the daytime hours causes predominantly southwesterly winds while the northern edge of the domain is bounded by mountainous terrain in the Angeles and San Bernardino National Forests, preventing pollutants from being transported further inland. Thus, NH$_3$ continues to be taken up by SOA as it is transported inland, causing the largest impacts on PM to occur in the downwind areas of the basin where a variety of anthropogenic and biogenic precursors accumulate, rather than near NH$_3$ emissions sources.

Fig. 4.9 shows that the greatest impacts on 24-h average PM$_{2.5}$ concentrations occur in the northeastern area of the basin. Here, reference case levels range from 40 to 55 μg/m$^3$ (Fig. 4.9) and decrease by up to 15 μg/m$^3$ in this scenario (Fig. 4.9b, right column). Previous studies showed that concentrated NH$_3$ plumes from agricultural activity shift the NH$_4$NO$_3$ equilibrium towards the particle phase, leading to coincident formation of NO$_3^-$ and NH$_4^+$ particles and depletion of gas-phase HNO$_3$ in downwind areas of the basin (Hughes et al., 2002; Neuman et al., 2003; Nowak et al., 2012). Additionally, these studies suggested that NH$_4$NO$_3$ particle formation in the SoCAB could be best controlled by reducing the highly concentrated NH$_3$ emissions from agricultural activity, rather than emissions from automobiles, which are well distributed throughout the domain. Here we show that decreases in NH$_3$ concentration due to uptake by SOA reduce the availability of gas-phase
NH₃ to react with HNO₃ and H₂SO₄ to form NH₃ nitrate and ammonium sulfate particles, and that the largest impacts occur directly downwind of strong NH₃ emissions sources. Changes in the concentration of gas-phase HNO₃ and H₂SO₄, shown in Fig. 4.10, are consistent with this result. Because gas-phase HNO₃ and H₂SO₄ concentrations are inversely correlated with gas-phase NH₃ concentrations, HNO₃ and H₂SO₄ concentrations are generally higher in scenarios (b), (c), (d) and (e) than in the reference case. In particular, areas that show decreases in ammonium nitrate particle concentrations typically show increases in gas-phase nitric acid concentrations. This confirms that reductions in gas-phase NH₃ concentrations cause the equilibrium between NH₃(g) and NH₄NO₃(s) to shift toward the gas phase.
Figure 4.10. 24-hour average concentrations of nitric acid (HNO₃, ppb) and sulfuric acid (H₂SO₄, ppb) in the base case shown in (a). Difference in concentration versus the base case shown in rows (b), (c), (d) and (e) when using (b) $\gamma=10^{-2}$, (c) $\gamma=10^{-3}$, (d) $\gamma=10^{-4}$ and (e) $\gamma=10^{-5}$. Negative values represent decreases in concentration with respect to the base case.
Fig. 4.11 shows reference case levels and the change in 24-h nitrate (NO$_3^-$), ammonium (NH$_4^+$), and sulfate (SO$_4^{2-}$) particle concentrations for scenarios (b), (c), (d) and (e) versus the reference case, (a). These figures show that although the spatial distribution of these species differs in the reference case (because of the different patterns of SO$_2$ and NO$_x$ emissions), the largest changes in 24-h average concentrations for all three particulate species generally occur in the same geographical area northeast of Riverside. Together, decreases in nitrate, ammonium, and sulfate particle concentrations account for essentially all of the decrease in total PM$_{2.5}$ concentrations shown in Fig. 4.9. The spatial distribution and magnitude of model-predicted nitrate particle concentrations in the reference case (Fig. 4.11a, left column) agree with those measured by Neuman et al. (2003), who reported a peak concentration of 12.7 μg/m$^3$ near Rubidoux.
Figure 4.11. 24-h average concentrations of particulate nitrate (NO$_3^-$, μg/m$^3$), ammonium (NH$_4^+$, μg/m$^3$) and sulfate (SO$_4^{2-}$, μg/m$^3$) in the base case shown in (a). Difference in concentration versus the base case shown in rows (b), (c), (d) and (e) when using (b) $\gamma = 10^{-2}$, (c) $\gamma = 10^{-3}$, (d) $\gamma = 10^{-4}$ and (e) $\gamma = 10^{-5}$. Concentration decreases relative to the reference case are indicated by negative values.

In scenario (c), when the uptake coefficient is set to $10^{-3}$, the magnitude of the impact on NH$_3$ and PM$_{2.5}$ concentrations is lower than in scenario (b), although the spatial distribution of changes remains similar. In this case, hourly domain wide average NH$_3$ concentrations decrease by 3–14% (Table 4.1), with some locations experiencing decreases of over 25%
compared to reference case levels. Fig. 4.9c (left column) shows that the largest impacts on
gas-phase NH₃ occur in the same areas as in scenario (b), with decreases in 24-h average
concentrations of about 7 ppb near Chino where the strongest NH₃ emissions sources in the
basin are located. Although 24-h average NH₃ concentrations decrease by only 2–4 ppb in
areas downwind of Riverside, the spatial distribution of changes in total PM₂.₅ (Fig. 4.9, right
column), as well as in nitrate, ammonium, and sulfate particle concentrations (Fig. 4.11) is
similar in scenarios (b) and (c). In both scenarios, the largest reductions in 24-h average
particle concentrations occur northeast of Riverside. Comparing parts (b) and (c) of Fig. 4.9,
Fig. 4.11 illustrates this result. Although the impact is lower than in scenario (b) due to the
uptake coefficient being reduced by an order of magnitude, significant reductions in PM₂.₅
concentrations still occur in this scenario. Decreases in 24-h average concentrations of 2–
4 μg/m³ cover large areas in the northeast portion of the basin, with peak decreases reaching
10 μg/m³. Given that the national standard for 24-h average PM₂.₅ concentrations is
35 μg/m³, decreases of this magnitude have important implications for reaching attainment
of national ambient air quality stands for fine particulate matter. Reducing 24-h average gas-
phase NH₃ concentrations by only a few ppb significantly reduces the formation of
ammonium nitrate and ammonium sulfate particles. Similar to scenario (b), the impact on
hourly PM₂.₅ concentrations is even greater, with decreases exceeding 20 μg/m³ (33%) in
downwind areas of the basin during the afternoon hours. Coastal areas and locations upwind
of NH₃ emissions sources again experience little to no change in NH₃ or PM₂.₅ concentrations.
In scenario (d) with γ = 10⁻⁴, domain wide average NH₃ concentrations decrease by only a
few percent at all hours of the day (Table 4.1). Although isolated locations in the basin
experience larger decreases, the overall impact on NH₃ concentrations is small when an
uptake coefficient of $10^{-4}$ is used. Decreases in 24-h average NH$_3$ concentrations peak at 2 ppb and show a similar spatial distribution to those seen in scenario (c) (Fig. 4.9, left column). Areas downwind of strong emissions sources show decreases of 0.5–1 ppb, causing 24-h average PM$_{2.5}$ concentrations to decrease by 1–5 μg/m$^3$. This indicates that the formation of ammonium nitrate and ammonium sulfate particles in the SoCAB is highly sensitive to changes in gas-phase NH$_3$ concentrations, consistent with Schiferl et al. (2014). The largest decreases in PM$_{2.5}$ concentrations again occur in the far northeast portion of the basin where pollutants accumulate. Peak decreases in hourly PM$_{2.5}$ concentrations reach 12 μg/m$^3$ (20%) in some locations, although decreases of this magnitude are localized to highly impacted areas and only occur at certain times of the day. Overall, the impact on 24-h average NH$_3$ and PM$_{2.5}$ concentrations is around a factor of 2–3 lower in this scenario than scenario (c).

In the final scenario (e), an uptake coefficient of $10^{-5}$ is utilized. Although this uptake coefficient is three orders of magnitude lower than that used in scenario (b), peak decreases in PM$_{2.5}$ concentrations are only a factor of three lower. However, decreases of this magnitude are isolated to only a small area in the northeast corner of the basin. There are only small changes in NH$_3$ concentrations in this scenario. Hourly domain wide average NH$_3$ concentrations change by less than 1%, and most individual locations show decreases of only a few percent. Changes in 24-h average NH$_3$ concentrations are less than 0.5 ppb, as shown in Fig. 4.9e (left column). In contrast to scenarios (b) and (c), the increases and decreases in NH$_3$ concentrations are similar in magnitude in this scenario. Additionally, changes in NH$_3$ concentrations in this scenario are less localized and occur throughout the inland portion of the basin. Reducing the magnitude of the uptake coefficient increases the lifetime of NH$_3$. 

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causing the spatial distribution of impacts to be more dependent on the meteorological conditions in the basin during the first two days and into day three. Fig. 4.9 (right column) shows that the spatial distribution of changes in PM$_{2.5}$ concentrations is also different in this scenario than in scenarios (b) and (c). Here, changes in 24-h average PM$_{2.5}$ levels of ±1 μg/m$^3$ occur at various locations, with decreases of 1–2 μg/m$^3$ occurring in downwind areas of the basin. However, domain wide average PM$_{2.5}$ concentrations decrease by less than 1% at all hours of the day, indicating that the overall impact on fine particle concentrations is small. As in the previous scenarios, changes in the concentration of ammonium and nitrate particles cause nearly all of the change in total PM$_{2.5}$ concentrations. Overall, the impact on both gas-phase and particulate species is of variable sign when the lowest uptake coefficient of 10$^{-5}$ is utilized.

4.6 Model Predictions for the Continental US

Results from the CMAQ model validation comparing simulated mixing ratios for various atmospheric species (i.e., O$_3$, NH$_3$, NH$_4^+$, NO$_3^-$, and PM$_{2.5}$) against observations obtained by the Ammonia Monitoring Network (AMoN), the US Environmental Protection Agency’s (EPA’s) Air Quality System (AQS), and US EPA’s Chemical Speciation Network (CSN) showed an overall good model performance for most of the criteria. Details of the model validation can be found in Zhu et al., 2018.

4.6.1 Impact on gas-phase NH$_3$ and HNO$_3$ concentrations

Figure 4.12 shows the time series of daily domain-averaged (averaged over 24 h and the simulation domain) NH$_3$ for both the winter and summer, for different uptake coefficient values.
Figure 4.12. Daily, spatially-averaged NH$_3$ concentrations for different uptake coefficient scenarios for the (a) winter period and (b) summer period.

