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Sources and Source Processes of Organic Nitrogen Aerosols in the Atmosphere

Mark E. Erupe
Utah State University - Continuing Education

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SOURCES AND SOURCE PROCESSES OF ORGANIC NITROGEN AEROSOLS IN
THE ATMOSPHERE

by

Mark E. Erupe

A dissertation submitted in partial fulfillment
of the requirements for the degree

of

DOCTOR OF PHILOSOPHY

in

Chemistry

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Logan, Utah

2008
ABSTRACT

Sources and Source Processes of Organic Nitrogen Aerosols in the Atmosphere

by

Mark E. Erupe, Doctor of Philosophy
Utah State University, 2008

Major Professor: Dr. Philip J. Silva
Department: Chemistry and Biochemistry

The research in this dissertation explored the sources and chemistry of organic nitrogen aerosols in the atmosphere. Two approaches were employed: field measurements and laboratory experiments. In order to characterize atmospheric aerosol, two ambient studies were conducted in Cache Valley in Northern Utah during strong winter inversions of 2004 and 2005. The economy of this region is heavily dependent on agriculture. There is also a fast growing urban population. Urban and agricultural emissions, aided by the valley geography and meteorology, led to high concentrations of fine particles that often exceeded the national ambient air quality standards. Aerosol composition was dominated by ammonium nitrate and organic species. Mass spectra from an aerosol mass spectrometer revealed that the organic ion peaks were consistent with reduced organic nitrogen compounds, typically associated with animal husbandry practices. Although no direct source characterization studies have been undertaken in Cache Valley with an aerosol mass spectrometer, spectra from a study at a swine facility
in Ames, Iowa, did not show any evidence of reduced organic nitrogen species. This, combined with temporal and diurnal characteristics of organic aerosol peaks, was a pointer that the organic nitrogen species in Cache Valley likely formed from secondary chemistry. Application of multivariate statistical analyses to the organic aerosol spectra further supported this hypothesis. To quantify organic nitrogen signals observed in ambient studies as well as understand formation chemistry, three categories of laboratory experiments were performed. These were calibration experiments, smog chamber studies, and an analytical method development. Laboratory calibration experiments using standard calibrants indicated that quantifying the signals from organic nitrogen species was dependent on whether they formed through acid-base chemistry or via secondary organic aerosol pathway. Results from smog chamber reactions of amines with ozone, nitrogen oxides, nitrate radical, and nitric acid showed that the secondary organic aerosol pathway was more plausible than acid-base chemistry, thus making the contribution of the organic nitrogen species to the total aerosol mass in Cache Valley significant. Gas phase and aerosol products formed from the smog chamber reactions were identified and used to devise reaction mechanisms. Finally, an ion chromatographic method for detecting and quantifying some key organic nitrogen species in aerosol was developed and tested.
DEDICATION

In memory of my dad
ACKNOWLEDGMENTS

First and foremost, I want to acknowledge my advisor, Dr. Philip J. Silva, in whose mentorship I have been under in the last five years. I have had an opportunity to learn from his expertise and he has also made numerous opportunities for learning available to me. Most importantly, I want to recognize him for always pushing me to the limits in order for me to give my best.

Secondly, I want to acknowledge my advisory committee members, Dr. Robert S. Brown, Dr. Cheng-Wei T. Chang, Dr. Stephen E. Bialkowski, and Dr. Randy S. Martin for their individual time and the directions and advice they offered during the committee meetings. Besides sitting in my committee, Dr. Martin was also a collaborator in some of the projects including the Ames study in Iowa.

In the course of my study, I had the opportunity to participate in a number of field studies that were co-sponsored by the Space Dynamic Laboratory (SDL). I want to acknowledge them for funding these studies. I also want to thank the NSF for funding the smog chamber studies and Dr. David R. Cocker for offering us the use of their state-of-the-art environmental chamber at the University of California, Riverside.

I also want to acknowledge my colleagues in our research group and in the analytical chemistry section for sharing ideas and for their friendship. Thanks Oluwatosin Dada, Sileola Ogunlaja, Prakash Joshi, John Dalgleish, Hanh Dinh, Derek Price, and all the undergraduate researchers.
To my dear friend Koichi Yamamoto, thank you for inspiring me to learn science. The role that you played in supporting my education during critical moments will always be remembered.

Finally, this section will not be complete without mentioning the invaluable support that my family gave me. Their love and encouragement was my anchor throughout the process. Thanks to my mom, my wife, Rebecca, and my son, Nathan.

Mark E. Erupe
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<tr>
<td>AMS</td>
<td>Aerosol Mass Spectrometer</td>
</tr>
<tr>
<td>CE-CERT</td>
<td>College of Engineering-Center for Environmental Research and Technology</td>
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<tr>
<td>CPCA</td>
<td>Custom Principal Component Analysis</td>
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<tr>
<td>DEA</td>
<td>Diethylamine</td>
</tr>
<tr>
<td>DMA</td>
<td>Differential Mobility Analyzer (also Dimethylamine)</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
</tr>
<tr>
<td>ESI</td>
<td>Electrospray Ionization</td>
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<td>HOA</td>
<td>Hydrocarbon-like Organic Aerosol</td>
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<tr>
<td>HR-ToF-AMS</td>
<td>High Resolution Time-of-Flight Aerosol Mass Spectrometer</td>
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<td>IC</td>
<td>Ion Chromatography</td>
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<tr>
<td>IE</td>
<td>Ionization Efficiency</td>
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<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<tr>
<td>IPP</td>
<td>Ions Per Particle</td>
</tr>
<tr>
<td>LC-ToF-AMS</td>
<td>Liquid Chromatography Time-of-Flight Aerosol Mass Spectrometer</td>
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<td>LDI</td>
<td>Laser Desorption Ionization</td>
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<tr>
<td>LOD</td>
<td>Limit of Detection</td>
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<td>MA</td>
<td>Methylamine</td>
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<td>MS</td>
<td>Mass Spectrum/Mass Spectrometer</td>
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<td>MSA</td>
<td>Methane Sulfonic Acid</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>OC</td>
<td>Organic Carbon</td>
</tr>
<tr>
<td>OOA</td>
<td>Oxygenated Organic Aerosol</td>
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<tr>
<td>PAH</td>
<td>Polycyclic Aromatic Hydrocarbon</td>
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<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PM$_{2.5}$</td>
<td>Particulate Matter (Below 2.5 Micrometers)</td>
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<td>PSL</td>
<td>Polystyrene Latex</td>
</tr>
<tr>
<td>PTR-MS</td>
<td>Proton Transfer Reaction Mass Spectrometer</td>
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<td>Q-AMS</td>
<td>Quadrupole Aerosol Mass Spectrometer</td>
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<tr>
<td>QMS</td>
<td>Quadrupole Mass Spectrometer</td>
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<tr>
<td>RO$_2$</td>
<td>Alkylperoxy Radical (R=Alkyl)</td>
</tr>
<tr>
<td>RSD</td>
<td>Relative Standard Deviation</td>
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<td>SMPS</td>
<td>Scanning Mobility Particle Sizer</td>
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<td>SOA</td>
<td>Secondary Organic Aerosol</td>
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<td>TBA</td>
<td>Tributylamine</td>
</tr>
<tr>
<td>TEAO</td>
<td>Triethylamine Oxide</td>
</tr>
<tr>
<td>TEOM</td>
<td>Tapered Element Oscillating Microbalance</td>
</tr>
<tr>
<td>TMA</td>
<td>Trimethylamine</td>
</tr>
<tr>
<td>TMAO</td>
<td>Trimethylamine Oxide (Trimethylamine-N-Oxide)</td>
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<tr>
<td>ToF</td>
<td>Time-of-Flight</td>
</tr>
<tr>
<td>UDAQ</td>
<td>Utah Division of Air Quality</td>
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<td>USU</td>
<td>Utah State University</td>
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<td>VOC</td>
<td>Volatile Organic Compound</td>
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Atmospheric Aerosols

Atmospheric aerosols are a fairly stable suspension of tiny particles in air (Hinds, 1999). They enter into the atmosphere through direct emissions (primary sources) or through condensation of vapor phase species (secondary sources) (Finlayson-Pitts and Pitts, 2000). Once in the atmosphere, particle size, number, and chemical composition can be changed by several mechanisms until they are eventually removed by natural and/or chemical processes, mainly through wet and dry deposition (Ravishankara, 1997; Seinfeld and Pandis, 1998). Particles usually remain suspended in the atmosphere for a period that ranges from days to weeks (Seinfeld and Pandis, 1998).

Aerosols have significant impacts that span local, regional and global scales. Locally, emission from vehicles, wood burning fires, agriculture and industries can pollute air leading to visibility degradation and possible adverse health effects (Dockery et al., 1993). On regional scale, aerosols and their precursors can be transported by wind from areas of high emissions to relatively clean remote regions. Globally, aerosols interact both directly and indirectly with incoming solar radiation. In the direct effect, aerosols such as ammonium sulfate scatter sunlight directly back into space while other aerosols such as black carbon absorb radiation (IPCC, 2007). In the indirect effect, aerosols in the lower atmosphere can modulate cloud properties due to changes in the concentration of cloud condensation nuclei. This has potential of altering cloud albedo as well as changes in cloud lifetime. As shown in Fig. 1-1, the radiative effects of aerosols...
have the largest uncertainties, especially the indirect effect, in understanding global climate and making predictions on future climatic changes (Ramanathan et al., 2001).

**Fig. 1-1.** Radiative forcing components from the fourth assessment report on climate change. The cloud albedo (indirect) effect has the largest uncertainty of all the components (IPCC, 2007).
Particles in the atmosphere arise from natural sources as well as anthropogenic activities (Jacobson et al., 2000). The former source includes wind-blown dust, sea spray, volcanic activities and biomass burning, while emissions of particles resulting from human activities include fuel combustion, industrial processes, non-industrial fugitive sources, and transportation sources. Globally, natural aerosols are estimated to be up to 5 times larger than anthropogenic aerosols, but regional variations in man-made pollution may change this ratio significantly in certain areas, particularly in the industrialized countries (Seinfeld and Pankow, 2003).

There are a wide variety of properties exhibited by atmospheric particles but perhaps the most commonly encountered are size, composition and concentration. Depending on specific interest area, other properties include shape, hygroscopicity, polarity, mixing state, density and ability to scatter and/or absorb radiation (Saxena and Hildemann, 1996; Blando et al., 1998). Figure 1-2 displays one of several the ways in which particle sizes are classified. The nucleation mode consists of new particles formed in the atmosphere. This mode accounts for the largest particle number, but because of their small size these particles contribute to a small fraction of the total particulate mass. Particles in the accumulation mode have typical atmospheric lifetimes between a few days and a few weeks. The accumulation mode particles account for most of aerosol surface area and a substantial fraction of aerosol mass. The nucleation and accumulation mode particles are collectively called fine particles. Particles larger than those in the accumulation mode are termed coarse mode particles and generally have relatively short atmospheric lifetimes before being removed by precipitation or gravity.
Particle constituents may be inorganic or organic. In many environments, a major fraction of the particulate mass comprises organic compounds (Seinfeld and Pankow, 2003). Organic compounds significantly influence aerosol properties; therefore they directly modulate the role aerosols play in the environment. Organic species can change the hygroscopic properties of aerosols, their toxicity, and their optical properties.

The large dynamic range of particles sizes, their heterogeneity and the wide range of functional groups makes the measurement of atmospheric particles all the more challenging. No single instrument can accomplish all the tasks. Ideally, the instrument should be fast enough to track changes in concentration, composition, or both as they...
occur. These changes can be due to chemistry or meteorology. The instrument should be sensitive enough to detect the species of interest, and free of interferences from other species present in the same air mass. Other consideration may include the weight and portability of the developed instrumentation. Such instrument is not available and probably never will. In recent years, however, aerosol mass spectrometry has emerged as a powerful analytical technique for characterizing atmospheric particles. There are many types of aerosol mass spectrometers and their details have been recently summarized in a review by Nash et al. (2006).

The Aerosol Mass Spectrometer

The aerosol mass spectrometer (Aerodyne Research Inc., Billerica, MA) is an instrument that measures size-resolved chemical composition of volatile and semi-volatile particulate matter in real-time. The AMS has the ability to combine size and chemical analysis of sub-micron aerosol with a high time resolution. Over the years, different versions of the AMS have been developed. This section discusses the quadrupole AMS.