In general, the NH$_3$ concentration is reduced after the introduction of the NH$_3$ uptake process, and the magnitude of the reduction is increased as the uptake coefficient increases. For the winter, the spatiotemporally averaged (averaged over entire period and the simulation domain) NH$_3$ concentration for the base case is 0.44 ppb, while the value decreases to 0.43 ppb (−2.3%) for the $\gamma = 10^{-5}$ case, 0.41 ppb (−6.8%) for the $\gamma = 10^{-4}$ case, and 0.31 ppb (−29.5%) for the $\gamma = 10^{-3}$ case. These results indicate that an uptake of $10^{-5}$ is not significant.

For the summer, the spatiotemporally averaged NH$_3$ concentration for the base case is 2.30 ppb, while the value decreases to 2.10 ppb (−8.7%) for the $\gamma = 10^{-5}$ case, 1.58 ppb (−31.3%) for the $\gamma = 10^{-4}$ case, and 0.76 ppb (−67.0%) for the $\gamma = 10^{-3}$ case. The impact of the uptake process is higher for the summer due to larger SOA concentrations during the summer (spatiotemporally averaged 9.25 µg m$^{-3}$ for the base case) than the winter (spatiotemporally averaged 2.72 µg m$^{-3}$ for the base case).
The spatial distribution of the impact over the simulated domain is also investigated. Figure 4.13a and c show the time-averaged spatial distribution of NH$_3$ for the winter and summer base cases, while the differences between the $\gamma = 10^{-3}$ case and the base case are shown in Fig. 4.13b and d. For both periods, the Central Valley of California is a hotspot for NH$_3$ emissions, and the region exhibits the most significant impact due to the introduction of the new NH$_3$ uptake mechanism. This is due to the intensive agricultural activities in this region including the heavy application of fertilizers (Krauter et al., 2002) and the year-round farming pattern supported by California’s relatively warm climate. The hog farm industry is largely responsible for the high NH$_3$ concentration in North Carolina and north Iowa in the summer, where significant NH$_3$ loss can also be spotted in the $\gamma = 10^{-3}$ case. Agriculture and wildfires also produce some hotspots of ammonia concentration in other areas, such as southern Florida in the winter and several locations in northern California and Washington states, where NH$_3$ concentrations also decreased significantly in the $\gamma = 10^{-3}$ case. The spatial distribution of differences between the base case and the $\gamma = 10^{-4}$ and $\gamma = 10^{-5}$ cases is similar to the $\gamma = 10^{-3}$ only with different scales.
Figure 4.13. Spatial distribution of time-averaged NH$_3$ concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged NH$_3$ concentrations between the $\gamma = 10^{-3}$ and the base case for (b) winter and (d) summer. Negative values represent decreases in concentration with respect to the base case.

As the condensation of HNO$_3$ into the particle phase is directly associated with NH$_3$ concentration, it is reasonable to infer that the introduction of the NH$_3$ uptake mechanism could also impact the concentration of HNO$_3$. In contrast to NH$_3$, the integration of the NH$_3$ uptake mechanism leads to an increase in HNO$_3$ concentration, and the scale of magnitude of the increase rises as the uptake coefficient is increased, although the extent of variation is smaller than that of NH$_3$. For the winter, the difference between the base case and the $\gamma = 10^{-5}$ case is very small (< 0.2 %) and remains insignificant for the $\gamma = 10^{-4}$ case (~ 1.2 %). Only the
The $\gamma=10^{-3}$ case shows a significant increase in HNO$_3$ as concentrations increase by 8.5% (the spatiotemporally averaged concentration is 0.27 ppb for the base case and 0.30 ppb for the $\gamma = 10^{-3}$ case). Similar to the NH$_3$ variation, the impact becomes larger for the summer, where the spatiotemporally averaged HNO$_3$ concentration for the base case is 0.51 ppb, while the value increases by 2.0% (0.52 ppb) for the $\gamma = 10^{-5}$ case, 7.8% (0.55 ppb) for the $\gamma = 10^{-4}$ case, and 19.6% (0.61 ppb) for the $\gamma = 10^{-3}$ case. These increase in HNO$_3$ concentrations is due to the reduction in NH$_3$ caused by the conversion of NH$_3$ into NOCs, making less NH$_3$ available for reaction with HNO$_3$ to form the particle-phase NH$_4$NO$_3$.

The time-averaged spatial distributions of HNO$_3$ for both the winter and summer base cases are presented in Fig. 4.14a and c. The northeast region exhibits relatively high HNO$_3$ concentration for both periods, largely due to the high NO$_x$ (NO + NO$_2$) emissions from transportation activities. The addition of the NH$_3$ uptake process does not cause an obvious impact in this region for the winter, as the reduction of NH$_3$ is very small (Fig. 4.13b) due to low SOA and NH$_3$ concentrations in the base case. In contrast, the increase in HNO$_3$ becomes much more significant for this region in the summer, as the loss of NH$_3$ becomes greater due to larger NH$_3$ and SOA concentrations in the base case.
Figure 4.14. Spatial distribution of time-averaged HNO$_3$ concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged HNO$_3$ concentrations between the $\gamma = 10^{-3}$ case and the base case for (b) winter and (d) summer. Positive values represent increases in concentration with respect to the base case.

The winter hotspot around northeastern Utah (Uintah Basin) could be caused by the stagnant atmospheric conditions during the winter in the valley (Lee et al., 2014), which traps NO$_x$ emitted from local and remote sources located on the east side of the valley. The resulting NO$_x$ undergoes a nighttime reaction with O$_3$, forming N$_2$O$_5$ (high N$_2$O$_5$ concentration is spotted in the model at the same place). Additionally, the lack of NH$_3$ also favors the HNO$_3$ accumulation, as a result, the addition of NH$_3$ does not have much impact on this spot. The largest increase in HNO$_3$ concentrations in winter is found over the Central
Valley of California, which also corresponds to the largest NH₃ reduction (Fig. 4.13b). For the summer, the largest impact occurs over the hotspot of southern California, where strong traffic emissions of NOₓ and active photochemistry provide a strong HNO₃ source. The significant reduction of NH₃ concentration from the south Central Valley could reduce the potential sink of HNO₃ into the particle phase and leave more HNO₃ in the gas phase. The spatial distribution of differences between the base case and the $\gamma = 10^{-4}$ and $\gamma = 10^{-5}$ cases is similar to the $\gamma = 10^{-3}$ only with smaller scales. The increase in time-averaged HNO₃ between the base case and the $\gamma = 10^{-4}$ case was on the scale of 0.03 ppb and 0.20 ppb in the winter and summer, respectively. The increase in time-averaged HNO₃ between the base case and the $\gamma = 10^{-5}$ case was on the scale of 0.007 ppb and 0.05 ppb in the winter and summer, respectively.

4.6.2 Impact on Inorganic PM

One of the effects of the gas-phase NH₃ reduction due to the inclusion of the NH₃ uptake was the decrease in the particle phase NH₄⁺ concentration, as all NH₄⁺ originates from gas-phase NH₃. In general, the addition of NH₃ uptake in the model causes a decrease in particle-phase NH₄⁺ concentration, and the impact is more significant for the summer than the winter. For the summer case, the average decrease in NH₄⁺ is 1.8 % for $\gamma = 10^{-5}$, 10.7 % for $\gamma = 10^{-4}$, and 28.2 % for $\gamma = 10^{-3}$; for the winter case, the average decrease is 0.2 % for $\gamma = 10^{-5}$, 2.3 % for $\gamma = 10^{-4}$, and 13.2 % for $\gamma = 10^{-3}$. Such behavior corresponds well to the level of NH₃ reduction in Fig. 4.12 caused by the higher SOA concentrations during the summer.

The time-averaged spatial distributions of the NH₄⁺ concentration for both the winter and summer base case are shown on Fig. 4.15a and c. Most of the NH₄⁺ is concentrated over the
eastern part of the US, as a result of high NH$_3$ concentrations (see Fig. 4.13) in this region combined with the abundance of NH$_3$ neutralizers (e.g., HNO$_3$ and H$_2$SO$_4$). Another hotspot is the Central Valley of California and the South Coast Air Basin of California (Nowak et al., 2012), resulting from high NH$_3$ emissions from the intensive agriculture (Fig. 4.13).

![Figure 4.15](image)

**Figure 4.15.** Spatial distribution of time-averaged NH$_4^+$ concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged NH$_4^+$ concentrations between the $\gamma = 10^{-3}$ case and the base case for (b) winter and (d) summer. Negative values represent decreases in concentration with respect to the base case.

In the presence of both HNO$_3$ and H$_2$SO$_4$, NH$_3$ is first neutralized by H$_2$SO$_4$ to form either (NH$_4$)$_2$SO$_4$ or NH$_4$HSO$_4$ in the particle phase, while the rest of the NH$_3$ reacts with HNO$_3$ and
forms particle-phase NH$_4$NO$_3$. The percentage of NH$_4^+$ associated with NO$_3^-$, SO$_4^{2-}$, and HSO$_4^-$ could be investigated by comparing the spatial distribution of the NO$_3^-$ concentration for the corresponding period in Fig. 4.16a and c and the SO$_4^{2-}$ in Fig. 4.17a and b. In the West Coast and Central Valley of California, the enriched NH$_4^+$ mostly exists in the form of NH$_4$NO$_3$, as the sulfate concentration is low in this region for both periods (Fig. 4.17). Figure 4.15b and d presents the spatial distribution of the difference in NH$_4^+$ concentration between the $\gamma=10^{-3}$ case and the base case, which is highly correlated with the NH$_3$ variation map (Fig. 4.13). The reduction in NH$_3$ due to the SOA uptake directly impacts the available NH$_3$ that could be condensed into the particle phase and reduces the NH$_4^+$ concentration consequently. The spatial distribution of differences between the base case and the $\gamma=10^{-4}$ and $\gamma=10^{-5}$ cases is similar to the $\gamma=10^{-3}$ only with different scales. In mid-east region during the winter, the H$_2$SO$_4$ concentration is insufficient to neutralize all the NH$_3$, so more NO$_3^-$ is involved in the NH$_3$ neutralization, and there are more nitrate particles than sulfate particles. For the summer, as the sulfate concentration nearly doubles over the mid-east US compared to the winter, most of the NH$_3$ is neutralized by H$_2$SO$_4$. This causes an absence of NO$_3^-$ above this region and only appears on the surrounding region where sulfate concentration is low.
Figure 4.16. Spatial distribution of time-averaged NO$_3^-$ concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged NO$_3^-$ concentrations between the $\gamma = 10^{-3}$ case and the base case for (b) winter and (d) summer. Negative values represent decreases in concentration with respect to the base case.

Figure 4.17. Spatial distribution of time-averaged SO$_4^{2-}$ concentrations in the base case for (a) winter and (b) summer. The difference due to NH$_3$ conversion into NOCs is not shown because it is very small.
The concentration of NO$_3^-$ changes as a result of adding the NH$_3$ conversion into NOCs, namely, adding the NH$_3$ uptake mechanism leads to a decrease in NO$_3^-$ concentrations for both periods. The spatial distributions of the NO$_3^-$ variation due to the addition of the NH$_3$ uptake mechanism ($\gamma = 10^{-3}$) are presented in Fig. 4.16b and d for the winter and summer. By comparing with the base cases (see Fig. 4.16a and c), it is clear that most of the NO$_3^-$ reduction occurs over regions with high NO$_3^-$ concentration, such as the Central Valley of California, the South Coast Air Basin of California, and vast regions over the mid-east US. One exception is the high NO$_3^-$ region over Canada on the north edge of Montana and North Dakota during the winter. Neither NH$_4^+$ concentration nor NO$_3^-$ concentration changes much, mostly because the SOA concentration is extremely low for that region (see Fig. 4.18a), so almost no NH$_3$ is lost due to the SOA uptake. The same occurs in south Florida during the summer.

Overall, similar to NH$_4^+$, the impact on NO$_3^-$ is more significant for the summer than the winter. The average reductions for the winter are 0.2 % for $\gamma = 10^{-5}$, 1.9 % for $\gamma = 10^{-4}$, and 10.9 % for $\gamma = 10^{-3}$. For the summer, the average reductions are 1.9 % for $\gamma = 10^{-5}$, 10.6 % for $\gamma = 10^{-4}$, and 24.3 % for $\gamma = 10^{-3}$. Moreover, the magnitude of the difference is also close to the difference in NH$_4^+$, indicating that almost all the NH$_4^+$ reduction is from NH$_4$NO$_3$.

4.6.3 Impact on Organic PM

Figure 4.18a and c show the time-averaged spatial distribution of SOA for the winter and summer base cases, respectively. For both seasons, high SOA concentrations are found over the southeastern US due to high vegetation coverage in this region, while hotspots in the
northwestern region are caused by widespread fire events. The averaged SOA concentration in the base case is more than 3 times higher in the summer (9.25 µg m\(^{-3}\)) than in the winter (2.72 µg m\(^{-3}\)), largely due to the higher biogenic SOA (BIOSOA) concentrations (4.43 µg m\(^{-3}\) summer vs. 0.22 µg m\(^{-3}\) winter) resulting from elevated biogenic emissions in the warm season.

Figure 4.18. Spatial distribution of time-averaged SOA concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged SOA concentrations between the \(\gamma = 10^{-3}\) case and the base case for (b) winter and (d) summer. Positive values represent increases in concentration with respect to the base case, and negative values represent decreases in concentration with respect to the base case.

As mentioned in the modeling methods (Sect. 4.3.2), the NH\(_3\) uptake parametrization added to the CMAQ model does not directly add mass to SOA because the original SOA carbonyl and
the NOCs they convert into have similar molecular weights. However, significant changes in SOA mass concentration are observed after implementing the NH₃ uptake mechanism and is indirectly caused by the changes in particle acidity. As demonstrated in Fig. 4.18b and d, implementing the NH₃ uptake mechanism has a stronger impact on SOA concentrations during the summer than in the winter. Almost the entire increase in SOA concentrations in the summer is due to the mass change in biogenic SOA (see Figs. 4.19a and 4.18d). Further investigation reveals that the majority of the increase (∼80 %) is caused by the nonvolatile AIS03 species (Fig. 4.19b), which is the isoprene epoxydiols (IEPOX)-derived SOA through the acid-catalyzed ring-opening reactions (Pye et al., 2013). This increase in AIS03 is caused by the increase in aerosol aqueous-phase acidity due to the reduction in NH₄⁺ after adding the NH₃ conversion into NOCs. This increase in particle acidity corresponds well with the sensitivity study between NH₃, SO₄²⁻, and particle pH presented in Fig. 2 of Weber et al. (2016), where particle pH is found to be more sensitive to NH₃ concentrations than to SO₄²⁻ concentrations. Figure 4.19c shows a large drop in pH value (∼0.9–2.3) in the southeast region where the increase in the AIS03 is most significant and there is a simultaneous decrease in IEPOX concentrations (Fig. 4.19d). The largest pH variation appears over the northwest region. However, there is no observable impact on SOA concentrations due to the extremely low concentration of both isoprene and IEPOX (see Fig. 4.19e and f) in this area. Moreover, the reduction in NH₄⁺ concentrations also increases the ratio of SO₄²⁻/HSO₄⁻, where SO₄²⁻ can act as a nucleophile and promote the IEPOX uptake process. This also contributes to the increase in AIS03.
Figure 4.19. Spatial distribution of the difference in time-averaged (a) biogenic SOA concentrations, (b) isoprene epoxydiols (IEPOX)-derived SOA concentrations, (c) particle acidity (pH), and (d) isoprene epoxydiols concentrations between the $\gamma = 10^{-3}$ case and the base case during the summer. Spatial distribution of time-averaged (e) isoprene, and (f) isoprene epoxydiols concentration in the base case during the summer.
Figure 4.20 shows the time evolution of daily–spatially averaged H\(^+\), IEPOX, and AIS03 for both the winter and summer. Although the average H\(^+\) concentration in the base case is similar between two periods, the variation between the NH\(_3\) uptake scenarios and the base case is much smaller for the winter largely due to the lower SO\(_4^{2-}\) concentrations in the winter which restrain the acidity variation level. Additionally, lower SOA concentrations in winter also reduce the magnitude of NH\(_4^+\) variation. As a result, addition of the NH\(_3\) uptake mechanism does not have a large impact on the AIS03 concentration for most of the simulation (except for the last several days). On the contrary, the summer shows a significant increase in H\(^+\) concentrations as the NH\(_3\) uptake coefficient increases, while the concentration of IEPOX decreases. And the increase in AIS03 concentration is remarkable, with more than 10 times the growth on average between the \(\gamma = 10^{-3}\) case (1875 ng m\(^{-3}\)) and the base case (182 ng m\(^{-3}\)). The amount of growth on AIS03 seems linear with different values of the NH\(_3\) uptake coefficient (\(\gamma = 10^{-5}\): 16%; \(\gamma = 10^{-4}\): 172%; \(\gamma = 10^{-3}\): 932%).

In addition to the isoprene epoxydiols pathway, other biogenic SOA species contribute the rest of the SOA changes (~ 20%), including other SOA species derived from isoprene (AISO1 and AIS02), from monoterpenes (ATRP1 and ATRP2), from sesquiterpenes (ASQT), and AOLGB, which represents the aged nonvolatile SOA origin from AISO1, AIS02, ATRP1, ATRP2, and ASQT. The common point with those SOAs (AISO1, AIS02, ATRP1, ATRP2, and ASQT) is that they all have a pathway to be formed through the oxidation between gas-phase NO\(_3\) radicals and their gas precursors. One possible explanation could be that the addition of NH\(_3\) uptake leads to an increase in gas-phase HNO\(_3\), which could shift the reaction balances between NO\(_3\) and HNO\(_3\) and leave more NO\(_3\) available for SOA oxidation.
4.6.4 Impact on Total PM

Figure 4.21 presents the time evolution of daily-averaged concentrations of PM$_{2.5}$ and PM$_{10}$ in different scenarios during both periods. First, both the pattern and level of impact caused by the NH$_3$ uptake mechanism is similar for PM$_{2.5}$ and PM$_{10}$, which indicates that most of the mass change due to this process occurs on fine particles. Secondly, the level of impact on both PM$_{2.5}$ and PM$_{10}$ is much more significant over the summer than the winter, which is consistent with previous analysis of individual species. Third, opposite impact patterns are found between the winter and summer. The inclusion of the NH$_3$ uptake mechanism leads to a decrease in the total PM mass for the winter, which is caused by the reduction of inorganic NH$_4^+$ and NO$_3^-$ due to the decrease in the NH$_3$ concentration. On the contrary, PM
concentrations during the summer increase after adding the NH$_3$ uptake mechanism. Although the concentration of inorganic species still decreases during the summer, the increase in biogenic SOA concentration, as detailed in Sect. 4.6.3, outpaces the decrease caused by inorganic species and leads to an overall increase in total PM mass for the summer. For the winter, the average PM$_{2.5}$ concentration reduction is 0.07 % for the $\gamma = 10^{-5}$ case, 0.59 % for the $\gamma = 10^{-4}$ case, and 3.39 % for the $\gamma = 10^{-3}$ case. For the summer, the average PM$_{2.5}$ concentration increase is 0.14 % for the $\gamma = 10^{-5}$ case, 2.05 % for the $\gamma = 10^{-4}$ case, and 12.38 % for the $\gamma = 10^{-3}$ case.

![Graphs showing PM$_{2.5}$ concentrations](image)

**Figure 4.21.** Daily, spatially-averaged concentrations of different scenarios for (a) PM2.5 in the winter (b) PM10 in the winter (c) PM2.5 in the summer, and (d) PM10 in the summer

The spatial distribution of time-averaged PM$_{2.5}$ concentration for the winter and summer is presented in Fig. 4.22a and c, respectively. Most of the high PM$_{2.5}$ concentration happens over the mid-east US during the winter, with additional hotspots over the Central Valley of California, resulting in an overall average of 7.5 $\mu$g m$^{-3}$. PM$_{2.5}$ concentrations are highly correlated with the population density map of the US, indicating a dominant anthropogenic origin. The relatively low fraction of biogenic SOA in winter also supports this point (Fig.
4.23a). The model predicts a much higher PM$_{2.5}$ concentration for the summer, with an average concentration of 16 µg m$^{-3}$. The hotspots observed over the northwest of the country and coastal area over southeast Texas are due to wildfire events. In general, high PM$_{2.5}$ concentrations are predicted over the southeast of the US, where high fractions of biogenic SOA are present (Fig. 4.23b). This could be a result of both high average temperatures during the summer and high vegetation density in that region. Figure 4.22b shows the variation in PM$_{2.5}$ concentrations between the $\gamma = 10^{-3}$ case and the base case for the winter. An overall reduction can be observed from the map, with the highest reduction around the Central Valley of California and a smaller reduction over the vast mid-east region. This is mostly caused by the decrease in NH$_4$NO$_3$ due to the reduction of gas-phase NH$_3$ concentrations as discussed earlier. During the summer, although the decrease still appears over the northwest of the country, the prominent feature becomes a significant increase in PM$_{2.5}$ concentrations over the southeast region. This is due to the increase in biogenic SOA resulting from the enhanced acid-catalyzed uptake reactions.
Figure 4.22. Spatial distribution of time-averaged PM$_{2.5}$ concentrations in the base case for (a) winter and (c) summer. Spatial distribution of the difference in time-averaged PM$_{2.5}$ concentrations between the $\gamma = 10^{-3}$ case and the base case for (b) winter and (d) summer. Positive values represent increases in concentration with respect to the base case, and negative values represent decreases in concentration with respect to the base case.