Overview of the AMS

Figure 1-3 is a schematic representation of the AMS. It consists of three sections that are pumped differentially; the sampling chamber, the time of flight chamber, and the analysis and detection chamber (Jayne et al., 2000). In the sampling chamber, aerosol particles in the size range ~ 40 to ~1000 nanometers (nm) are sampled into a high vacuum system where they are aerodynamically collimated into a tight beam of ~ 1 millimeter (mm) diameter.
Fig. 1-3. Schematic representation of the AMS. This instrument measures size and composition of atmospheric aerosol in real-time.

After exiting through the lens, the aerosols enter the time-of-flight (ToF) chamber where particle sizing takes place. A rotating chopper wheel, with two radial slits located 180 degrees apart, intercepts the focused particle beam. The chopper wheel can be positioned in one of the three positions as follows; completely blocking the beam so that no particles pass through (beam closed); not blocking the beam so that all particles pass through (beam open), and a chopping position in which a fraction of the particle beam is allowed to pass through the radial slits (beam chopped). The flight times between the chopper and the detector gives the measurement of a particle's velocity; this measurement can be converted into aerodynamic diameter after performing instrument calibration with particles of known size. From the ToF chamber, the particle beam is directed into the analysis and detection chamber; here, the particle beam is vaporized by impacting a resistively heated surface, and immediately ionized by electron ionization. The resulting positive ions are then sorted by the quadrupole mass analyzer and detected by an electron
multiplier. The electron ionization process is a universal process, meaning that any species that can be vaporized within a short time will be detectable.

*The sampling chamber.* Aerosols enter into the AMS through a particle sampling inlet that restricts the flow with a 100 µm critical orifice at a flow rate of ~1.4 cm³/s. They proceed through aerodynamic lens that focuses the aerosols into a tight beam of ~1 mm in diameter, using six apertures whose diameter decreases sequentially (Liu et al., 1995). The pressure in this chamber is approximately 10⁻³ torr at the final stage of the aerodynamic lens. This low pressure is maintained by a V301 turbo molecular pump (Varian Inc., Palo Alto, CA) backed by MD1 diaphragm pump (Vacuubrand, Essex, CT). Due to the higher mass of the particles relative to the gas molecules, particles follow trajectories that deviate from the gas streamlines in the lens. Particles with enough inertia will partially follow the gas streamline while remaining focused on-axis as they expand through the nozzle into vacuum, producing a narrow, low-divergence particle beam as shown in Fig. 1-4.

![Calculated particle trajectories for 100 nm diameter, unit density spheres through the aerodynamic lens (Jayne et al., 2000).](fluuent_focus.pxp)

**Fig. 1-4.** Calculated particle trajectories for 100 nm diameter, unit density spheres through the aerodynamic lens (Jayne et al., 2000).
According to fluid dynamic calculations, the AMS has 100% transmission efficiency for particles between 40 nm and 600 nm (Jayne et al., 2000). The smaller size cut-off is as a result of Brownian diffusion by the small particles. The decreased efficiency in the higher particle sizes is as a result of particle impaction losses at the critical orifice and at the first stage of the lens. Progress has been made in the development of aerodynamic lens that can transmit aerosols efficiently below and above this range (Zhang et al., 2002). Figure 1-5 shows focusing efficiency diagram of the aerodynamic lens from FLUENT calculations (Jayne et al., 2000).

![Figure 1-5](image_url)

**Fig. 1-5.** Size dependent particle transmission efficiency of the AMS aerodynamic lens. There is 100% focusing efficiency for particles in the 60-600 nm aerodynamic diameters.
**Particle sizing chamber.** The aerodynamic lens is aligned so that the focused particles enter into a particle sizing chamber in a supersonic expansion through 1 mm diameter skimmer. The particle-sizing chamber is a 395 mm long flight tube maintained at $\sim 10^{-5}$ torr by a Varian V70 turbo molecular pump. Upon exiting the lens, particles acquire a velocity distribution that is dependent on their size with small particles traveling faster than larger ones. The flight times of the particles can be used to calculate their velocity using the flight tube as the distance of travel. A calibration curve, relating particle velocity to vacuum aerodynamic diameter can then be used to determine vacuum aerodynamic diameters for measured particles.

An optical sensor is used to determine the start of particle ToF cycle by locating the position of the slits on the mechanical chopper relative to the particle beam. The ToF measurement relies on fast particle vaporization and detection (of the order of microseconds) that provides the end of the time of flight cycles. The chopper operates at a fixed frequency, typically in the range of 100 - 150 Hz, defining a ToF cycle of 10 ms or less. The chopper also has a fixed duty cycle (2% for the work reported here) which determines the aerosol throughput from the lens to the detector. The chopper duty cycle is determined by the width and relative position of the slits, and also the diameter of the chopper wheel. A servo motor is used to control the chopper position, relative to the aerosol particle beam.

Since the flight times used to calculate velocities and the size of the particles takes place in the free molecular regime, the resulting size is referred to as vacuum aerodynamic diameter. This differs from the classical aerodynamic diameter that is
measured by other measurement methods. The relationship in Eq. (1) is used to convert
the AMS diameter to classical aerodynamic diameter. The difference between vacuum
and classical aerodynamic diameters is discussed by DeCarlo et al. (2004).

\[ D_a = D_m \times \rho \times \chi \]  

(1)

\( D_a \) is the vacuum aerodynamic diameter, \( D_m \) is mobility diameter, \( \chi \) is the dynamic shape
factor. The shape factor is interpreted as a density modifier and is usually in the range of
0.8 to 0.85. The assumption is that only 80 to 85% of the particle is solid NH\(_4\)NO\(_3\), the
remaining percentage is void volume.

*Particle detection/analysis chamber.* Figure 1-6 shows the ionizer/heater
assembly used in the AMS. During the ionization stage, typically a few ions are produced
from each million neutral molecules or atoms present in this ionization volume. The low
ionization efficiency requires high efficiency amplification for detection by conventional
means. The ions produced in the ionizer are focused into the quadrupole mass analyzer,
which acts as a mass-to-charge filter. Ions of a given mass-to-charge (\( m/z \)) ratio emerge at
the exit of the quadrupole filter and are directed to an ETP electron multiplier (SGE Inc.,
Austin, TX) for fast and high gain multiplication (up to 10\(^6\) times). From the multiplier,
the electron flow is then directed into a current-to-voltage amplifier set to a gain of 10\(^{-6}\)
amps per volt gain. The signals within the data acquisition program are usually displayed
as bits, which relate directly to the analog-to-digital conversion process.

*Modes of Operation*

There are two major types of data that can come from the AMS; chemical
composition from the mass spectra and size distribution of a series of fragments
representing various chemical species. Typically, the data acquisition software is set up to alternate between the mass spectrum (MS) and time-of-flight (ToF) modes at a user defined interval. Other special modes that are beyond the scope of the work presented here include a four second mode, selective scan mode, jump mass spectrum mode and the eddy correlation mode.

Fig. 1-6. The AMS detection scheme. The vaporization and ionization steps are separate making quantification of the resulting ions possible.
The mass spectrum mode. The MS mode gives information on chemical composition of the particle ensemble without particle size information. This is done by setting the mass spectrometer to repeatedly scan a predetermined range (typically 1-300 amu) at a rate of 1 ms per 1 amu. In this mode, the position of the particle beam chopper is alternated every 5 seconds in such a way that it either blocks the aerosol beam completely and an average background mass spectrum is obtained (beam blocked position) or it fully moves out of the way of the aerosol beam and an average mass spectrum of particle ensemble is recorded (beam open position). The spectrum that results from the difference between the open and blocked positions is an average mass spectrum of the non-refractory, mostly volatile and semi-volatile constituents. With proper instrument calibration, the resulting mass spectra can be quantified and classified for different chemical species.

The time of flight mode. In the ToF mode, chemically speciated, size-resolved data is obtained. In this mode, the quadrupole mass spectrometer is programmed to "sit" on one of several pre-programmed masses. Ion signal intensity is monitored as a function of the rotational phase of the chopper. This measurement of particle flight time is used to determine particle aerodynamic diameter. In ToF mode, the chopper is positioned so that the beam is "chopped." While this allows particle size to be measured it also reduces the overall particle throughput by the ratio of the chopper duty cycle. For example, a 2% chopper will block 98% of the particles. Several different spectrometer settings are usually selected to characterize different chemical species (sulfate, nitrate, ammonium, organic, etc.). Data obtained in this mode can be transformed into mass distributions of
selected mass fragments as a function of their vacuum aerodynamic diameter after applying the appropriate calibrations.

*The AMS Quantification Theory*

After vaporization and ionization, the AMS measures the number of ions produced at each scanned mass every second (Hz). This measurement can be converted into a quantitative measure of the aerosol mass loading (e.g. in µg/m³) of a particular species. This is done by determining the ionization efficiency of the species, defined as the ratio of ions detected/molecule vaporized. The conversion of the raw signal (in ion counts) to mass concentration was adapted by Jimenez et al. (2003) from Bley (1988).

The molecular flux $M_s$ (molecules/s) of species $s$ entering the AMS detection region per unit time is calculated from the signal at a single $m/z$ as shown in Eq. (2).

$$M_s = \frac{I_{sf}}{\chi_{sf} \times I_{Es}}$$  \hspace{1cm} (2)

$I_{sf}$ is the number of ions detected per unit time at the $f^{th}$ fragment ($m/z$) of species $s$, $\chi_{sf}$ is the fraction of ions formed from species $s$ detected at its $f^{th}$ fragment, and $I_{Es}$ is the ionization efficiency for species $s$.

The gain of the electron multiplier detector and the transmission efficiency of the quadrupole are a function of the $m/z$ in the range of interest and must be accounted for before using Eq. (2) as shown in Eq. (3).

$$I_{sf}^{corr} = \frac{I_{sf}}{T_{m/z} \times G_{m/z}}$$  \hspace{1cm} (3)

$T_{m/z}$ and $G_{m/z}$ are the relative quadrupole transmission and the relative response (gain) of the electron multiplier detector, respectively (Jimenez et al., 2003).
The mass concentration of species \( s \) in the aerosol \( (C_s) \) can then be calculated as shown in Eq. (4).

\[
C_s = \frac{M_s MW_s}{Q N_A} = \frac{c_{sf}^{corr}}{QN_A X_s \chi_{sf}} \frac{MW_s}{IE_s} \tag{4}
\]

\( MW_s \) is the molecular weight of species \( s \), and \( Q \) is the air volume sampling rate into the AMS. The inherent assumption here is that only one species contributes to the signal at that particular \( m/z \). The \( \chi_{sf} \) like \( IE_s \), is measured during the calibration procedure, described in more detail in the next section. If the species are not known, the values for \( IE_s, MW_s \) and \( \chi_{sf} \) are estimated by assuming the ratio \( IE_s/MW_s \) is equal to \( IE_{NO3}/MW_{NO3} \). This is commonly referred as nitrate equivalent concentration. However, if the class of the molecule (or group of molecules) is known, e.g. hydrocarbon(s), oxygenated organic(s), or inorganic salt as described by McLafferty and Turecek (1993), a response factor \( (R_f) \) is used to correct the \( IE_{NO3} \) as shown in Eq. (5).

\[
\frac{IE_s}{MW_s} = R_f \frac{IE_{NO3}}{MW_{NO3}} \tag{5}
\]

The response factors for broad categories of compounds are obtained based on the linearity between the numbers of electrons produced by 70 eV EI ionization and electron impact ionization cross-sections \( (\sigma) \) of the molecule as shown in Fig. 1-7. This means that the ionization efficiency of a molecule is directly proportional to \( \sigma \), the ionization efficiency on a molecular basis. The number of electrons in a molecule is highly correlated with the molecular weight of the molecule, especially for the volatile and semi-volatile molecules present in aerosols. Since IE is directly proportional to the electron impact cross section \( (\sigma) \) and the number of electrons in the molecule \( (N_e) \) is
approximately proportional to $MW_s$, $IE_s/MW_s$ will be proportional to $\sigma/N_e$ (Jimenez et al., 2003). For small molecules of a given type, $\sigma/N_e$ is approximately constant. From the data and regressions in Fig. 1-7, $R_f$ is estimated to be 2.0 for hydrocarbons, 1.5 for oxygenated hydrocarbons, and 1.0 for most inorganic species. However, some variability is observed with different chemical species.

**Fig. 1-7.** The EI ionization cross-sections as a function of the number of electrons in a molecule for various groups of compounds. This relationship is used in quantifying species detected by the AMS as discussed by Jimenez et al. (2003).
**AMS Calibrations**

*Ionization efficiency calibration.* Ionization efficiency is the ratio of the number of ions made to the total number of available parent molecules for that ion species (e.g., if the IE is $1 \times 10^{-6}$, then 1 molecule in 1 million molecules is ionized). In order to convert AMS signals into mass loading, an IE calibration, also called the mass or nitrate calibration is performed. The calibration procedure measures the ionization and ion transmission efficiency of ammonium nitrate. Ammonium nitrate particles, typically 350 nm as determined by a DMA, are generated, size-selected, dried using a diffusion drier, and then passed into the AMS. The relevant mass fragments (e.g. $m/z$ 15 (NH$^+$), $m/z$ 16 (NH$_2^+$), $m/z$ 17 (NH$_3^+$), $m/z$ 28 (N$_2^+$) $m/z$ 30 (NO$^+$), and $m/z$ 46 (NO$_2^+$) are set in ToF mode and the AMS is set to alternate between MS and ToF mode. After sufficient signal is accumulated, an automated command in the data acquisition software can be used to perform the calculations or they are manually calculated and entered into the data acquisition program. Alternatively, if a precise fragmentation fraction for a given fragment ion is known, it can be used to calculate the number of ions by multiplication of the inverse of the fragmentation ratio with the ion intensity of that fragment.

The linear relationship of the ionization efficiency with the size of the molecule is the basis of the quantification of unknown samples in the AMS. Larger molecules have larger ionization efficiencies than smaller molecules, and the increase in ionization efficiency is linear with increasing molecule size. Therefore, if the ionization efficiency can be determined for one molecule, the ionization efficiencies for all other species can be related to the measured ionization efficiency of the initial species.
As described above, ammonium nitrate is used as the primary mass calibration species because the ionization efficiency, density, and shape are well known, and ammonium nitrate does not leave residue to interfere with subsequent measurements. Also, ammonium nitrate vaporizes with close to 100% efficiency and it is well-focused by the aerodynamic lens so that all the particles can be detected.

The ionization efficiency for nitrate ($I_{E_{NO3}}$) is calculated by determining the number of ions produced per particle of a select size as shown in equation (6).

$$ I_{E_{NO3}} = \frac{IPP}{\frac{\pi d_m^3 \rho e^{-21X}f_{NO3}}{6} * \frac{MW_{NO3}}{N_A}} $$

(6)

Ions per particle is determined from the calibration, $d_m$ is the mobility diameter of the calibration particles (typically 350 nm), $\rho$ is the density of ammonium nitrate, $X$ is the shape factor (<1 for non-spherical particles), $f_{NO3}$ is the fraction of NO$_3$ in NH$_4$NO$_3$.

**Particle size calibration.** Particle size calibrations are performed by sampling particles of known size, usually polystyrene spheres (PSLs) and particles delivered from a DMA, usually NH$_4$NO$_3$. The use of PSLs represents a primary size standard, but the range of sizes is somewhat limited (from ~ 100 nm). Therefore, the DMA particles can be used to extend the range of measurements to smaller sizes.

For PSL measurements, the first step is to increase the vaporizer temperature to ~800 ºC. In the data acquisition program, $m/z$ 104 (styrene parent ion) is monitored. ToF data is then recorded for a series of different sized PSLs. Similarly for NH$_4$NO$_3$ ToF data is collected for a range of sizes, but in this case $m/z$ 46 is selected and a vaporizer temperature of ~600 ºC is set. Figure 1-8 shows mass peak arrival times for four PSL sizes.
It is important to cover as wide a range as possible in size since extrapolating the fitted curve beyond the data points can lead to significant errors. NH₃NO₃ is used to extend the measurements to smaller sizes and the PSLs extend the measurements to larger sizes. The solid line in Fig. 1-9 is a non-linear least squares fit to the combined PSL/NH₄NO₃ data set using Eq. (7).

\[
Velocity = V_{g(lens)} + \frac{[V_{g(exit)}-V_{g(lens)}]}{1+(D^{*}/D)^b}
\] (7)

\(V_{g(lens)}\) is the velocity of the gas in the lens, \(V_{g(exit)}\) is the gas velocity at the lens exit, \(D^{*}\) is an effective scaling diameter and \(b\) is the power dependence. The \(V_{g}\) terms provide limits to the particle velocity for small and large size particles. A small particle cannot
travel faster than the expanding gas ($V_{g(\text{exit})}$) and a very large particle cannot go slower than the velocity of the gas in the lens ($V_{g(\text{lens})}$). The product of the velocity calibration is the fitted coefficients, which, for this example, are shown in Fig. 1-9. These coefficients are then entered into the data acquisition program.

**Flow rate calibration.** It is important to know the precise rate of flow of gas into the AMS. This helps in normalizing the measured particle mass to the volume of sample taken. This allows one to report particle mass loadings in the conventional units of $\mu g/m^3$, where $\mu g$ comes from the mass spectrometer measurement and the $m^3$ represents the volume of air sampled.

![Graph of particle velocities plotted against aerodynamic diameter. PSL particles are usually used as primary standard but NH$_4$NO$_3$ are used to extend the curve to smaller sizes.](image)

**Fig. 1-9.** Particle velocities plotted against aerodynamic diameter. PSL particles are usually used as primary standard but NH$_4$NO$_3$ are used to extend the curve to smaller sizes.
The flow of sample into the AMS is fixed by a critical orifice (~100 µm diameter) mounted upstream of the aerodynamic lens. The pressure drop across this aperture is large enough that a choked-flow condition exists (ambient pressure to ~1 torr). Under these choked-flow conditions the volumetric flow through this orifice is constant. The acquisition program continually monitors this flow rate by measuring the pressure at the entrance to the aerodynamic lens. There is a unique relationship between lens pressure and flow and lens transmission properties. In this system an absolute pressure gauge is used to monitor the lens inlet pressure, and from calibration the volumetric flow can be extracted. This relationship between pressure and flow is based on the Poiseuille equation, relating the volume flow rate of a viscous gas through a laminar flow element. In this case the laminar flow element is the aerodynamic lens tube which has an entrance pressure of ~1 torr and an exit pressure of 10⁻³ torr.

*Quadrupole tuning.* This procedure aims to optimize the throughput of ions through the mass spectrometer by tuning the various voltages that control the formation of ions in the ionization region and their subsequent extraction, and focusing into the quadrupole mass spectrometer, followed by their deflection into the electron multiplier detector. This is regarded as one of the most crucial optimization procedures that directly affects the ionization efficiency of instrument and therefore, influences its sensitivity. Table 1-1 lists QMS voltages and their functions. These voltages are applied on various parts in the region between the ionizer and the electron multiplier detector. The ion reference, cathode and field axis voltages have fixed values and are not, contrary to the rest of the voltages, part of regular optimization procedure.
**Electron multiplier calibration.** To perform this calibration, the acquisition program is configured to look for single ion pulses that exceed the electronic noise level, using a threshold approach. This involves applying a threshold that is just above the electronic noise level by shutting off the ion production (turning off the filaments) and manually adjusting the threshold level. When the filaments are turned back on, any signal exceeding this threshold level can be counted and processed. The data acquisition program can measure the area of single ion pulses. There is a large distribution of pulse heights that can be observed, resulting in a Poisson probability distribution of pulse heights.

**Table 1-1.** QMS voltages and functions.

<table>
<thead>
<tr>
<th>Voltage</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Reference</td>
<td>Nominal potential at which ions are formed and reference potential for all other potentials</td>
<td>90 V</td>
</tr>
<tr>
<td>Cathode</td>
<td>Determines acceleration voltage of electrons and therefore the nominal ionization energy</td>
<td>70 eV</td>
</tr>
<tr>
<td>Focus</td>
<td>Affects peak level</td>
<td>12 V</td>
</tr>
<tr>
<td>Field Axis</td>
<td>Nominal voltage of ions in the rod system</td>
<td>14 V</td>
</tr>
<tr>
<td>Extraction</td>
<td>Accelerates ions from ionization area towards the rod system</td>
<td>130 V</td>
</tr>
<tr>
<td>Inner Deflection</td>
<td>Uses inner plate voltage to direct ions through the 90 turn to reach electron multiplier</td>
<td>15 V</td>
</tr>
<tr>
<td>Outer Deflection</td>
<td>Uses outer plate voltage to direct ions through the 90 turn to reach electron multiplier</td>
<td>30 V</td>
</tr>
</tbody>
</table>
For this reason we determine the gain from the "average" pulse height. The integrated area of the average pulse height has units of charge (amps x time) and, when divided by the Faraday Constant (1.6x10^{-19} Coulombs per charge), gives the number of electrons per incident ion, or the multiplier gain.

Over time, the performance of the electron multiplier slowly degrades, reducing the magnitude of the signal generated per ion detected. This deterioration is taken account of by the multiplier calibrations described above, but as the multiplier degrades continuously, a correction must be applied as a function of time. The relative degradation can be assumed to be uniform for all parent species, so a correction factor can be calculated by inspecting the signals due to the air beam that enters the instruments with the aerosol sample (either m/z 28, which corresponds to N_2^+ or m/z 32, which corresponds to O_2^+), which would be constant in ambient air if the amplification of the ion signal did not decrease with time. While this correction is designed to take account of changes to the multiplier’s amplification, it will also account for any changes in its ion collection efficiency and the transmission of the quadrupole.

Overview of AMS Data Analysis

AMS data is usually analyzed using the IGOR PRO, a data plotting and analysis software (Wavemetrics, Portland, OR); therefore the data acquisition is usually in a format that can be directly read by IGOR, usually in .itx or .hdf formats. Functions are available to calculate time trends of particle mass loadings for selected chemical species, to analyze individual or group-average mass spectra. Individual or group-average particle
ToF data can also be analyzed and images can also be displayed that show size distribution time series for the different masses that were monitored in ToF mode.

The analysis package also provides data diagnostic and data correction functions that help verify the quality of the data. One of the most important components of this analysis procedure is the fragmentation table (Allan et al., 2003). This feature is at the heart of the AMS analysis and provides a way of interpreting the mass spectra so that different chemical classes can be extracted from the spectra. Interpretation of mass spectra can be complicated by the fact that different species can be detected at the same amu. The “frag” table makes it possible to separate the relative contribution or ion intensity that gives rise to a particular mass peak. The list is based on laboratory measurements of different aerosol types, known isotopic ratios, and ratios from the NIST database for electron impact ionization mass spectra for certain species. For some species it is simply a "best guess," based on comparison with data from other particle instrumentation. The “frag” table has developed over time and continues to evolve as our understanding of the data grows.

IGOR procedures are open source code, and other AMS users have contributed specialized routines for different applications. Since this is open source code, all users have the ability to optimize the data processing for their individual applications. The majority of AMS users use this data plotting and analysis tool; however, it is not the only way to process AMS data. All AMS data files are written in ASCII format so they are easily imported into different data analysis and plotting software packages.
Research Objectives and Dissertation Outline

The main goal of this research is to use the capabilities of the aerosol mass spectrometer to study the sources of organic nitrogen aerosols in the ambient air as well as in the laboratory. The main focus is on organic aerosols because their concentrations, composition and the processes that control their formation and transformation in Cache Valley air are not well understood. An understanding of the sources, atmospheric processes and the corresponding effects on aerosol properties is essential in order to understand the importance of ambient aerosols and to enable appropriate remediation scenarios into future regulations.