Figure 4.23. Spatial distribution of time-averaged biogenic SOA fraction of total PM$_{2.5}$ for (a) the winter and (b) summer.
4.7 Conclusions

This study presents the initial findings of including this previously unaccounted for process in air quality models. Our results indicate the chemical uptake of NH$_3$ by SOA can reduce the concentration of gas-phase NH$_3$, thereby reducing the potential to form ammonium nitrate and ammonium sulfate in the particle phase. The main chemical mechanism for this is the conversion of NH$_3$ in SOA particles to less basic nitrogen-containing organic compounds that are less efficient in neutralizing inorganic acids than NH$_3$ is. We show that the inclusion of this previously unaccounted for sink for gas-phase NH$_3$ into an urban airshed model for the SoCAB region reduces 24-h average PM$_{2.5}$ concentrations by up to 15 μg/m$^3$ in highly impacted areas. However, this result should be seen as an upper limit as it reflects the use of the largest plausible uptake coefficient ($10^{-2}$) without any consideration of possible reaction saturation effects. It is more likely that the changes in PM$_{2.5}$ concentrations caused by the uptake of NH$_3$ by SOA are in the 1–5 μg/m$^3$ range, as projected in scenarios $\gamma = 10^{-4}$ (d) and $\gamma = 10^{-5}$ (e). Results also indicate that the formation of inorganic PM$_{2.5}$ is highly sensitive to changes in the concentration of gas-phase NH$_3$, as reductions in 24-h average NH$_3$ concentrations of 0.5–2 ppb cause 24-h average PM$_{2.5}$ concentrations to decrease by 1–5 μg/m$^3$ in downwind areas (see Fig. 4.9d). Previous studies have shown that ammonium nitrate particles form when concentrated NH$_3$ plumes are mixed into areas of active urban photochemistry, such as the northeast portion of the SoCAB (Nowak et al., 2012; Schiferl et al., 2014). Both primary and secondary pollutants accumulate in the northeast portion of the basin, which is photochemically active and where high temperatures are observed during the summer months. Thus, while the largest decreases in gas-phase NH$_3$ concentrations occur near the strongest emissions sources, the largest decreases in PM$_{2.5}$ concentrations
occur in downwind areas, particularly northeast of Riverside. Together, changes in the concentration of nitrate, ammonium, and sulfate particles account for essentially all of the decrease in total PM$_{2.5}$ concentrations.

Simulations over the continental US were performed for the winter and summer seasons of 2011 with a range of NH$_3$ uptake coefficients ($\gamma = 10^{-3} - 10^{-5}$). The inclusion of the SOA-based NH$_3$ conversion into NOCs had a significant impact on the concentrations of NH$_3$, NH$_4^+$, and NO$_3^-$, but did not affect O$_3$ and SO$_4^{2-}$. The overestimation of NH$_3$ and NH$_4^+$ for the summer was reduced by this new mechanism. Moreover, the prediction of NO$_3^-$ was improved by this mechanism, given that the overestimation of NO$_3^-$ concentration gradually subsides as the uptake coefficient increases.

The comparison between different uptake coefficient scenarios and the base case allowed a more detailed understanding of the impact of this mechanism on both gas-phase and particle-phase species. Simulations indicated a significant reduction in gas-phase NH$_3$ due to conversion of NH$_3$ into NOCs. The highest spatially averaged reduction in gas-phase NH$_3$ is 31.3\% in the winter and 67.0\% in the summer when the largest uptake is used ($\gamma = 10^{-3}$). The actual value for each individual SOA may be lower or higher than the uniform uptake coefficient used in this study, regardless the magnitude of the impact indicates the importance of including this process in air quality models. The seasonal differences are obvious as the impact is much more significant in the summer than in the winter, due to the higher NH$_3$ and SOA concentrations in the summer. The concentration of gas-phase HNO$_3$ was also impacted by this new mechanism. As the NH$_3$ concentration drops because it is being converted into NOCs, less HNO$_3$ is neutralized by NH$_3$, resulting in an overall increase in HNO$_3$ concentration. Geographically, the biggest reduction in NH$_3$ happens in the Central
Valley of California during both seasons, the same location as the biggest increase in HNO$_3$ in the winter. While for the summer, HNO$_3$ increases more dramatically over the South Coast Air Basin of California and the northeast region of the country.

PM concentrations were found to decrease during the winter period, largely due to the reduction in ammonium nitrate formation caused by the decrease in gas-phase ammonia. The largest uptake scenario ($\gamma = 10^{-3}$) led to a 13.2 % reduction of NH$_4^+$, 10.6 % reduction of NO$_3^-$, and 3.4 % reduction of PM$_{2.5}$ in the winter, and the largest reduction in PM$_{2.5}$ occurred over the Central Valley region of California. In contrast, PM concentrations increased during the summer due to an increase in biogenic SOA production resulting primarily from the enhanced acid-catalyzed uptake of IEPOX. Although the reduction in ammonium nitrate was even larger in magnitude during the summer than in the winter, the dramatic increase in biogenic SOA outpaced the decrease caused by ammonium nitrate to result in an overall increase in total PM$_{2.5}$. The largest increase of biogenic SOA occurred over the southeast region of the US, where high vegetation density is located.

Results from the SoCAB and continental US simulations revealed that the chemical uptake of NH$_3$ by SOA can have a significant impact on the model-predicted concentrations of important atmospheric pollutants, including NH$_3$, HNO$_3$, NH$_4^+$, NO$_3^-$, SOA, and PM. Furthermore, while the inclusion of ammonia uptake led to a decrease in inorganic PM concentrations, the effect on total PM concentrations (increase/decrease) was dependent on seasonality. Because inorganic particles (comprised of ammonium, sulfate and nitrate) represent a large portion of total fine particulate matter mass in the SoCAB (Kim et al., 2010; Schiferl et al., 2014), continental US, and many other locations around the world, accurate modeling of gas-phase NH$_3$ concentrations is essential for predicting future air quality.
Although we focus on the SoCAB and US, results shown here have important global implications as NH$_3$ emissions have shown increasing trends over the last few decades and are expected to increase even more in the future (Amann et al., 2013; Warner et al., 2017). It is especially important to account for the uptake of NH$_3$ by SOA in models used to simulate air quality in agricultural areas with strong NH$_3$ emissions sources. Additionally, models used in the development of air quality management strategies should account for changes in the concentration of NH$_3$ due to its uptake by SOA to ensure accurate prediction of PM$_{2.5}$ concentrations. Because significant uncertainty remains regarding the mechanism, rate and extent of reactions between gaseous NH$_3$ and organic compounds found in SOA, additional studies are needed to better constrain and quantify uptake coefficients for a variety of SOA compounds. Furthermore, better knowledge about basicity of NOCs is needed to verify whether they can neutralize inorganic acids. For example, single particle measurements conducted by Neuman et al. (2003) showed that organic aerosols also contributed to increases in fine-particle mass in regions with high NH$_3$ emissions rates, suggesting that NH$_3$ uptake can increase organic aerosol mass concentrations directly. Current air quality models only include one pathway for the acid-catalyzed SOA generation (based on the high NO$_x$ case in the study of Pye et al., 2013), and a more detailed representation of other acid-catalyzed pathways could lead to an even larger impact on the SOA concentration.
5.1 Background

In addition to ammonia, amines provide a source of atmospheric reactive N and are therefore important to consider when investigating potential atmospheric sources of N in particulate matter. Anthropogenic sources of amines include animal husbandry, industrial operations, automobiles, cooking, composting, and sewage (Ge et al., 2011). Examples of natural sources of amines include the ocean, vegetation, biomass burning, and geologic sources, such as volcanic eruptions (Ge et al., 2011). The most common atmospheric amines contain one to six carbons (C\textsubscript{1}-C\textsubscript{6}), such as methylamine, dimethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, 1-propanamine, and 1-butanimine (Ge et al., 2011).

The mixing ratios of amines in the atmosphere vary widely by location; they can range from ppt to ppm levels near their sources and decrease rapidly with distance due to their high reactivity. Trimethylamine, often associated with the putrid smell of fish, has been detected near fish markets and fish processing plants with peak mixing ratios ranging from 0.59 ppb to 10 ppm (Namiesnik et al., 2003; Kamiya and Ose, 1984; Okita, 1970). When measured at these same locations, peak mixing ratios of methylamine and dimethylamine were of the same order of magnitude as trimethylamine. Near industrial sites, peak mixing ratios of methylamine, C\textsubscript{2} amines (dimethylamine, ethylamine), and C\textsubscript{3} amines (trimethylamine, N-methylethaneamine, propanamine) ranged from 0.03-120 ppb, 0.04-130 ppb, and 0.01-120
Aniline, an aromatic amine widely used as raw material in the polymer, rubber, agricultural, and dye industries, has been detected in industrial workplaces at even higher mixing ratios of up to 240 ppb (Patil and Lonkar, 1994). Near animal husbandry operations, peak mixing ratios of methylamine and trimethylamine ranged from 4.2-12.4 ppb and 1.6-69.7 ppb, respectively (Hutchinson et al., 1982; Kuwata et al., 1983; Fujii and Kitai, 1987; Kallinger and Niessner, 1999). Other locations where mixing ratios of small aliphatic amines have been measured in the tens of ppb or higher include food waste composting plants and landfills (Tsai et al., 2008; Rampfl et al., 2008).

When concentrations of ammonia and amines are measured simultaneously, emissions of individual amines are typically 2-3 orders of magnitude smaller than those of ammonia (Hutchinson et al., 1982; Schade and Crutzen, 1995; Chang et al., 2003; Tsai et al., 2008; Zheng et al., 2015). Moreover, Schade and Crutzen (1995) relied on animal husbandry emissions to estimate that the combined annual global emissions of methylamines were approximately 2 orders of magnitude smaller than NH$_3$ emissions (145 Gg N/yr from amines versus 23.3 Tg N/yr from NH$_3$). When emissions from marine and biomass were also considered, the estimated global NH$_3$ emissions remained about 2 orders of magnitude larger than those from methylamines (Ge et al., 2011; Yu and Luo, 2014). It is worth noting that while the concentrations of amines are expected to be two to three orders of magnitude smaller relative to ammonia in the gas phase, particulate concentrations can be much more similar in magnitude (Makela et al., 2001; Sorooshian et al., 2008).