This dissertation is divided into 6 chapters. Chapter 2 gives results from the field campaign that was carried out in Cache Valley in Northern Utah during the year 2004. This chapter emphasizes organic aerosols. Chapter 3 continues with field measurements in Cache Valley during the sampling year 2005. This chapter also introduces some of the laboratory experiments conducted as a follow-up to the observations during the ambient sampling. Chapter 4 builds on the chamber experiments from the previous chapter. Here, more details on the chemistry of tertiary amines including gas phase and aerosol phase products are discussed. A reaction mechanism is also proposed. Chapter 5 outlines an ion chromatographic method that was developed for detecting and quantifying some of the potential products identified in the previous chapter. Finally, Chapter 6 gives a summary of the research findings and offers suggestions for future research.
References


CHAPTER 2
CHARACTERISTICS OF ORGANIC AEROSOLS DURING SEVERE WINTER INVERSIONS IN NORTHERN UTAH’S CACHE VALLEY

Abstract

Physical and chemical characteristics of organic aerosols sampled in the Cache Valley using an AMS are presented. Qualitatively, at least four distinct sources appear to contribute to the formation process of organic aerosol. Peaks representing these different contributions to aerosol are mass-to-charge \( m/z \) 57; a peak that is usually associated with hydrocarbon-like species; \( m/z \) 44 usually associated with oxygenated organic carbon, \( m/z \) 58 probably representing nitrogen-containing organic aerosol, and \( m/z \) 60 a key fragment associated with wood smoke combustion. Polycyclic aromatic hydrocarbons (PAHs) were also observed in the mass-to-charge range of 190-300 and perhaps lower. Mass distributions of the organic aerosols peaked in the accumulation mode size range with one exception. Distributions obtained using \( m/z \) 57 also appears in the ultra fine mode (~150 nm) and probably represents primary emissions from vehicles. Principal component analysis was applied to the data. Application of principal component analysis to the data resolves two meaningful components. Attempts to resolve \( m/z \) 44 and \( m/z \) 58 were not successful, perhaps because \( m/z \) 44 may be also produced by species with \( m/z \) 58. The two components are closely associated with \( m/z \) 44 and 57, the relative contribution by mass being 65% and 35% for components 1 and 2, respectively. Component 1 correlated well with the nitrate concentration, and appears largely due to oxygenated organic aerosol. This component is probably representative of secondary
reaction chemistry. Component 2 appears hydrocarbon-like, implying a source associated with primary organic aerosols, however it correlated weakly with carbon monoxide and nitrogen oxides associated with combustion of fossil fuel. There appeared to be no influence of temperature and relative humidity on the formation processes of the organic aerosol.

**Introduction**

Fine particulate matter (PM) is ubiquitous in the troposphere and the role that it plays in health, visibility, and global climate change has been a subject of interest by many researchers in the recent years (Jacobson et al., 2000; Seinfeld and Pankow, 2003; Kanakidou et al., 2005). Fine PM scatter solar radiation thus limiting visibility (Eldering and Cass, 1996; Watson, 2002). When inhaled, they can give rise to inflammation of respiratory tissues, heart complications, low birth weight, and even death (Dockery et al., 1993; Long et al., 2002; Parker et al., 2005). On a global scale, fine particles scatter or absorb incoming solar radiation and also modify cloud properties such as reflectivity and lifetime. These effects, the direct and indirect radiative forcing, can alter climate (Ravishankara, 1997; Jacobson et al., 2000; IPCC, 2007)

Depending on the location, the organic fraction of particles accounts for ~10%-70% of the total fine PM mass concentration (Murphy et al., 1998, Jacobson et al., 2000). The organic fraction is composed of a complex mixture made up of many individual compounds (Rudich, 2003) that exhibit a wide range of physical, chemical and thermodynamics characteristics (Saxena and Hildemann, 1996). The study of organic aerosols is also complicated due to lack of a single analytical method that can be used to
study the wide array of compounds (Turpin et al., 2000). Knowledge of the characteristics of these particles together with their sources is needed in order to fully understand the role that they play in local, regional and global air quality (McMurry, 2004).

Organic aerosol sources can broadly be classified as primary and secondary (Jacobson et al., 2000; Kanakidou et al., 2005). Primary sources are those in which particles are emitted directly into the atmosphere (for example from vehicle exhaust) while secondary sources are those in which particles are formed when precursor volatile organic compounds react in the atmosphere to form low volatility products (e.g. Odum et al., 1996). These can either nucleate to form new particles or coat the surface of pre-existing particles (Rudich, 2003). Primary and secondary organic aerosols can be emitted naturally from sources such as vegetation and sea sprays (Seinfeld and Pankow, 2003) or they can be from anthropogenic sources such as fossil fuel and biomass combustion (Jacobson et al., 2000). The relative contribution of primary and secondary organic aerosols to the total organic fraction has proven to be a challenge to many researchers, mainly because there is no direct chemical analysis method for studying these source and formation processes. Indirect methods have been employed for these purposes such as cluster analysis (Marcolli et al., 2006), custom principal component analysis (Zhang et al., 2005a) and positive matrix factorization (Lanz et al., 2007).

Cache Valley is located in Northern Utah where occasional severe winter inversions occur that may last for several days that leads to a large accumulation of fine PM close to the surface. During January and February of 2004, Cache Valley experienced
one of the worst air quality problems in the country (Malek et al., 2006). This was due to prolonged temperature inversion periods facilitated by the valley geography, leading to several exceedances of the standard EPA regulatory limits (Silva et al., 2007). Mangelson et al. (1997) had previously conducted winter-time studies in this area using off-line filter based methods and they identified ammonium nitrate as the major component of the fine PM, with the organic aerosol fraction being the second major contributor. With data acquired by an AMS, this chapter reports on the characteristics of organic aerosols in Logan, Utah during the winter inversions of 2004.

**Experimental**

*Field Sites and Sampling Dates*

Details about the sampling sites and AMS deployments and sampling procedures can be found in Silva et al. (2007) and only a brief summary will be given here. Valley-wide meteorological parameters during the same period have been reported by Malek et al. (2006). The AMS was operated at two main sites during this study experiment in Logan, Utah during January and February of 2004. The first site was located on the third floor of the chemistry and biochemistry building at Utah State University (USU) campus. This site was situated away from major roads close to the mountain benches. This was to contrast it with the downtown Logan sampling site in which AMS was close to the main street and proximity to other busy roads. The AMS was deployed at the USU site from 10\textsuperscript{th} to 26\textsuperscript{th} January 2004, while the sampling at the downtown site took place between February 4\textsuperscript{th} and March 11\textsuperscript{th}. The two sites are separated spatially by a distance of ~2.5 km but with an altitude difference of ~ 60 m. The downtown site was co-located at the
Utah Department of Air Quality (UDAQ) monitoring site for Logan where on-site continuous measurements of criteria pollutants, including fine particulate matter (PM\textsubscript{2.5}), NO\textsubscript{x}, and meteorological parameters were made during the sampling period.

**Results and Discussion**

*Contribution of Organic Aerosols*

A number of species contribute to aerosol loading during winter-time (Silva et al., 2007). The total amount of AMS aerosol was determined using a fragmentation list developed by Allan et al (2004) and calibration procedures in Jayne et al. (2000) and Jimenez et al. (2003). This total amount of aerosol was about 90% of the PM\textsubscript{2.5} measured by the state, although AMS measures ~PM\textsubscript{1} and doesn’t measure non refractory components such as elemental carbon and crustal species. This means that most of the aerosol in the Valley is semi-volatile and in the accumulation mode. Table 2-1 gives the contribution by mass of the different species that were measured by the AMS. As shown, the organic aerosols accounted for ~15-25% of the total mass of fine particles measured by the AMS, variation being controlled by the severity of the inversions. For example, during the peak of an inversion, as much as 20 $\mu$g/m\textsuperscript{3} of the organic aerosol was recorded.

<table>
<thead>
<tr>
<th>Avg. Conc.</th>
<th>Sulfate</th>
<th>Nitr ate</th>
<th>Ammonium</th>
<th>Organic Aerosol</th>
</tr>
</thead>
<tbody>
<tr>
<td>% of Total</td>
<td>6±0</td>
<td>52.5±1.5</td>
<td>18.5±0.5</td>
<td>22.5±0.5</td>
</tr>
<tr>
<td>Avg. Conc.</td>
<td>1.74±0.04</td>
<td>15.57±0.43</td>
<td>5.47±0.14</td>
<td>6.69±0.14</td>
</tr>
</tbody>
</table>
A time series plot of the total AMS concentration versus that of the organic aerosols is shown in Fig. 2-1. Here the organic aerosol fraction is defined as all signals that cannot be attributed to the known inorganic substances such as sulfate, nitrate, water, ammonium, and chloride (Allan et al., 2003). Clearly, the organic aerosol concentration increased with the total amount of aerosol during the inversions. However, the two did not track each other well ($r^2 < 0.3$). Since the major contributor of the total aerosol mass is ammonium nitrate, this means that some of the peaks that contribute to the organic fraction may have similar temporal profile to that of ammonium nitrate while others deviate from it, perhaps suggesting different sources or processes.

Fig. 2-1. Organic aerosol mass concentration versus total aerosol concentration detected by the AMS.
The mass spectrum of the organic fraction (Fig. 2-2) shows remarkable complexity. This is because EI ionization causes more fragmentation compared to other ionization techniques. Even when compared to the NIST EI database, the AMS shows more fragmentation except for a few compounds that are stable (Dzepina et al., 2007). Interpretation of the organic spectra poses an enormous challenge and different methods of interpreting the ion peaks are usually employed, some of which will be discussed in the subsequent sections of this chapter. Generally, fragmentation patterns indicate that the spectra is composed of broad groups such as long chain and branched alkanes, aromatics, oxygenated species, nitrogen-containing species and polycyclic aromatic hydrocarbons (PAHs).

**Fig. 2-2.** Mass spectrum of organic aerosol and PAHs averaged over an inversion episode in the downtown Logan sampling site. Some representative ion peaks are shown.
At this point no source profiles of organic aerosol emissions specific to Cache Valley, UT exist, so a quantitative attribution of organic aerosol sources using mass spectrometry or other methods cannot be accomplished. However, in the mass spectral data signals are observed out to \( m/z \sim 200 \) and a qualitative look at temporal trends reveals at least four distinct profiles. Figure 2-3 show profiles of four fragment ions representative of these trends. Mass-to-charge \( m/z \ 44 \) \((\text{CO}_2^+)\) is an ion fragment typically representative of oxygenated organic aerosol (OOA) (Zhang et al., 2005b). This ion predominates from organic molecules with oxygen-containing functional groups, especially poly-carboxylic acids. In many locations, the temporal profile of this ion shows a clear diurnal difference increasing during the day and decreasing at night. In Logan, \( m/z \ 44 \) resembles the variation of nitrate ion, showing continual increases anytime an inversion is present without much diurnal behavior.

In contrast to \( m/z \ 44 \), the temporal profile of \( m/z \ 57 \) shows only minimal increases during inversion conditions. The peak at \( m/z \ 57 \) is dominated by \((\text{C}_4\text{H}_9^+)\) an organic ion representing hydrocarbon-like organic aerosol (HOA) observed frequently from sources such as vehicle emissions (Zhang et al., 2005b). Maximum signal from this ion peak tends to occur during rush-hour time periods and shows a transitory profile with short spikes followed by decreases. Peaks associated with this temporal profile do not show a large tendency to build up in concentration as those associated with the \( m/z \ 44 \) time trend.

In Fig. 2-3c, the temporal profile of a third ion, \( m/z \ 58 \) is shown. This ion has not been encountered as a major component of signals in other locations studied by the AMS, (e.g. Alfarra et al., 2004; Zhang et al., 2005b) although it has been observed as a minor
component. In Logan it frequently is one of the highest intensity organic ions detected. The temporal variation of this ion shows sharp increases during inversion conditions, however sometimes a strong diurnal profile is superimposed on the increases. At the downtown sampling site, maximum signal from this peak is generally, though not always observed during the middle of the night (~2-5 AM) with decreases in concentrations during the afternoons (~1-4 PM). We hypothesize that the dominant ion fragment represented here is (C$_3$H$_8$N$^+$) from a nitrogen-containing organic aerosol and that it may represent amine compounds in the particulate phase. Although other peaks could contribute to m/z 58, it is likely dominated by the amine fragments; given the other even numbered peaks such as m/z 86 are also observed. In addition, Cache Valley is an agricultural area with high concentrations of ammonia. It is possible that amines may also be emitted in large amounts. Amines have been reported by researchers in several locations using laser-desorption ionization mass spectrometry (Murphy and Thomson, 1997; Angelino et al., 2001; Tan et al., 2002).

The final temporal profile found in Fig. 2-3d is for m/z 60. This ion is known from laboratory experiments to be a major fragment ion from levoglucosan, an organic tracer for particles emitted from wood-burning. This marker ion detected by the AMS worked well for identifying particles from a large natural fire event in Houston, Texas. In the Logan study, the peak values (marked with asterisks) for the ion detected do occur during the late evening (typically 9 PM-12 AM) consistent with wood burning smoke. However, a general increase in ion signal is also observed during inversion conditions from 2/12-2/18/2004. This could suggest a secondary source for this ion peak since the
increase is well correlated with ammonium nitrate and oxygenated organic aerosol. Without proper source emission studies, quantitative estimate of the fraction of aerosol detected by the AMS due to wood smoke from wood burning is possible with some degree of uncertainty. However, as can be seen, the y-axis for the major levoglucosan ion peak in Fig. 2-3d is a factor of ~4 lower than that from Fig. 2-3a-c. Although this not indicative of the amount of contribution from this source, wood smoke may generally be contributing less given that most of the chemistry in the Valley appears to be from secondary reaction chemistry. Chemically speciated filter data obtained by UDAQ also support this contention, as potassium and elemental carbon (EC) concentrations in PM$_{2.5}$ are typically low, though they are major components of wood smoke (UDAQ 2005).

**Fig. 2-3.** Temporal profiles of representative organic aerosol peaks during inversions in Logan in February 2004.
Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are known for their toxicity, carcinogenicity and mutagenicity (Hannigan et al., 1998). They result from combustion of carbonaceous materials at high temperatures. Typical anthropogenic sources include coal-fired power plants, cigarette smoke, wood smoke, and car emissions. Natural sources include forest fires and volcanic eruptions.

PAH detection using an AMS has been performed by Dzepina et al. (2007). The method that was used to detect PAHs was used in the Logan data and the mass spectrum at the USU campus sampling site is shown in Fig. 2-4. The total mass concentration of the PAHs at the USU campus site was ~15 nanograms per cubic meter (ng/m$^3$). Due to the low concentration of PAHs in both sampling sites, no diurnal pattern was observed, but the highest concentration was recorded in the evenings at the USU site. The major peak observed at the downtown site was $m/z$ 202, usually associated with pyrene and/or fluoranthene, whereas at the USU campus site, the dominant peak was $m/z$ 252, usually associated with benzo[a]pyrene and its structural isomers.

Marr et al. (2006) and Dzepina at al. (2007) performed analysis of particle bound PAHs using AMS acquired data from Mexico City. They measured concentration of between 90-910 ng/m$^3$. The peaks they used for the averaging includes $m/z$ 202-300. They observed a strong diurnal pattern that peaked in the morning hours, suggesting traffic-related sources. The PAH distribution detected in Logan shows lower $m/z$ peaks including 152, 166, and 178. Larger PAHs usually are stable and do not easily fragment. This observation is probably from lower mass PAHs, typically in the gas phase partitioning into the particles due to the low winter temperatures (~ -10º C).
Fig. 2-4. PAH ion peaks observed at the USU campus sampling site. Some peaks were detected below this range and it is possibly due to gas phase PAHs partitioning into aerosol phase due to the low winter temperatures.

Size Distributions

The mass size distributions of the representative ion peaks introduced earlier are shown in Fig. 2-5. These peaks had their masses in the accumulation mode. The highest concentrations for these peaks were in the 500-600 nanometers (nm) size range. Although m/z 57 did not have a distinct bimodal size distribution as reported in other AMS studies (e.g. Alfarra et al., 2004; Allan et al., 2004), there was tailing towards the ultra fine mode. This fine mode is typically associated with fresh emissions from vehicles, but a clear break in the distribution is not observed because of inversion chemistry.
Fig. 2-5. Size distributions of representative organic aerosol peaks. There was some ‘ultrafine’ mode in m/z 57, typically associated with fresh traffic emissions.

**Ion-Series Analysis**

The organic aerosol fraction was analyzed using an ion-series analysis method, also called delta analysis (McLafferty and Turecek, 1993). In this mass spectrometric analysis technique, organic molecules are assumed to consist of a backbone, R, made up of CH₂ groups with functional chains attached to it. Electron impact ionization of these molecules results in formation of mass spectra in which groups of peaks have a 14 amu separation due to fractionation at different positions in the CH₂ chains. The masses at which these peaks appear are characteristic of the R backbone of the molecule. Series with different Rs are classified in this approach according to their delta value

\[
\Delta = \text{peak mass} - 14n + 1
\]
where $n$ is the number of CH$_2$ groups remaining on the backbone. Different $\Delta$ groups are associated with different groups of organic species. Lab- and field-measurement results indicate that some of the $\Delta$ groups can be used as signatures of certain types of organic aerosol particles e.g. $\Delta = 0, 2 \ (m/z=13, 27, 41, \ldots \text{ and } 15, 29, 43, \ldots \text{ amu})$ correspond to traffic related aerosol; $\Delta = 3 \ (m/z = 16, 30, 44, \ldots \text{ amu})$ correspond to photochemically produced particles; and $\Delta = -7 \ (m/z = 76, 90, \ldots \text{ amu})$ correspond to aromatics. However, no direct association between $\Delta$ groups and single-chemical species can be made.

In Fig. 2-6, on 1/16/04 during morning and afternoon periods the average composition of the organic particles is shown by displaying the average pattern of contributions of the mass signals to the 14 $\Delta$ groups determined from ion series analysis as described above. Morning spectra show the most prominent delta groups as those with $\Delta = -4, -2, 0, 2, \text{ and } 3$. In the afternoon, the most prominent delta group is was still 2, but delta 0 and 3 had also increased. This points out to traffic related sources although there are indications that the afternoon aerosol may be from photochemical activity (a stronger delta 3). Although $m/z$ 44 and 58 may both comprise delta 3 according to ion-series analysis, their characteristics as discussed earlier indicate that they may be different subsets of the series and indicative of different sources. Ozone mixing ratios in Cache Valley are typically on the order of 50-70 ppb during winter, a similar mixing ratio to that observed throughout the Mountain West region. This means that ozone is expected to play an important role in photochemical reactions. As it will be shown later in the chapter, perhaps it does this indirectly.
Fig. 2-6. Ion-series analysis of organic aerosols during the morning and afternoon hours at the USU campus sampling site. Morning aerosol was dominated by delta 2, suggesting traffic-related sources.

Principal Component Analysis

As described in previous sections of this chapter, a few peaks are typically used as representative of broad groups of organics. But there are about 270 organic-containing peaks in the AMS data obtained at a sampling rate of 5-10 minutes. It can therefore be difficult to identify patterns and for these reason multivariate statistical methods such as
principal component analysis are used. PCA is a data reduction method that can be used to create a few virtual variables (peaks) based on their covariance or correlation that are easy to interpret. These virtual variables, referred to as principal components when used with other external variables can be useful in understanding source characteristics of the aerosol. The goal of PCA is to map variables into principal components without losing much information. To see relationships clearly, the solution is sometimes rotated (e.g. varimax rotation, a type of rotation in which eigenvectors remain orthogonal as the axes are rotated). PCA was applied to the USU campus data and the results are shown in Table 2-2. There were attempts to resolve the peaks into several components indicative of the various sources as outline by the representative peaks discussed earlier. However, most of the times, two components were resolved that explained variance in over 90% of the data set. When temperature and relative humidity were introduced, three components were resolved, the third being these meteorological parameters. There was high $m/z$ 44 loading in component 1 with a smaller loading in component 2. The peak at $m/z$ 44 can be CO$_2^+$ and/or C$_3$H$_8^+$. Studies with the AMS have shown that the peak is mainly a result if (CO$_2^+$) due to pyrolysis of oxygenated organic aerosol. Oxygenated organic aerosol mostly arises from photochemical oxidation; however a smaller fraction can result from wood burning smoke, which is definitely present in Logan. The result that $m/z$ 57 was almost entirely a component 2 loading is consistent with the fact that it has been used as marker for hydrocarbon like organic aerosol with the main peak being C$_4$H$_9^+$. Mass-to-charge ($m/z$) 58 was almost entirely component 1, correlating with peaks that appear oxygenated. It is important to note that although $m/z$ 44 is usually associated with oxygenated aerosols, the
fact that it could not be resolved from \( m/z \) 58 means that they could be related. In fact \( m/z \) 44 may be from C\(_2\)H\(_6\)N\(^+\), an amine fragment. The relative contribution of the amine fragment or the oxygenated fragment to \( m/z \) 44 is currently not clear. The \( m/z \) 60 peak contributed significantly to both components 1 and 2. This supports the observation that points out the contribution from both primary and secondary sources. Temperature and relative humidity were the only items that comprised component 3. Both temperature and relative humidity showed low factor loadings indicative of weak correlation to components 1 and 2.

**Table 2-2.** Principal component analysis of the organic aerosol peaks at the downtown Logan sampling site.

<table>
<thead>
<tr>
<th>Peak (m/z)</th>
<th>Component 1</th>
<th>Component 2</th>
<th>Component 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>0.904</td>
<td>0.411</td>
<td>0.067</td>
</tr>
<tr>
<td>17</td>
<td>0.902</td>
<td>0.414</td>
<td>0.070</td>
</tr>
<tr>
<td>18</td>
<td>0.869</td>
<td>0.345</td>
<td>-0.083</td>
</tr>
<tr>
<td>30</td>
<td>0.901</td>
<td>0.412</td>
<td>0.075</td>
</tr>
<tr>
<td>31</td>
<td>0.836</td>
<td>0.519</td>
<td>0.112</td>
</tr>
<tr>
<td>43</td>
<td>0.739</td>
<td>0.662</td>
<td>0.047</td>
</tr>
<tr>
<td>44</td>
<td>0.800</td>
<td>0.548</td>
<td>0.042</td>
</tr>
<tr>
<td>46</td>
<td>0.912</td>
<td>0.380</td>
<td>0.048</td>
</tr>
<tr>
<td>55</td>
<td>0.545</td>
<td>0.807</td>
<td>0.045</td>
</tr>
<tr>
<td>57</td>
<td>0.358</td>
<td>0.849</td>
<td>0.070</td>
</tr>
<tr>
<td>58</td>
<td>0.813</td>
<td>0.389</td>
<td>0.211</td>
</tr>
<tr>
<td>60</td>
<td>0.702</td>
<td>0.612</td>
<td>0.146</td>
</tr>
<tr>
<td>71</td>
<td>0.452</td>
<td>0.840</td>
<td>0.041</td>
</tr>
<tr>
<td>77</td>
<td>0.597</td>
<td>0.782</td>
<td>0.100</td>
</tr>
<tr>
<td>79</td>
<td>0.617</td>
<td>0.776</td>
<td>0.050</td>
</tr>
<tr>
<td>115</td>
<td>0.468</td>
<td>0.839</td>
<td>0.117</td>
</tr>
<tr>
<td>124</td>
<td>0.378</td>
<td>0.881</td>
<td>0.128</td>
</tr>
<tr>
<td>139</td>
<td>0.421</td>
<td>0.879</td>
<td>0.090</td>
</tr>
<tr>
<td>TEMP</td>
<td>-0.078</td>
<td>-0.362</td>
<td>-0.778</td>
</tr>
<tr>
<td>RH</td>
<td>0.041</td>
<td>-0.099</td>
<td>0.829</td>
</tr>
</tbody>
</table>
A custom 2-component PCA (CPCA) developed by Zhang et al. (2005a) was used to analyze the data. Mass spectra obtained are shown in Fig. 2-7. Both CPCA and PCA show \( m/z \) 44 and \( m/z \) 58 as strong peaks in component 1 while \( m/z \) 57 as strongly associated with component 2. Factor loading of \( m/z \) 60 was very low in both components. Spectrum of component 1 resembles that of typical hydrocarbon aerosol (alkyl fragments) while component 2 spectrum resembles oxygenated aerosol with the exception of the strong \( m/z \) 58.

![Components 1 and 2 mass spectra from principal component analysis.](image)

**Fig. 2-7.** Components 1 and 2 mass spectra from principal component analysis.
The time series and residual plots of components 1 and 2 are shown in Fig. 2-8. The diurnal profiles for components 1 and 2 are distinctly different. Component 1 did not show much diurnal variation. On the other hand component 2 showed peak concentrations in morning and evening hours, the typical commute periods. There is possibility that wood smoke contributed to this component especially in the evening hours.