Ammonia, as discussed in the previous chapter can contribute to PM mass and aging. In addition to ammonia, which remains an important atmospheric basic gas due to its
abundance, amine derivatives of ammonia may contribute to PM in similar ways. For instance, amines may also neutralize atmospheric acids and therefore lead to new particle formation (Murphy et al., 2007; Kumar et al., 2018).

\[
\begin{align*}
\text{NR}_3 \text{(g)} + \text{HNO}_3 \text{(g)} &\rightarrow \text{HNR}_3\text{NO}_3 \text{(s)} \\
\text{NR}_3 \text{(g)} + \text{H}_2\text{SO}_4 \text{(g)} &\rightarrow \text{HNR}_3\text{HSO}_4 \text{(s)} \\
2 \text{NR}_3 \text{(g)} + \text{H}_2\text{SO}_4 \text{(g)} &\rightarrow (\text{HNR}_3)_2\text{SO}_4 \text{(s)}
\end{align*}
\]

Theoretical studies indicate that amines are more effective than ammonia at stabilizing sulfuric acid–amine clusters (Kurten et al., 2008; Kupiainen et al., 2012; Paasonen et al., 2012) that lead to new particle formation. A theoretical study comparing the relative efficiencies of methylamines to stabilize sulfuric acid, found the stabilizing strength of ammonia and amines to increase in the following way: ammonia < monomethylamine < trimethylamine ≤ dimethylamine (Olenius et al., 2017). Evidence for particle formation from DMA–H$_2$SO$_4$–H$_2$O clusters was observed in the megacity of Shanghai, China (Yao et al., 2018).

Other pathways explored in laboratory experiments by which amines may contribute to aerosol mass include the gas phase oxidation of amines by O$_3$, OH, and NO$_3$ (Atkinson et al., 1987; Murphy et al., 2007; Tang et al., 2013; Tuazon et al., 1984; Tuazon et al., 1994), gas phase oxidation of a known SOA precursor in the presence of dimethylamine (Duporte et al., 2017), and reactions between amines and carbonyl species carried out in the gas, surface, and bulk phase (De Haan et al., 2011; Galloway et al, 2014; Duporte et al., 2016; Kampf et al., 2016; De Haan et al., 2017; De Haan et al., 2019). This latter pathway may contribute to aerosol aging, for instance by leading to the formation of light absorbing species when pre-existing aerosol is exposed to amines (De Haan et al., 2019), akin to the browning of lab-generated SOA when exposed to ammonia (Bones et al., 2010; Updyke et al., 2012).
The change in the optical properties of aerosol exposed to NH₃ or amines is one clear piece of evidence that reactions occur between species in the aerosol and ammonia or amines. In this study, we focused on the incorporation of organic N into aerosol particles for evidence of ammonia and dimethylamine reactions with SOA and also considered the effects of relative humidity on this process. Liu et al. (2018) explored the NH₃ uptake by toluene SOA and found that when the relative humidity was increased from 20-60%, the uptake of NH₃ also increased. The explanation offered for this trend was that due to the high viscosity of toluene SOA, the reactive uptake and diffusivity of NH₃ is kinetically inhibited at RH < 20% where toluene SOA can be classified as a glassy material. Then the transition from diffusion-limited to saturated uptake occurred across 20-60% RH, which suggested that toluene secondary organic material (SOM) is semi-solid across this RH range. Above 60% RH, reactive uptake of NH₃ no longer increased with RH and this was attributed to the toluene SOM behaving as a viscous liquid at this RH range. On the other hand, for less viscous SOA, increasing the RH may theoretically suppress reactive uptake of NH₃ due the fact that this reaction follows a condensation mechanism accompanied by a loss of water. Previous studies investigating the browning of SOA after NH₃ exposure have proposed reaction pathways for browning in which carbonyl groups in the SOA react with NH₃ and water is a byproduct (Bones et al., 2010, Updyke et al., 2012; Lin et al., 2015; Laskin et al., 2015). Therefore, increasing RH can favor the reverse reaction and suppress NH₃ uptake by SOA.

Studies exploring the effect of relative humidity on amine uptake by SOA are lacking, however if amine uptake is similar to that of ammonia, we would expect to see the same trends. Specifically, our working hypothesis for this study is that as RH increases, amine
uptake by highly viscous SOA will also increase, but amine uptake by less viscous SOA will be suppressed.

5.2 Experimental Methods

Smog chamber experiments were performed in order to explore the reactive uptake of ammonia and dimethylamine by SOA particles, as well as the dependence of this process on relative humidity.

A biogenic (d-limonene or α-cedrene) or an anthropogenic (toluene) VOC was oxidized in a 5 m³ Teflon chamber to generate SOA under low-NOₓ conditions. In these low-NOₓ experiments, no NO was added to the chamber; background concentrations of NO as measured by an NO/NOᵧ analyzer (Thermo Scientific, Model 42i) were typically below 1 ppb. Organic seed aerosol containing nitrogen was used to serve as an internal standard of nitrogen in the particles when analyzing particle composition data. The seed solution was made by dissolving nicotinic acid (99.5%, Sigma Aldrich) in deionized water (1 g/L). Relative humidity (RH) in the chamber was achieved by flowing purified air through a Nafion humidifier. The relative humidity (±2% RH) and temperature (±1°C) were monitored with a Vaisala HMT330 probe. The RH was varied between <2-50% to investigate the effect of relative humidity on the uptake of ammonia or dimethylamine by SOA. D-Limonene (97%, Sigma) or α-cedrene (98%, Sigma-Aldrich) was introduced to the chamber to reach a mixing ratio of 50 ppb and was subsequently oxidized via ozonolysis (500 ppb O₃) or photooxidation (1 ppm H₂O₂). Anthropogenic SOA consisted of injecting 1 ppm toluene (99.8%, Fisher Scientific) and 2 ppm of aqueous H₂O₂ (30% wt, Fisher Scientific). The mixing ratio used for toluene was higher than that of the biogenic VOCs due to the lower SOA mass yield of toluene
SOA than d-limonene and α-cedrene SOA, as well as the suppression of the SOA mass yield for toluene SOA at higher relative humidity under low-NOx conditions (see Chapter 2). In the photooxidation experiments, aqueous hydrogen peroxide was introduced into the chamber by evaporation into a flow of clean air, and then UV-B lamps were turned on to initiate the photooxidation. In all experiments, prior to oxidation, gases in the chamber were mixed with a fan for 10 minutes and a PTRMS was used to confirm that the VOC was well mixed before initiating oxidation. The fan was turned off after that to slow down particle wall loss. After the particle mass concentration of SOA reached a peak value, a gas mixture containing NH$_3$ (1000 ppm NH$_3$ in N$_2$, Airgas), aqueous NH$_3$ (NH$_4$OH, 28 wt %, Fisher Scientific), or aqueous DMA (C$_2$H$_7$N, 40 wt %) was introduced into the chamber. The target mixing ratio of NH$_3$ or DMA in the chamber was supposed to be 500 ppb, however, due to losses in the inlet lines and chamber walls the actual mixing ratio was around 200 ppb as verified with an Ecotech 9842 NH$_3$/NO$_x$ analyzer. Particle volume concentration was monitored with a scanning mobility particle sizer (SMPS; TSI 3936) equipped with a condensed particle counter (CPC; TSI 3775). The chemical composition of SOA particles was probed online with a Time-of-Flight Aerosol Mass Spectrometer (ToF-AMS). The ToF-AMS data were analyzed using PIKA 1.22A with SQUIRREL 1.62A software.

**Calculating uptake coefficients for NH$_3$ and DMA from NH$_3$ monitor data**

The uptake coefficients for NH$_3$ and DMA were calculated from NH$_3$ monitor data. The monitor can detect NH$_3$, small amines, and other simple nitrogen containing organic compounds by converting them to NO on a Pt-based catalyst and then detecting NO by chemiluminescence. The loss of NH$_3$ or DMA mixing ratios as captured by the NH$_3$ analyzer was fitted to a first order decay rate equation in order to obtain the first-order loss rate
constant, k (s⁻¹) The rate constant was used in the following equation to determine the uptake coefficient, \( \gamma \).

\[
\gamma = \frac{4 \times k}{v_{NH3} \times c_{area}} 
\]

(5.1)

At room temperature, the average speed of NH₃ molecules, \( v_{NH3} \) (m s⁻¹), and DMA molecules is \( 6.1 \times 10^2 \) m s⁻¹ and \( 3.7 \times 10^2 \) m s⁻¹, respectively. The concentration of surface area of the particles, \( C_{area} \) (m² m⁻³), was calculated by averaging the total surface area of the particles (obtained from the SMPS) from the time of NH₃ or DMA injection through the end of the experiment. This time segment matched the period of time for which the first-order loss rate constant was calculated.

Note, that this method cannot distinguish uptake due to wall loss or the formation organic nitrogen compounds in particle due to neutralization of acids and physical dissolution of ammonia or amine in the particle material. Therefore, it measures the total uptake coefficient. Given that the elemental ratios in the particles as determined with the AMS should be less sensitive to wall loss effects, AMS data was used to obtain a normalized uptake coefficient.

\[
\text{normalized } \gamma_{NH3} = \gamma_{NH3} \times \frac{n_N^{added \ (AMS)}}{n_N^{added \ (NH_3 \ monitor)}} 
\]

(5.2)

The moles of nitrogen, \( n_N^{added} \), added to the particles are described below.
Calculating moles of nitrogen added from NH₃ monitor and AMS data

The moles of nitrogen added to the particles, \( n_{N}^{added} \) (mol), is equal to the loss in the moles of NH₃ or DMA after injection. For simplicity, NH₃ is used in the following equations, but note that these equations can be used in the same manner for DMA.

\[
n_{N}^{added} = ([NH_3]_0 - [NH_3]_t) \times V_{chamber}
\]  \hspace{1cm} (5.3)

The starting concentration of NH₃, \([NH_3]_0\), is equivalent to the amount we inject (e.g., 200 ppb as determined by the NH₃ analyzer). The concentration of NH₃ at some later time \( t \), \([NH_3]_t\), can be obtained from the first order decay fit of the NH₃ loss. The concentration of NH₃ is multiplied by the chamber volume, \( V_{chamber} \), to convert to moles of NH₃. Equation 5.3 above can be expressed as:

\[
n_{N}^{added} = [NH_3]_0 \times (1 - e^{-k \times \Delta t}) \times V_{chamber}
\]  \hspace{1cm} (5.4)

The first-order loss rate constant, \( k \), is the same one used earlier in the uptake coefficient calculations.