**Fig. 2-8.** a) Temporal, and b) diurnal profiles of components 1 and 2. c) Time series of the measured organic mass concentration and components 1 and 2 estimates. d) Variations of the residual of the fit and the absolute residual as a function of time. e) Time series of the ratio of the residual to the measured organic concentration.
In order to provide more insight into these aerosol components, correlation analyses with some of the known tracers were performed. Component 1 was plotted with the nitrate concentration, which is secondary reaction component of the particles in Cache Valley (Mangelson et al., 1997; Silva et al., 2007). As shown in Fig. 2-9, there was very good correlation between the two ($r^2=0.88$). There was no correlation between component 1 and ozone. This is a rather interesting observation given that ozone plays an important role in photochemical reactions. This could possibly mean that it plays an indirect role in the chemistry of the peaks in this component or perhaps the peaks may not be oxygenated, but rather form from different pathways in the atmosphere.
Fig. 2-9. a) Time series of component 1 with nitrate. Scatter plots of component 1 with b) nitrate and c) ozone.
**Source Characterization Study**

A source study was conducted in Ames, Iowa at a deep pit swine facility as part of another research project. Sampling was conducted between August and September of 2005 during an intensive campaign that involved a number of researchers. Generally, particles from this source were larger and therefore could not be captured with the existing AMS inlet system described in Chapter 1. The composition of the submicron particles was largely organic aerosol. Figure 2-10 displays a mass spectrum from this source. Mass-to-charge 58 and other amine-like peaks similar to those detected in Cache Valley were clearly not there. This perhaps indicates that the organic nitrogen aerosol that was detected in Cache Valley resulted from secondary reactions. There is a journal article in Appendix A that has further information on this study.

![Mass spectrum of particles at a swine facility in Ames, IA.](image)

**Fig. 2-10.** Mass spectrum of particles at a swine facility in Ames, IA.
Conclusions

This chapter reports the characteristics (concentrations, mass distributions, and temporal variations) of organic aerosols in Logan during January and February 2004. Peaks representative of four different organic aerosol sources were qualitatively identified. PCA was applied to the organic peaks but only two meaningful components were resolved, probably due to the overwhelming influence of meteorology causing most sources of particulate matter to build up together during stagnation episodes. One of the components showed strong correlation with $m/z$ 57 and the other with $m/z$ 44, used as markers of hydrocarbon-like and oxygenated organic species. Influence of temperature and relative humidity on both components was not significant. However, the good correlation of component 1 with nitrate suggests secondary formation. The fact that the nitrate peaks correlated well with component 1 is further evidence that supports this. Mass-to-charge 57 had the strongest association with component 2, which exhibits a strong diurnal pattern that peaks during morning and evenings, perhaps an indication of traffic contributions.

References


Utah Division of Air Quality (UDAQ): Query air monitoring data, State of Utah Department of Environmental Quality, 2005.


CHAPTER 3
TRIMETHYLAMINE AS PRECURSOR TO SECONDARY ORGANIC AEROSOL FORMATION VIA NITRATE RADICAL REACTION IN THE ATMOSPHERE

Abstract

Amines in fine particulate matter have been detected and quantified during ambient studies of winter inversions in Logan, Utah, using aerosol mass spectrometry. Amine-related compounds account for 0.5-6 µg/m³ of fine particulate mass during some wintertime periods. The amine contributions sometimes show a clear diurnal pattern, reaching peak concentrations during the middle of night while decreasing during morning and afternoon. Smog chamber reactions show that the reaction of tertiary amines with nitrate radical can account for this behavior in the atmosphere. The reaction of trimethylamine and nitrate radical yielded a particle formation rate constant of 4.4x10⁻¹⁶ cm³/molec/s with a conversion rate to the aerosol phase of ~70%. This suggests that amines could be a significant contributor to secondary organic aerosol formation in areas where nitrate radical is a significant player in oxidation chemistry.

Introduction

Amines are known to be emitted from both natural and anthropogenic sources. Early measurements from catalyst-equipped vehicles showed that amines are emitted at low concentrations. Cadle and Mulawa (1980) measured amines at the part-per-billion (ppb) level in exhausts from cars equipped with catalysts. Westerholm et al. (1993) also

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3 Coauthored by Mark E. Erupe, Philip J. Silva, Derek Price, John Elias, Quentin G. J. Malloy, Li Qi, Bethany Warren and David R. Cocker III. Reproduced and modified with permission from Environ. Sci. Technol., 42, 4869-4696.
reported low concentrations from both gasoline and diesel fuel emissions, with amine emission rates less than the detection limit of 1 µg/km in all cases. Industrial sources of amines include sewage treatment facilities and waste incinerators (Leach et al., 1999).

Numerous studies have shown that significant concentrations of amines are present near agricultural facilities such as dairies and feedlots. Research during the 1970s qualitatively examined the presence of amines from such sources, showing a number of simple primary, secondary, and tertiary amines and indicating that amines make up to 10% of total gas-phase nitrogen emitted (Luebs et al., 1973; Mosier et al., 1973). More recent studies have reported quantitative data, showing that a range of amines are present at high-ppb levels near such agricultural operations. Schade and Crutzen (1995) identified the tertiary amines, trimethylamine and triethylamine as present in the highest concentration. Rabaud et al. (2003) estimate emission rates of 0.3 pounds of amines (including pyridine) per head of cattle per year (lb/hd/yr) at a dairy. Other estimates show possibly higher emission factors for amines, up to 12 lb/hd/yr (San Joaquin Valley Air Pollution Control District, 2005).

The major reactions of aliphatic amines in the gas-phase are believed to be with atmospheric oxidants such as OH radical and O₃. Atkinson reported rate constants for the reaction of OH ($k_{OH}$) with various alkyl amines on the order of 2-9 x10⁻¹¹ cm³/molecules/s (Atkinson et al., 1989). This leads to atmospheric lifetimes on the order of ~3-13 hours assuming an OH concentration of 1x10⁶ molecules/cm³. Rate constants for gas-phase reactions between amines and ozone were reported by Tuazon et al. (1994).
Relatively rapid reactions with ozone were observed for the secondary and tertiary amines. Reactions by other atmospheric gases have not been reported.

During the 1970s, significant studies into amine chemistry focused on amines as precursors to nitrosamines. Nitrosamines are carcinogens in animals and the reaction was of concern for the potential health impacts of products in the air. It was showed that under photochemical oxidation conditions, amines react with nitrous acid to form nitrosamines (Pitts et al., 1978; Tuazon et al., 1978). Since HONO forms readily from NO$_2$ in the presence of water, the reaction proceeds if amines are also present. However, nitrosamines rapidly undergo photolysis in the atmosphere yielding back the relevant amine and NO (Tuazon et al., 1984).

Sporadic reports of particulate amines have appeared for several decades. The earliest work was performed by Novakov and co-workers who conducted a series of particle studies using X-ray photoelectron spectroscopy (Novakov et al., 1972; Dod et al., 1984; Appel et al., 1976). The studies indicated the presence of a non-ammonium reduced form of nitrogen in aerosol particles and even suggested that ammonium measurements using water-based extraction techniques may suffer from positive artifacts due to hydrolysis reactions of amines. Later studies suggested that the reduced form of nitrogen was accounted for by amino acids (Milne and Zika, 1993). However, at the same time reports indicated the presence of amines in precipitation droplets (Gorzelska and Galloway, 1990; Gorzelska et al., 1992). Recently, Murphy et al. (2007) performed chamber reactions looking at particulates from amines and reported that primary and
secondary amines produce salts but that tertiary amines produce non-salt secondary organic aerosol in yields of ~5–23% via reactions with OH and ozone.

In the last 10 years, a number of studies using single particle laser desorption/ionization-mass spectrometry (SPLDI-MS) have indicated the presence of amines at many different sites. Murphy and Thomson (1997) were the first to report that single particle mass spectra acquired at Idaho Hill showed evidence of fragment ions of amines. Since that study, many other groups utilizing laser mass spectrometry have reported similar findings in other locations. Angelino et al. (2001) reported strong signals of amine components in up to 80% of particle in Riverside, California. The amine particles exhibited a strong diurnal pattern correlating with wind direction, interpreted as indicating fresh emissions. Outdoor smog chamber experiments performed during this study also confirmed that alkyl amines can react with ambient concentrations of oxidants and acids to form condensed-phased products. Other studies by Tan et al. (2002) at an urban site in Toronto, Ontario, Glagolenko and Phares (2004) in College Station, Texas, and Beddows et al. (2004) at a rural site in Scotland have observed amine fragmentation patterns in single particle mass spectra. These are just a few examples of studies with such results. None of the SPLDI-MS studies have addressed the issue of quantifying the signals to determine mass concentrations of the amine components. However SPLDI-MS methods are known to suffer from significant matrix-effects that can make quantitative analysis difficult (Morrical et al., 1998; Gross et al., 2000).

Quantitative studies of particulate amines are rare. Zhang and Anastasio (2003a) discussed the concentrations of free and combined amino compounds in particles and
fogwater at Davis, California. Fine particles were enriched in protein-related amino compounds while fogwater contained more non-protein related amino compounds such as methylamine. Zhang and Anastasio (2003b) also showed that organic nitrogen compounds react with ozone in fogwater to form various products, including inorganic ions. Makela et al. (2001) reported the interesting finding that amines may play a role in particle nucleation events. Specifically, the presence of dimethylammonium (the protonated cation of dimethylamine) in particles was the major difference between particle nucleation events and non-events in a forest in Finland.

Despite the mounting anecdotal evidence that amines are present in the particulate phase, no attempt at systematic identification and quantification of amine contributions to ambient particulate matter has been described. Here we present evidence from ambient studies in Utah that amines can be a significant component of ambient particles. Data from smog chamber experiments suggests that trimethylamine reaction with nitrate radical may be a critical process for producing secondary organic aerosol. The major instrument utilized for these studies was the AMS.

Experimental

For ambient data described here, the AMS sampled during the winter seasons (January-March) of 2004, 2005, and 2006 at various locations in the Cache Valley, Utah. For ambient sampling during 2004 and 2006 the AMS sampled ambient particles with 10 minute time resolution. During 2005, ambient sampling was alternated with indoor sampling each 10 minutes.
A series of experiments using trimethylamine were conducted in the UC Riverside/CE-CERT environmental chamber. The chamber facility has been previous described by Carter et al. (2005). Briefly, the environmental chamber consists of a temperature controlled enclosure that is continually flushed with purified air. Two 90 m³ Teflon (2 mil FEP Teflon) film reactors are hung on a rigid frame that descends during the experiment to maintain a slight positive differential pressure between the bags and the enclosure. The experimental runs were all batch and were conducted under dry (RH<0.1%) conditions and a bank of 80 blacklights was used as the irradiation source. Injection and sample ports are located at bottom of the each reactor. Hydrocarbons are injected into a glass manifold where they were evaporated into a stream of pure N₂ and flushed into the reactors. A Dasibi Environmental Corp. 1003-AH Ozone analyzer monitored ozone concentration. Carbon monoxide was monitored with a Thermal Environmental model 40C CO analyzer, while a Thermal Environmental Instruments model 42C chemiluminescent NOₓ analyzer monitored NO, NO₂ and NOₓ, for all experiments. Particle size and concentration was measured throughout the experiment using an in-house built scanning mobility particle spectrometer (SMPS) located inside the chamber enclosure. The SMPS consists of a TSI model 3077 ⁸⁵Kr neutralizer, a TSI model 3081 long column cylindrical differential mobility analyzer, and a TSI model 3760 A condensation particle counter. A voltage scan from 40 V to 7000 V provided particle size distribution from 28 nm to 730 nm.

Chemicals used directly for calibration of the AMS included ammonium nitrate, trimethylamine (TMA), triethylamine (TEA), diethylamine (DEA), methylamine (MA),
and trimethylamine-n-oxide (TMAO) (Aldrich). Several calibration standards were synthesized using acid-base reactions and purified using a rotovap (chloride and nitrate salts of TMA, TEA, DEA, and MA). The synthesis of triethylamine-n-oxide (TEAO) was accomplished in the laboratory using TEA.

**Results and Discussion**

*Ambient Data from Utah*

Over the last several years, an AMS has been used to sample fine particles in Logan, Utah (Silva et al., 2007). As previously reported, Logan experiences strong wintertime inversions with average surface temperatures of -10 °C leading to acute episodes of PM$_{2.5}$ (Malek et al., 2006). For example, during January and February 2004, PM$_{2.5}$ concentrations in Logan exceeded the previous 24-hour National Ambient Air Quality Standard (NAAQS) value of 65 µg/m$^3$ on 17 days and reached upper values of ~140 µg/m$^3$. The major constituent of fine particles in Logan as measured by both gravimetric and AMS measurements is ammonium nitrate, making up 50-80% of the particle mass concentration detected. However, another 15-25% of the mass loading is normally made up of organic aerosols.

The AMS can differentiate between different types of organic aerosols as described by Zhang et al. (2005a). The USU AMS detects hydrocarbon-like organic aerosols (HOA) and oxygenated organic aerosols (OOA) similar to other locations where AMS instruments have sampled (Zhang et al., 2005b). However in Logan, the AMS often detects other organic aerosol that does not fit the fragmentation patterns of either HOA or OOA. The mass spectrum at these times is dominated by even-number mass fragments.
correlating with the pattern \((C_nH_{2n+2}N)^+\). This is the set of peaks often observed by the SPLDI-MS techniques and includes \(m/z\) 58, 86, and 100 which strongly indicate presence of amines (McLafferty and Turecek, 1993). The presence of even number peaks is probably evidence of an odd number nitrogens.