For an independent and potentially more accurate measurement of the amount of N inserted to the particles, we relied on AMS data. AMS can sensitively detect presence of nitrogen in particles, and furthermore, it can separately measure organic and inorganic nitrogen. Prior to NH₃ or DMA injection, nicotinic acid was the only source of N in the particles and was responsible for the initial average total N:C ratio of the particles. While nicotinic acid could react with the oxidant, we would expect this to be minimal given that nicotinic acid is in the condensed phase when introduced into the chamber and is expected to be less reactive than the other precursors used in this study (Atkinson et al., 1986; Atkinson, 1988; Atkinson,
After the injection of NH$_3$ or DMA, the increase in the N:C ratio of the particles was used to calculate the moles of N added into the particles. The following equation was used to calculate the moles of N added to particles from the AMS data.

$$n_{N}^{\text{added}} = n_{N}^{0} \times \left( \frac{\text{N:C after NH}_3 \text{ injection}}{\text{N:C before NH}_3 \text{ injection}} - 1 \right) \quad (5.5)$$

The initial moles of nitrogen in the particles, $n_{N}^{0}$, were calculated from the concentration of nicotinic acid seeds present in the chamber before organic aerosol formation and before NH$_3$ or DMA injection. This equation assumes that the amount of organic carbon in particles is not affected by the reaction of SOA with ammonia or amine. It also assumes that AMS is equally sensitive to the nicotinic acid and to the organic nitrogen compounds formed in the reaction.

**5.3 Results**

When toluene SOA was exposed to dimethylamine in the chamber, there was no observed change in particle number and mass concentrations, as was the case when SOA was exposed to NH$_3$ (Fig. 4.2). Figure 5.1 is an example of SMPS-recorded data for a typical NH$_3$ or DMA uptake in a toluene SOA experiment. The experiment began with the injection of nicotinic acid seeds (light blue region), which led to an initial rapid increase in particle number concentration (blue trace); subsequently the number concentration decreased as seed particles coalesced and some partitioned to the walls. As the SOA was generated through photooxidation (yellow region), the particle number concentration (blue trace) did not change significantly while the particle mass concentration (red trace) rose significantly suggesting that most of the new SOA particles formed on the pre-existing seeds.
After photooxidation was stopped, the SOA was exposed to dimethylamine (green region) and the particle number and mass concentrations remained unaffected. This is fully consistent with our expectation that the chemical uptake of ammonia/amine should not significantly change the mass of the reacting SOA compound (ammonia/amine are taken up but water molecules are released as products).

**Figure 5.1.** Particle number concentration (blue trace) and particle mass concentration (red trace) for toluene/OH SOA at low relative humidity exposed to dimethylamine (green region), showing that dimethylamine amine exposure did not affect these parameters.

SMPS data for d-limonene or α-cedrene SOA exposed to NH₃ or dimethylamine in the chamber was very similar to that from toluene SOA. Again, as shown in Figure 5.2, there was no significant change in particle number and mass concentrations after exposure of the SOA to DMA. One distinction between the SOA made from the biogenic VOCs (d-limonene, α-cedrene) versus toluene was that the d-limonene and α-cedrene oxidation formed particles
much more rapidly. This can be seen in Figure 5.2, where upon the addition of O₃ in the chamber, there is a sudden increase in the particle number concentration (blue trace), suggesting that upon oxidation new particles formed instead of solely growing onto the pre-existing seed particles.

Figure 5.2. Particle number concentration (blue trace) and particle mass concentration (red trace) for d-limonene/O₃ SOA at low relative humidity exposed to dimethylamine (green region), showing that dimethylamine amine exposure did not significantly affect these parameters.

Figure 5.3 compares the reactive uptake of NH₃ to that of DMA by d-limonene SOA particles under low RH. We focus on d-limonene SOA for this comparison because d-limonene SOA showed the strongest interaction with NH₃ in comparison to toluene SOA and n-hexadecane SOA (discussed in Chapter 4). When exposed to the same mixing ratios of NH₃ and DMA (200 ppb), d-limonene SOA reacted more efficiently with DMA as evidenced by the faster and larger increase in the N:C ratio in the particles. More specifically, when exposed to NH₃, the
N:C ratios of the d-limonene SOA particles increased by 0.005 after nearly 2 h (Fig. 5.3 left panel); however, the increase in the N:C ratios was an order of magnitude greater after 2 h when exposed to DMA (Fig. 5.3 right panel). It is likely that the lower volatility of DMA (vapor pressure = 1520 mm Hg at 25°C; Daubert and Danner, 1989) than NH₃ (vapor pressure = 7500 mm Hg at 25°C; Daubert and Danner, 1999) contributes to the observed higher uptake by d-limonene SOA.

**Figure 5.3.** Elemental ratios of d-limonene ozonolysis SOA particles when exposed to NH₃ (left panel) and DMA (right panel), showing how N:C ratios increases more significantly from DMA uptake than NH₃ uptake. Note that the left y-axis is an order of magnitude larger in the right panel than in the left.

Figure 5.4 shows d-limonene ozonolysis SOA exposed to DMA at varying RH. After exposure of d-limonene SOA to DMA (yellow region) under low RH (a), we see a significant increase in the N:C ratio of the particles (red trace). As the RH was increased from <2% to 20% (b) and then to 50% (c), the increase in the N:C ratios for the particles after DMA exposure was suppressed. These observations agree with the hypothesis that the uptake of amines leads to condensations reactions where one or more water molecules are produced, therefore as RH increases and the reverse reaction is favored, the uptake of DMA is suppressed.
Figure 5.4. d-Limonene ozonolysis SOA exposed to DMA at varying RH. As the RH humidity was increased from <2% (a) to 20% (b) to 50% (c), the increase in the N:C ratio (red trace) after DMA exposure (yellow region) became smaller indicating that an increase in RH suppresses DMA uptake.

Figure 5.5 shows α-cedrene ozonolysis SOA exposed to DMA at varying RH. Similar to the trend observed in the d-limonene SOA data, as the RH was increased from <2% (a) to 20% (b) to 50% (c), the increase in the N:C ratios for the particles was suppressed. Again, these observations agree with the proposed mechanism that the uptake of amines leads to condensations reactions, and therefore as RH increases, the uptake of DMA is suppressed.
Figure 5.5. Plots showing the H:C (blue trace), O:C (green trace), and N:C (red trace) ratios as a function of time for α-cedrene ozonolysis SOA particles exposed to DMA at varying RH. As the RH humidity was increased from <2% (a) to 20% (b) to 50% (c), the increase in the N:C ratio (red trace) after DMA exposure (yellow region) became smaller indicating that an increase in RH suppresses DMA uptake.

Figure 5.6 shows toluene photooxidation SOA exposed to DMA at low and 20% RH. Note that experiments performed at 50% RH need to be repeated because insufficient time was given for photooxidation and the growth in particle mass concentration was small and therefore is not discussed here. Unlike in the NH₃ uptake experiments (Chapter 4), exposure of toluene SOA to DMA (yellow region) resulted in a noticeable increase in the particles N:C ratio (red trace), again suggesting that uptake of DMA is more efficient than that of NH₃.

At <2% RH (left panel) after DMA exposure (yellow region), the N:C ratio (red trace) of the particles increased from approximately 0.08 to 0.12 (Δ = 0.04) after 2.5 h. At 20% RH (right panel) after DMA exposure (yellow region), the N:C ratio (red trace) of the particles
increased from about 0.06 to 0.10 ($\Delta = 0.04$) after 2.5 h. Given the similar change in the N:C ratios, more experiments at higher RH are necessary to establish a trend. Within this range of RH (0-20%), Liu et al. (2018) reported no significant change in NH$_3$ uptake by toluene SOM. In that same publication, they report an increase in NH$_3$ uptake by toluene SOM with an increase in RH when the RH was between 20% and 60%, explaining that the limitations in mass transfer rate for uptake due to the high viscosity of toluene SOM at low RH disappear at RH>20% (Liu et al., 2018).

![Figure 5.6](image)

**Figure 5.6.** Toluene photooxidation SOA exposed to DMA at varying RH. As the RH humidity was increased from <2% (left) to 20% (right), the increase in the N:C ratio (red trace) after DMA exposure (yellow region) was similar (~0.04).

When looking at the N-containing families, the largest increase after DMA exposure was in the CHN family, shown in Fig. 5.7 (purple trace), indicating that DMA uptake predominantly led to an increase in organic nitrogen in the particles. Individual N-containing fragments that had a strong signal after DMA exposure are listed in Table 5.1. These fragments were taken from mass spectra representing the particle composition averaged from the time beginning with DMA injection through the end of the experiment.
Figure 5.7. Nitrogen-containing families plotted versus time for LIM/O\textsubscript{3} SOA (a), CED/O\textsubscript{3} SOA (b), and TOL/OH SOA (c) exposed to DMA (yellow region) under low RH. The initial decrease seen in the N-containing families for the LIM/O\textsubscript{3} SOA particles (~2:30 pm) and the CED/O\textsubscript{3} SOA particles (~1:30 pm) prior to DMA injection were caused by diluting the particle flow to the AMS, not by a change in particle composition. This data show that the largest increase after DMA exposure was in the CHN family (purple trace) for the three SOA systems.
Table 5.1. Table listing the 15 most prominent N-containing peaks and their families for LIM/O₃ SOA, CED/O₃ SOA, and TOL/OH SOA after exposure to DMA under low RH. Peaks are listed in descending order with respect to their signal.

<table>
<thead>
<tr>
<th></th>
<th>LIM/O₃ SOA, low RH</th>
<th></th>
<th>CED/O₃ SOA, low RH</th>
<th></th>
<th>TOL/OH SOA, low RH</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>family</td>
<td>m/z, fragment</td>
<td>family</td>
<td>m/z, fragment</td>
<td>family</td>
<td>m/z, fragment</td>
</tr>
<tr>
<td>1</td>
<td>CHN</td>
<td>42.034, C₂H₄N</td>
<td>CHN</td>
<td>44.050, C₂H₆N</td>
<td>CHN</td>
<td>44.050, C₂H₆N</td>
</tr>
<tr>
<td>2</td>
<td>CHN</td>
<td>27.011, CH₄</td>
<td>CHN</td>
<td>42.034, C₂H₄N</td>
<td>NO</td>
<td>29.998, NO</td>
</tr>
<tr>
<td>3</td>
<td>NO</td>
<td>29.998, NO</td>
<td>CHN</td>
<td>79.042, C₂H₅N</td>
<td>NH</td>
<td>17.027, NH₂</td>
</tr>
<tr>
<td>4</td>
<td>CHN</td>
<td>44.050, C₂H₆N</td>
<td>NO</td>
<td>29.998, NO</td>
<td>NH</td>
<td>16.019, NH₂</td>
</tr>
<tr>
<td>5</td>
<td>CHN</td>
<td>30.034, CH₄N</td>
<td>CHN</td>
<td>55.042, C₂H₅N</td>
<td>CHN</td>
<td>45.058, C₂H₇N (DMA)</td>
</tr>
<tr>
<td>6</td>
<td>CHN</td>
<td>41.027, C₂H₅N</td>
<td>CHN</td>
<td>53.027, C₂H₅N</td>
<td>CHN</td>
<td>42.034, C₂H₄N</td>
</tr>
<tr>
<td>7</td>
<td>NO</td>
<td>45.993, NO₂</td>
<td>CHN</td>
<td>51.011, C₂H₆N</td>
<td>CHN</td>
<td>27.011, CHN</td>
</tr>
<tr>
<td>8</td>
<td>CHN</td>
<td>43.042, C₂H₅N</td>
<td>CHN</td>
<td>27.011, CHN</td>
<td>CHN</td>
<td>28.019, C₂H₅N</td>
</tr>
<tr>
<td>9</td>
<td>CHN</td>
<td>28.019, CH₂N</td>
<td>NH</td>
<td>18.034, NH₄</td>
<td>NH</td>
<td>18.034, NH₄</td>
</tr>
<tr>
<td>10</td>
<td>CHN</td>
<td>29.027, CH₃N</td>
<td>CHO₁N</td>
<td>55.006, C₂HON</td>
<td>CHN</td>
<td>43.042, C₂H₅N</td>
</tr>
<tr>
<td>11</td>
<td>CHN</td>
<td>58.066, C₃H₈N</td>
<td>CHN</td>
<td>30.034, CH₄N</td>
<td>CHN</td>
<td>30.034, CH₄N</td>
</tr>
<tr>
<td>12</td>
<td>NH</td>
<td>17.027, NH₃</td>
<td>CHN</td>
<td>43.042, C₂H₅N</td>
<td>NO</td>
<td>45.993, NO₂</td>
</tr>
<tr>
<td>13</td>
<td>CHN</td>
<td>45.058, C₂H₇N (DMA)</td>
<td>CHN</td>
<td>95.074, C₅H₉N</td>
<td>CHN</td>
<td>41.027, C₂H₅N</td>
</tr>
<tr>
<td>14</td>
<td>CHN</td>
<td>40.019, C₂H₅N</td>
<td>CHN</td>
<td>50.003, C₂N</td>
<td>CHN</td>
<td>40.019, C₂H₅N</td>
</tr>
<tr>
<td>15</td>
<td>CHO₂₁N</td>
<td>123.032, C₆H₅O₂N (nicotinic acid)</td>
<td>CHN</td>
<td>41.027, C₂H₅N</td>
<td>CHO₂₁N</td>
<td>123.032, C₆H₅O₂N (nicotinic acid)</td>
</tr>
</tbody>
</table>

The presence of DMA in the particles at m/z 45.058 (Table 5.1) suggests that a portion of DMA uptake may lead to non-reactive uptake within the time of the experiment. It is also possible that this C₂H₇N fragment may be a fragment of something larger. Figure 5.8 shows that removing the DMA peak from the data (solid black squares) does not affect the change in N:C trends (solid red circles) observed after DMA exposure (yellow region). Therefore, while some DMA may remain in the particles, most of the change in N:C results from reactive uptake of DMA.
Figure 5.8. Elemental ratios plotted versus time for LIM/O$_3$ SOA (a), CED/O$_3$ SOA (b), and TOL/OH SOA (c) exposed to DMA (yellow region) under low RH. The elemental ratios for each SOA system are plotted to compare how including the DMA peak (circle traces) versus removing the DMA peak (square traces) affects the elemental ratios. Removing the DMA peak leads to a small overall decrease in the N:C ratios but does not affect how the N:C ratio changes after DMA exposure.

Table 5.2 lists the uptake coefficients obtained from NH$_3$ monitor data for NH$_3$ (left) by LIM/OH and LIM/O$_3$ SOA under different RH conditions. Uptake coefficients for DMA (right) by LIM/O$_3$, CED/O$_3$, and TOL/OH SOA under varying RH conditions are also listed. The normalized uptake coefficients for NH$_3$ were on the order of $10^{-5}$, which falls within the lower end of the range of NH$_3$ uptake coefficients previously reported for $\alpha$-pinene ozonolysis SOA and m-xylene SOA (Liu et al., 2015). The DMA uptake coefficients ranged from $10^{-5}$ to $10^{-4}$.

The moles of nitrogen per cubic meter of air incorporated into the particles was calculated by using NH$_3$ monitor and AMS data. The values calculated from the NH$_3$ monitor were
consistently higher than those calculated from the AMS data. One possibility for this discrepancy is that when using NH₃ monitor data, we assume that all NH₃ loss is due to uptake by the particles; this may be an overestimation as some NH₃ can partition to the chamber walls. Since the uptake coefficients calculated using the NH₃ analyzer data reflects total NH₃ or DMA uptake in the chamber (rather than solely that from the SOA), normalized uptake coefficients were calculated using AMS data in order to obtain more realistic values. These normalized coefficients resulted in values approximately one order of magnitude smaller and were comparable to the lower NH₃ uptake coefficient values previously reported for α-pinene ozonolysis SOA and m-xylene SOA (Liu et al., 2015). Furthermore, while the normalized uptake coefficients are likely to be more realistic than the un-normalized coefficients reported in Table 5.2, it is evident that these normalized uptake coefficients still do not capture the RH dependence that the AMS data does. Future control experiments performed at various RH, which are necessary to estimate the contribution to the uptake coefficient from wall loss, may allow us to better capture the RH dependence with the NH₃ analyzer.
Table 5.2. NH₃ uptake coefficients and increase in moles of N in the particles after exposure to NH₃ (left). DMA uptake coefficients and increase in moles of N in the particles after DMA exposure (right).

<table>
<thead>
<tr>
<th>VOC / Oxidant</th>
<th>RH (%)</th>
<th>( Y_{NH3} )</th>
<th>( n_{N\text{added}} ) (mol)</th>
<th>( n_{N\text{added}} ) (mol)</th>
<th>NH₃ monitor</th>
<th>AMS</th>
<th>VOC / Oxidant</th>
<th>RH (%)</th>
<th>( Y_{DMA} )</th>
<th>( n_{N\text{added}} ) (mol)</th>
<th>( n_{N\text{added}} ) (mol)</th>
<th>DMA (from NH₃ monitor)</th>
<th>AMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIM/OH</td>
<td>50</td>
<td>3.9E-4</td>
<td>9.7E-6</td>
<td>1.7E-5</td>
<td>4.2E-7</td>
<td></td>
<td>LIM/O₃</td>
<td>50</td>
<td>2.2E-4</td>
<td>2.8E-5</td>
<td>3.2E-5</td>
<td>4.1E-6</td>
<td></td>
</tr>
<tr>
<td>LIM/OH</td>
<td>50</td>
<td>4.9E-4</td>
<td>1.5E-5</td>
<td>1.9E-5</td>
<td>6.0E-7</td>
<td></td>
<td>LIM/O₃</td>
<td>20</td>
<td>1.8E-4</td>
<td>3.0E-5</td>
<td>2.9E-5</td>
<td>4.8E-6</td>
<td></td>
</tr>
<tr>
<td>LIM/OH</td>
<td>50</td>
<td>2.9E-4</td>
<td>4.7E-6</td>
<td>1.3E-5</td>
<td>2.1E-7</td>
<td></td>
<td>LIM/O₃</td>
<td>&lt;2</td>
<td>3.4E-4</td>
<td>8.0E-5</td>
<td>3.6E-5</td>
<td>8.5E-6</td>
<td></td>
</tr>
<tr>
<td>LIM/OH</td>
<td>20</td>
<td>9.0E-4</td>
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5.4 Conclusions

This study illustrates that under the conditions explored in this study, dimethylamine uptake is more efficient than that of ammonia by secondary organic aerosol. These findings suggest that while ammonia is more abundant in the atmosphere, amine uptake may still be a potential source of organic nitrogen in particulate matter. This idea is indirectly supported by field studies in which amine concentrations are much more similar to ammonia concentrations in the particulate phase than in the gas phase (Makela et al., 2001; Sorooshian et al., 2008). Emission inventories for amines are not as robust as those of NH₃, making air
quality simulations (such as those described in the previous chapter for NH$_3$ uptake) difficult. However, these experiments suggest that the uptake of amines may be an important source of organic N in particulate matter. Here, we chose to focus on DMA, a C$_2$ amine, but other common atmospheric C$_1$-C$_6$ amines remain to be explored and those with even lower volatilities than DMA may lead to more efficient uptake by SOA.

Moreover, when relative humidity was increased, the reactive uptake of dimethylamine by d-limonene and $\alpha$-cedrene SOA was suppressed, as indicated by AMS data. These observations are consistent with previous studies suggesting that reaction of ammonia with carbonyls in the SOA resulting in the loss of water is an important pathway in the uptake of ammonia of SOA. We propose here that amine reactions undergo similar dehydration reactions and therefore as relative humidity was increased, the reverse reaction was favored resulting in the observed suppression of amine uptake.
CHAPTER 6

Summary

6.1 Research Goals
Secondary organic aerosols (SOA) constitute a significant fraction of fine particulate matter (PM$_{2.5}$) and because SOA is not well-understood, it remains a large source of uncertainty in models that aim to predict global climate. SOA are formed in the atmosphere through the oxidation of volatile organic compounds (VOCs). VOCs are emitted from various anthropogenic (e.g., incomplete combustion, industrial processes) and natural (e.g., vegetation) processes. Biogenic terpenes, such as isoprene, d-limonene, and α-pinene, as well as anthropogenic compounds such as saturated hydrocarbons, toluene and xylenes, and condensed aromatics are some of the most commonly studied SOA precursors. A motivation for studying these hydrocarbon compounds is their prevalence in the environment. Beyond various types of hydrocarbons, scant research exists on SOA made from VOCs containing other common elements such as O, N, and S, thereby potentially missing others sources of SOA. One of the goals of my research was to investigate the formation of SOA from VOCs containing nitrogen atoms.