However, in the mass spectrum of amines, molecules tend to fragment at the carbon-carbon bond adjacent to the amine, giving similar fragment ions regardless of other functional groups present in the molecule (e.g. amine alcohols, amine n-oxides, and amides derived from the same amine will fragment similarly.) As discussed in the previous chapter, this signature was observed during the strong winter inversions of 2004, but as one small contributor to the overall particle mass spectral signal. During 2005, this signature was the dominant organic aerosol observed in the mass spectra acquired from two different locations in the valley. The “amine” contribution was larger in raw ion counts (Hz) than either the HOA or OOA fractions.

Analysis of the 2005 data when the amine signature was strong indicates that not all amine-related ions detected show the same temporal profiles. Figure 3-1 shows temporal profiles obtained from four different ion peaks representing the amine series: \(m/z\) 58, 86, 100, and 114. The temporal profiles indicate two distinct sources and/or chemical processes. Mass-to-charge peaks 58 and 114 are highly correlated \((r^2=0.783)\) and show a series of gradual, but continuous buildups in ion counts during mild inversion conditions. Mass-to-charge ions 86 and 100 also are well correlated \((r^2=0.836)\), however with time trends showing short, transient spikes in ion counts. The two sets of peaks are poorly correlated with each other \((m/z\) 58:100 gives \(r^2=0.093\); \(m/z\) 86:114 gives \(r^2=0.008\)).
Figure 3-2 shows hourly mean, median, and range data for the amine peaks at $m/z$ 58 and 114. A clear diurnal profile is observed with mass loadings reaching peak concentrations during the middle of the night while decreasing during the day. This behavior is observed for some other components in the data set (sulfate in particular). This may be due to diurnal boundary layer changes affecting particulate concentrations, temperature effects shifting gas-particle partitioning, or chemical processes involving nocturnal reactions, or some combination of the three.
Fig. 3-2. Mass concentration of amine-related peaks and TEOM data ($\mu$g/m$^3$).

Amine Calibration Experiments

As discussed by Jayne et al. (2000) and Allan et al. (2003a, 2003b) the AMS is able to quantify aerosol mass loadings using an empirically determined ionization efficiency for each chemical class. Typically, ammonium nitrate serves as the primary calibration standard while quantitative measurements of other chemical compounds (sulfate, chloride, organic carbon) are referenced to the nitrate measurements using a relative ionization efficiency of the chemical of interest compared to nitrate. Among organic compounds, ionization cross-sections show a rough dependence on molecular
weight with some variation due to different functionality (Bartmess and Georgiadis, 1983). A typical ionization cross-section factor used for organic aerosol when detected by the AMS is 1.4, meaning that organic aerosols are 1.4 times as easily ionized and detected as nitrate. Using the typical correction factor of 1.4, Fig. 3-3 shows the temporal profile of the amine signature as detected by the AMS which gives 10-minute averaged amine mass concentrations of up to 6 \( \mu g/m^3 \). For comparison, data acquired by the Utah Division of Air Quality (UDAQ) in Logan using a PM\(_{2.5}\) filter dynamics measurement system (FDMS, Thermo R&P) shows that the amines detected by the AMS may make up as much as 20% of the total PM\(_{2.5}\) loadings at times, assuming the standard ionization factor for organic aerosols applies. The FDMS shows increases of 5-20 \( \mu g/m^3 \) in mass during the night.

Fig. 3-3. Diurnal profile of amine-related peaks.
A series of ionization efficiency calibration experiments was run with a number of amines to determine a response factor. However, data obtained for ionization efficiencies of model amine compounds indicate that detection factors for amines may vary significantly depending on the exact species. In particular, a critical factor appears whether amines are present as neutral compounds (e.g. secondary organic aerosol) or as salts resulting from acid-base neutralization reactions.

Figure 3-4 displays the spectrum for triethylammonium chloride (TEACl). These particles were generated using a solution containing TEA and HCl. Chloride was used for calibration experiments because nitrate yields $m/z$ 30 (NO$^+$), a potentially significant interferent in the MS of amines where $m/z$ 30 can also be CH$_4$N$^+$. A series of ion peaks from the $\Delta 3$ series are observed due to fragmentation of triethylamine (e.g. $m/z$ 30, 58, 72, 86, 100). Chloride is detected at $m/z$ 36 and 38, the isotopes of hydrochloric acid. However, signal intensity from the amine ions is much greater than that from the chloride peaks even though the salt particles should have the same number of molecules of each chemical.

The ionization efficiency of the amine component in this case is found to be approximately eight times greater than the chloride. It is also ~8 times greater than the ionization efficiency of nitrate from ammonium nitrate obtained during the same set of experiments. This behavior was observed with several other amine salts (methylammonium chloride, dimethylammonium chloride, and trimethylammonium chloride) with response factors for the amine fraction ranging between 5 and 10 rather than the typical 1.4 encountered for other organic species.
The reason for the higher ionization efficiency factor is due to surface ionization of the amine salts on the vaporizer. Even with the ionization filaments turned off in the mass spectrometer, signals from amines were observed in the mass spectra due to direct ionization from elevated temperatures on the surface of the oven. The ionization potentials of alkyl amines tend to be lower (7-9 eV) than those of most other organic compounds (e.g. 10-11 eV for alkanes) which may account for the ease of ionization (Franklin and Haug, 1991).

Figure 3-5 shows the mass spectrum of trimethylamine-n-oxide (TMAO), a potential oxidation product of amines proposed as an atmospheric particulate component by Angelino et. al. (2001). The spectrum shows several peaks from the $\Delta 3$ series ($m/z$ 30,
58) and one other major fragment ion (m/z 42) and a small parent ion. However, the relative ionization efficiency for TMAO versus nitrate from ammonium nitrate was calculated as 1.3, not significantly different from 1.4 used as the standard OC response factor. Other neutral amine compounds tested (triethylamine-n-oxide) showed similar response factors.

**Fig. 3-5.** Mass spectrum of trimethylamine oxide calibrant.
Therefore, the mass loading calibration of the AMS for amine compounds is strongly dependent on the exact species present. The presence of neutral (free-base) amines would exhibit response factors similar to those of other organic compounds and would make the mass loadings displayed in Fig. 3-2 accurate. However, the presence of amine salts as the dominant component would require displayed mass loadings to be divided by a factor as much as 10 because of ease of ionizing these compounds. This would account for 0.1-0.6 µg/m³ of material. Amines in the particle phase at either level of mass concentration are unaccounted for by currently known atmospheric chemistry. As such, we conducted a series of smog chamber experiments to determine which if any mechanism could be responsible for aerosol formation from amines and attempt to identify products. Trimethylamine was chosen as a model compound because its major fragment is m/z 58, the dominant peak observed in ambient signals. Because of the uncertainty of AMS response depending on types of particulate amines formed, mass loading data for smog chamber experiments described below will be quoted using SMPS volume distribution data rather than AMS data.

**Smog Chamber Experiments**

Over a period of several weeks, we performed a series of experiments reacting trimethylamine with trace oxidants under different conditions to determine particulate products (Table 3-1). Reactive oxidants of interest included ozone, nitrogen oxides, nitrate radical, and nitric acid. Figure 3-6 display temporal profiles obtained using the SMPS for the reaction of TMA and ozone/NOₓ photochemical system. Figure 3-6 shows the total mass concentration acquired by the SMPS (corrected for wall losses) during
Nitric Oxide was injected at the beginning of the experiment (11:10 local time) to ensure removal of trace ozone. The mixing ratio of NO was measured at 46.7 ppb. No particle formation was observed on either the SMPS or AMS with the introduction of NO. Trimethylamine was injected into the chamber (11:44 local time) at an estimated mixing ratio of 100 ppb. Again, no particle formation was observed on any instrument. Approximately 30 minutes later (12:21), ozone was injected into the chamber at a measured mixing ratio of 333 ppb. Rapid particle formation was observed on both the SMPS and AMS instruments. The SMPS measured a peak volume concentration of 179.6 µg/m³.

**Fig. 3-6.** SMPS data for trimethylamine reaction with nitrogen oxides and then ozone.
Table 3-1. List of smog chamber experiments performed and variables changed

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Amine/ppb</th>
<th>Oxidant1/ppb</th>
<th>Oxidant2/ppb</th>
<th>Other Conds.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TEA/100</td>
<td>O₃/262</td>
<td>NOₓ/41</td>
<td>Black Lights</td>
</tr>
<tr>
<td>2</td>
<td>TEA/100</td>
<td>NOₓ/28</td>
<td>O₃/371</td>
<td>Black Lights</td>
</tr>
<tr>
<td>3</td>
<td>TEA/100</td>
<td>NOₓ/34</td>
<td>O₃/356</td>
<td>Black Lights</td>
</tr>
<tr>
<td>4</td>
<td>TEA/100</td>
<td>O₃/243</td>
<td>NOₓ/49</td>
<td>Black Lights</td>
</tr>
<tr>
<td>5</td>
<td>TMA/100</td>
<td>NOₓ/47</td>
<td>O₃/333</td>
<td>Black Lights</td>
</tr>
<tr>
<td>6</td>
<td>TMA/100</td>
<td>O₃/427</td>
<td>NOₓ/35</td>
<td>CO</td>
</tr>
<tr>
<td>7</td>
<td>TMA/100</td>
<td>O₃/465</td>
<td>NOₓ/40</td>
<td>CO/50%RH</td>
</tr>
<tr>
<td>8</td>
<td>TMA/100</td>
<td>O₃/371</td>
<td>NO/28</td>
<td>CO/seed</td>
</tr>
<tr>
<td>9</td>
<td>TMA/100</td>
<td>NOₓ/48</td>
<td>O₃/289</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>TMA/100</td>
<td>N₂O₅/100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>TMA/100</td>
<td>HNO₃/93</td>
<td>O₃/357</td>
<td>NOₓ</td>
</tr>
</tbody>
</table>

For the next experiment, the order of introduction of NO and O₃ were reversed. Figure 3-7 shows the SMPS temporal profile for experiment 6. Carbon monoxide was injected at 13:18 at a mixing ratio of 180 ppm to act as a hydroxyl radical scavenger. At 14:25, TMA was injected at the estimated mixing ratio of 100 ppb. No particle formation was observed. At 15:07, ozone was injected at a measured concentration of 427 ppb. Some particle formation was observed, leveling off at ~11 µg/m³ in the SMPS data after 1 hour. The average particle formation rate was 6.8 µg/m³/hr. Nitric oxide was injected at 17:41 at a concentration of 35 ppb. A larger rise in particle concentration was detected reaching 85 µg/m³ in the condensed phase. The average particle formation rate was 61.8 µg/m³/hr. Some aerosol was formed after the addition of ozone.
Fig. 3-7. SMPS data for trimethylamine reaction with ozone and then nitrogen oxides.

Figure 3-8 shows the mass spectrum obtained using the AMS for the particulate products from the reaction of TMA and the ozone/NOx system. The highest intensity peaks observed are $m/z$ 30, 44, and 58, consistent with the major peaks expected from TMA and nitrate ion. The spectrum also shows that reaction products produce fragment ions at masses much larger than the parent ion for TMA. The largest ion observed is $m/z$ 207, but others include $m/z$ 97, 104, 141, 146, 159, 161, 175, and 191. This indicates the formation of molecular species significantly larger than the parent TMA. The AMS spectrum appears consistent with the data reported by Murphy et. al. (2007).
Fig. 3-8. Mass spectrum of particles formed from trimethylamine/O₃/NOₓ photochemical reaction.