In addition to studying previously unaccounted sources of SOA, other ways in which laboratory studies can continue to improve our understanding of SOA behavior in the environment is to generate SOA under more realistic conditions. Examples of how experiment designs have improved over time in order to generate SOA under more environmentally relevant conditions include using lower VOC concentrations, using VOC mixtures instead of single VOC precursors, and varying the temperature and relative
humidity (RH) at which SOA is generated. A second goal of my research was to investigate the effect of RH on the formation of SOA.

Once SOA is generated, a myriad of critical questions can be asked about its subsequent chemical transformations or ‘aging’ in the environment. Many pathways of SOA aging exist that can lead to SOA mass gain or loss, changes in chemical composition (e.g., increasing oxidation), and changes in light-absorption properties, among others. In particular, I was interested in how the presence of nitrogen-containing organic compounds (NOC) in SOA can alter its light-absorption properties. Therefore, the third goal of my research was to investigate the introduction of NOC in SOA by aging SOA in the presence of ammonia (NH₃) and dimethylamine (DMA), two reduced nitrogen species common in the atmosphere.

6.2 Goal 1: Studying the effect of RH on SOA particle formation

Chapter 2 described the study where SOA made from toluene, an anthropogenic VOC was generated under a range of RH, and the RH was found to affect both the amount of toluene SOA formed (mass yield) and its chemical composition.

SOA was produced in a smog chamber from the photooxidation of toluene at <2-90% RH, collected on filters, and analyzed with high-resolution mass spectrometry (HRMS) to look for changes in chemical composition. A scanning mobility particle sizer (SMPS) was employed to look at the RH dependence of particle mass concentration. SMPS data showed that the particle mass loading decreased by nearly an order of magnitude when RH increased from <2 to 75–90% for low-NOₓ toluene SOA. HRMS measurements revealed a significant reduction in the fraction of oligomers present in the SOA generated at 75 % RH compared to SOA generated under dry conditions. The volatility distributions of the SOA compounds,
estimated from their molecular formulas using the “molecular corridor” approach, confirmed that low-NOx toluene SOA became more volatile on average under high-RH conditions. In contrast, the effect of RH on SOA mass loading was found to be much smaller for high-NOx toluene SOA. The observed increase in the oligomer fraction and particle mass loading under dry conditions were attributed to the enhancement of condensation reactions, which produce water and oligomers from smaller compounds in low-NOx toluene SOA. The reduction in the fraction of oligomeric compounds under humid conditions may partly counteract the previously observed enhancement in the toluene SOA yield driven by the aerosol liquid water chemistry in deliquesced inorganic seed particles.

6.3 Goal 2: Investigate the formation of SOA from a N-containing VOC

Chapter 3 described how highly light-absorbing SOA was efficiently generated from the oxidation of indole, a N-containing heterocyclic compound emitted from plants and animal waste.

SOA was generated in a smog chamber from the oxidation of indole by OH, O3, and NO3 in order to explore the formation, optical properties, and chemical composition of indole SOA. Indole photooxidation resulted in a high SOA mass yield (1.3 ± 0.3), suggesting that most oxidized indole products eventually end up in the particle phase. Moreover, indole SOA generated by reactions with any of the three oxidants studied all resulted in SOA that was highly absorbing in the UV-Vis spectrum. The optical properties of indole SOA were probed with two independent methods: UV-Vis spectrophotometry was used to study the bulk SOA, and broadband cavity enhanced spectroscopy was used to measure the light-absorption/scattering of SOA particles. When RH was increased from <2 to 25 to 50%,
indole/OH SOA and indole/O\textsubscript{3} SOA had a higher light-absorption. However, the absorption properties of indole/NO\textsubscript{3} SOA showed a non-linear dependence with RH. These trends were captured by both methods. High-performance liquid chromatography coupled to photodiode array spectrophotometry and high-resolution mass spectrometry (HPLC-PDA-HRMS) was used to identify chromophoric compounds that are responsible for the color of indole SOA. Indole derivatives containing one or two N atoms, such as tryptanthrin, indirubin, indigo dye, indoxyl red, and nitroindole were found to contribute significantly to the visible absorption spectrum of indole SOA. These observations suggest that NOC produced from indole oxidation may be important contributors to the pool of organic species that absorb radiation strongly in the near-UV and visible spectral ranges (aka brown carbon) in the atmosphere and that the light-absorption properties of indole SOA will vary depending on the ambient RH.

The potential effect of indole/OH SOA on the total SOA mass concentration and on the light-absorbing properties of SOA in the South Coast Air Basin of California (SoCAB) was explored with an airshed model. The model projected elevated concentrations of indole SOA during the afternoon hours, which contributed considerably to the total organic aerosol under selected scenarios. Despite its high light-absorption, indole/OH SOA is unlikely to contribute significantly to decreased visibility in an urban area such as the SoCAB where absorbance by black carbon dominates. However, the impact on visibility may be greater in more remote environments, especially under plant-stressed conditions or during flowering events when emissions of indole are elevated.

This study illustrated how indole oxidation can effectively lead to the formation of SOA. However, several questions remain including: 'What role does RH play in the oxidation
reactions of indole that lead to the production of chromophoric species?’ and ‘How photostable are the NOC chromophores produced from indole oxidation?’ Furthermore, indole is one of many N-containing VOCs present in the atmosphere that could potentially contribute to the formation of SOA in the environment.

6.4 Goal 3: Investigate NOC formation in SOA particles via SOA uptake of ammonia (NH₃) and dimethylamine (DMA)

Chapter 4 described how the reactive uptake of NH₃ by SOA leads to the formation of NOC in the SOA particles and how the efficiency of this uptake varies depending on the SOA precursor. Chapter 5 compared the reactive uptake of NH₃ to that of DMA by SOA and explored the RH dependence of this uptake.

Anthropogenic (toluene, n-hexadecane) and biogenic (d-limonene, α-cedrene) VOCs were oxidized in a smog chamber at various RH (<2-50%) resulting in SOA. After the initial SOA formation, a pulse of NH₃ or DMA was introduced into the chamber. An NH₃ monitor was used to track the decay of NH₃ and DMA in order to calculate their uptake coefficients, i.e., the probability that a molecule of NH₃ or DMA will react with an SOA particle upon contact. The normalized measured uptake coefficients ranged from 10⁻⁶ to 10⁻⁴. More careful experiments are necessary in order to distinguish the loss of NH₃ and DMA to the particles versus to the chamber walls and to determine the extent of RH dependence of the wall loss. Offline mass spectrometry was used to estimate the percentage of N-containing compounds in the SOA samples after exposure to NH₃, which resulted in approximately 20% for limonene SOA, 5% for toluene SOA, and 5% for n-hexadecane SOA. Based on these results, modeling of NH₃ uptake by SOA was given an upper limit of a 10% conversion of NOC
formation in the SOA. Online mass spectrometry was used to characterize chemical composition of the SOA particles. The appearance of NOC in the SOA particles after DMA exposure was larger and faster compared to after NH₃ exposure. These results suggest that in addition to NH₃ uptake contributing to NOC formation in SOA, amines while present in lower mixing ratios, may also be an important source of NOC in SOA due to their more efficient uptake by SOA. Moreover, when RH was increased from <2 to 50%, less NOC was incorporated into the SOA particles after exposure to DMA, indicating that water suppresses the uptake of DMA by SOA. This suggests that DMA reactions with SOA species likely follow similar condensation reactions shown to produce NOC from NH₃ reactions with carbonyl species in SOA, which are accompanied by a loss of water.

Air quality simulations for the SoCAB and continental US were conducted using a range of uptake coefficients (10⁻⁵ to 10⁻²) to explore the sensitivity of changes in NH₃ and PM₂.₅ concentrations to the magnitude of the uptake coefficient. Results indicate that introducing this chemical uptake of NH₃ by SOA depletes gaseous NH₃ concentrations, causing indirect reductions in the amount of ammonium nitrate and ammonium sulfate in PM₂.₅, and decreases particle pH. The magnitude of the impact on NH₃ and PM₂.₅ concentrations exhibited a strong but non-linear dependence on the value of the uptake coefficient. Furthermore, simulations over the continental US showed that the mass concentration of PM₂.₅ is significantly affected, with a distinct spatial pattern over different seasons. For example, PM₂.₅ concentrations decreased during the winter, largely due to the reduction in ammonium nitrate concentrations. On the other hand, PM₂.₅ concentrations increased during the summer especially in the southeastern U.S. due to increased biogenic SOA production resulting from enhanced acid-catalyzed uptake of isoprene-derived epoxides. It is important
to understand and capture processes that can significantly impact PM mass given that enforceable parameters used to protect air quality, such as the US National Ambient Air Quality Standards (NAAQS), focus on regulating PM mass concentrations.

This study showed experimentally that reactive uptake of NH$_3$ can occur in SOA, and that the extent of the uptake varies depending on the SOA precursor. The precursor dictates the resulting SOA composition and therefore its properties, such as viscosity. Previous studies have shown that toluene SOA has a high viscosity, and therefore its higher viscosity relative to limonene SOA likely contributed to the lower uptake of NH$_3$. Examples of other parameters that can be explored in future experiments to further probe the relationship between viscosity and uptake include varying the temperature at which experiments are conducted and generating SOA from VOC mixtures. This set of experiments also demonstrated that DMA uptake was considerably more efficient than NH$_3$ uptake by SOA. Other common amines that may potentially contribute to NOC formation in SOA include monomethylamine, trimethylamine, ethylamine, diethylamine, triethylamine, 1-propanamine, and 1-butanamine. Provided more robust inventories for amines are available in the future, these findings could help improve projections of NOC in PM by air quality models.

6.5 Conclusions

Overall, this body of work highlights the novel chemistry and important properties of NOC in the atmospheric environment and illustrates the importance of considering the dependence of SOA properties on RH, which can vary widely in the ambient atmosphere. As mentioned above, SOA constitutes a significant fraction of PM$_{2.5}$, and because SOA is not well-understood, it remains a large source of uncertainty in models that aim to predict air quality
and global climate. Laboratory experiments like the ones discussed here are a critical tool that, in conjunction with field studies, contributes to our scientific understanding of SOA in the environment, allowing us to use more realistic parameterizations or atmospheric processes and reduce uncertainties in the models. Addressing uncertainties in regional and global models is imperative given that model projections are often shared with policymakers who have the authority to make the decisions that ultimately impact our air quality.
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