To gauge the impact of acid-base reaction contributions, we ran a chamber reaction with a direct interaction between TMA and nitric acid (experiment 11). Figure 3-9 shows the SMPS time trend of the experiment. At 11:08, ~100 ppb of TMA was injected into the chamber. At 11:23, NO was added to the chamber to remove ozone. Measured concentration of NO was 54 ppb. At 11:29, nitric acid was injected directly to the chamber at an estimated mixing ratio of 93 ppb. Particle formation was observed, leveling off at ~50 µg/m³ after 150 minutes. This corresponds to an average particle formation rate of 21.3 µg/m³/hr.
The average mass spectrum from the particles formed during this reaction is shown in Fig. 3-10. The spectrum is very simple, showing only fragments from nitrate ($m/z$ 30, 46) and trimethylamine ($m/z$ 30, 42, 58, and 59). This is expected since that the simple acid-base reaction should result in an amine-nitrate salt. This implies that the higher mass peaks shown in Fig. 3-8 are from chemical interactions other than simple acid-base production of organic aerosol. After concentrations leveled off, ozone was added to the chamber at a measured concentration of 357 ppb. Particulate mass concentration increased even more, leveling off at ~140 $\mu$g/m$^3$. The average particle formation rate during this period was 40.1 $\mu$g/m$^3$/hr. After interaction with ozone, the mass spectrum from the reaction resembled the spectrum displayed in Fig. 3-8, the TMA/O$_3$/NO$_x$ reaction system.
Because the TMA/HNO₃ reaction product cannot account for the higher mass spectral peaks observed in the TMA/O₃/NOₓ reaction system and the observed kinetics was slower, we hypothesized that the interaction of O₃ and NO₂ in the previous experiment could form nitrate radical which could be a potential player in the reaction system. So for the next experiment, the interaction of TMA and NO₃ was directly studied and data shown in Fig. 3-11 and 3-12. Figure 3-11 shows the SMPS time trend. TMA was injected into the chamber at 100 ppb (calculated) at 10:49. At 12:05, 100 ppb (calculated) of dinitrogen pentoxide was injected through a heated line into the chamber. Through the heated inlet, N₂O₅ should have converted immediately to NO₂ and NO₃. Particle formation was nearly instantaneous. Over 100 µg/m³ was detected using the SMPS 7 minutes later. The concentration leveled off at ~160 µg/m³. The average particle formation rate during the reaction was 460 µg/m³/hr.
Fig. 3-11. SMPS time profile for the reaction of TMA and nitrate radical.

The AMS spectrum of the particles is shown in Fig. 3-12. The reaction of TMA and NO$_3$ produces a mass spectrum very similar to Fig. 3-8, indicating that nitrate radical may be the major player in starting the formation of particulate matter from amine precursors. The result of this reaction is consistent with the observation in Logan, Utah that amine-related AMS peaks are dominant during nocturnal hours. Interpretation of the mass spectra obtained in Figs. 3-8 and 3-12 could plausibly be consistent with either a typical photochemical oxidation involving RO$_2$ radicals or the addition of NO$_2$ and/or NO$_3$ groups onto an amine backbone.

To further elucidate the reaction mechanism, we performed several isotope-labeled experiments with deuterated trimethylamine (TMA-d$_9$) and $^{15}$N-labeled nitric oxide ($^{15}$NO).
Fig. 3-12. AMS spectrum of particles formed from the reaction of TMA and nitrate radical.

Figures 3-13a and 3-13b show product mass spectra obtained from the reaction of TMA-d₉ (98%) with O₃/NOₓ and TMA with O₃/¹⁵NOₓ (98.5%) respectively. In Fig. 3-13a, a clear difference of major ion peaks is shown from the normal TMA. For example, m/z 58 is the major fragment ion for TMA through loss of one proton (C₃H₈N⁺), and the analogous ion m/z 66 (C₃D₈N⁺) is observed for the TMA-d₉ spectrum. Similarly, a number of other ion shifts are observed in the spectrum. Major ion peaks at m/z 73, 88, 104, and 191 appear to shift to m/z 78, 94, 110, and 204 respectively. In contrast, Fig. 3-13b obtained from the reaction of TMA/O₃/¹⁵NOₓ shows the same high-mass ion peaks as observed for the reaction with TMA/O₃/NOₓ. This indicates that addition of NO₂ or NO₃ groups is not a major contributor to the high mass peaks.
Fig. 3-13. Mass spectrum of particles formed during isotope-labeled experiments. a) Shows mass spectrum from deuterated TMA (TMA-d$_9$) and O$_3$/NO$_x$ system and b) shows mass spectrum from TMA and O$_3$/15NO$_x$ photochemical system

The HR-ToF-AMS has high enough resolving power to definitively identify most peaks present in the mass spectrum. Figure 3-14 shows high resolution spectra of peaks present in the TMA/O$_3$/NO$_x$ reaction at $m/z$ 30, 46, 104, and 191. Of particular note is the observation in Fig. 3-14a that $m/z$ 30 is not due to the NO$^+$ ion which would have an exact mass of 29.998 Da. This ion is not observed while two peaks at 30.009 and 30.036
These ions are due to (CH$_2$O$^+$) and (CH$_4$N$^+$) respectively. This observation indicates that the formation of amine-nitrate acid-base salts is not a major particle-formation mechanism under the conditions here because nitrate salts yield both NO$^+$ and NO$_2^+$ as major fragments. Figure 3-14b shows that the peak at nominal m/z 46 does show significant signal due to NO$_2^+$ (45.996), in addition to signal at 46.030(CH$_4$NO$^+$) and 46.062(C$_2$H$_8$N$^+$). This indicates that fragmentation may include the presence of nitro-groups on an organic backbone. Definitive identification of higher mass ions detected in the spectrum include m/z 74 and 88 as well as 104 (Fig. 3-14c), and 191 (Fig. 3-14d).

**Fig. 3-14.** High resolution mass spectral peaks from HR-ToF-AMS. a) m/z 30, b) m/z 46, c) m/z 104, d) m/z 191.
To obtain added information on the chemical composition of particles formed in the TMA/O₃/NOₓ reaction, particles were collected on a Teflon filter for off-line chemical analysis. Particles were extracted in water and analyzed using high-resolution electrospray ionization mass spectrometry. Figure 3-15 shows the high resolution mass spectrum obtained from this analysis. Ions are observed out to ~800 m/z, a very high molecular weight considering the starting compound (TMA) has a molar mass of only 59 Da. Of note is the repeating series of ions with difference of 103 m/z units. This loss sequence is identified by mass defect and the loss pattern indicates the sequence is due to the loss of C₃H₅NO₃. This repeated loss unit contains one proton less than the ion observed in the AMS spectra at m/z 104. This repeating unit indicates formation of an oligomer or macromolecule during the smog chamber reaction. This unit is composed of TMA with three oxygens attached, and again indicates secondary oxidation chemistry providing the major mechanism for the aerosol formation process.

During most of these experiments, particle size measurements were made using both the SMPS and the AMS. These measurements showed gradual growth from the initial nucleation burst into the accumulation mode. Some unusual behavior was observed in that particle growth during several experiments continued unto unusually large particle sizes for smog chamber experiments. The SMPS showed significant particle mass distribution at the upper end of its detection capability (~700 nm) while the AMS showed particle growth continuing into the supermicron size range. In addition, a tandem differential mobility analysis (TDMA) was performed on the particles produced during the smog chamber reactions. The secondary aerosol from the reaction is hygroscopic with
significant particle growth observed. However, it is not indicative of the presence of salts but merely of water soluble organic carbon. Observed reaction rates indicate that the reaction between TMA and NO$_3$ displayed extremely fast kinetics. Although we could not monitor the rate from the precursor gases, the particle formation rate constant is among the fastest reported. A lower boundary for the reaction kinetics can be estimated by assuming that all the N$_2$O$_5$ was converted to NO$_3$ and that all of the NO$_3$ was consumed.

**Fig. 3-15.** High resolution ESI Mass Spectrum of water-soluble particulate matter from reaction of trimethylamine and ozone/NO$_3$ photochemical system.
Using second order reaction kinetics, the estimated lower boundary of the rate constant was $4.4 \times 10^{-16}$ cm$^3$/molec/s. This reaction would rival fast reactions such as those of unsaturated hydrocarbons with ozone and nitrate radicals. The overall conversion of TMA into particulate (measured by particulate produced relative to TMA introduced was 95% for the TMA/N$_2$O$_5$ reaction and 84% for the TMA/O$_3$/NO$_x$ system.

**Conclusions**

The data here suggest that secondary organic aerosol production from amines may be important in areas where nitrate radical mixing ratios are enough to contribute to oxidative chemistry. While amines also perform chemistry with ozone, it is the combination of ozone and nitrogen oxides that creates much greater amounts of secondary organic aerosol. Salts can be formed from the combination of amines and nitric acid, however the reaction appears relatively slow and does not account for high mass fragments observed in the mass spectra. Nitrate radical conducts very fast chemistry with tertiary amines and RO$_2$ chemistry following a hydrogen abstraction can account for higher mass fragments observed.

The experiments here imply that further research is needed into the reaction chemistry of amines with oxidants, especially nitrate radical for which no kinetics data has been reported in the literature. In the Cache Valley, Utah, the mixing ratios and sources of amines are not known. However, it is anticipated that agricultural facilities such as dairies and feedlots are significant sources of amines just as they are for ammonia. Given that secondary oxidation chemistry appears to dominate over acid-base chemistry as a source of particles from amine precursors, the response factor for amines
in ambient data sets is probably closer to that of trimethylamine-n-oxide rather than the equivalent amine-salts. If so, the mass concentration data shown in Fig. 3-2 is based on a valid calibration, implying several $\mu g/m^3$ of amines in Logan ambient air.

References


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CHAPTER 4
SECONDARY ORGANIC AEROSOL FORMATION FROM REACTION OF TERTIARY AMINES WITH NITRATE RADICAL

Abstract

Secondary organic aerosol formation from the reaction of tertiary amines with nitrate radical was investigated in an indoor environmental chamber. Particle chemistry was monitored using a high resolution aerosol mass spectrometer while gas-phase species were detected using a proton transfer reaction mass spectrometer. Trimethylamine, triethylamine and tributylamine were studied. Results indicate that tributylamine forms the most aerosol mass followed by trimethylamine and triethylamine respectively. Spectra from the aerosol mass spectrometer indicate the formation of complex non-salt aerosol products. We propose a reaction mechanism that proceeds via abstraction of a proton by nitrate radical followed by RO₂ chemistry. Rearrangement of the aminyl alkoxy radical through hydrogen shift leads to the formation of hydroxylated amides, which explain most of the higher mass ions in the mass spectra. These experiments show that oxidation of tertiary amines by nitrate radical may be an important night-time source of secondary organic aerosol.

Introduction

Aliphatic amines constitute an important class of volatile organic compounds due to their malodorous properties (Rappert et al., 2005; Filipy et al., 2006). Amines have also shown a propensity to form aerosols (Murphy et al., 2007; Silva et al., 2008) which
could have implications on health, visibility and climate change (Dockery et al., 1993; Watson, 2002; Seinfeld and Parker, 2003; IPCC, 2007). Amines are emitted from a variety of anthropogenic sources that include feedlots, car exhaust, biomass burning, sewage treatment plants and industries (Mosier et al., 1973; Cadle and Mulawa, 1980; Westerholm et al., 1993; Kataoka, 1996). In the biosphere, they result from bacterial degradation of nitrogen containing organic matter such as proteins and amino acids (Wright, et al., 1976). There is limited data on emissions of amines from the various sources, but they are generally associated with animal husbandry practices. Schade and Crutzen (1995) estimated the global emission of methylamines to be 150 Gg N/year, most of which was trimethylamine.

The lifetime of alkylamines in the atmosphere range from a few hours to tens of hours. Since they do not undergo photolysis in the atmosphere, their main removal processes are reactions with atmospheric reactants such as hydroxyl radical, ozone, atmospheric acids and nitrate radical (Pitts et al., 1978; Tuazon et al., 1994; Angelino et al., 2001; Murphy et al., 2007). Some of the products resulting from these reactions may be highly volatile in which case they remain in the gas phase. Others may have sufficiently low vapor pressure to exist in particulate phase. A number of studies have reported detecting particulate and aqueous phase amines in the atmosphere (Murphy and Thomson, 1997; Tan et al., 2002; Zhang and Anastasio, 2003). As discussed in chapter 3, amine compounds can be a significant portion of aerosol mass especially during the night-time. However, the chemistry that leads to particulate amines is not well understood.
Few smog chamber experiments have been conducted to probe the chemistry of amines. These experiments have shown that amine reactions result in the formation of both volatile and condensed products. For example, photo-oxidation experiments by Pitts et al. (1978) of ethylamine and triethylamine in an outdoor chamber resulted in aerosol formation. Triethylamine yielded more aerosol than ethylamine. Amine aerosol chemistry did not get much attention during this time as the focus was on formation of carcinogenic nitrosamines. Years later, studies have shown that the chemistry that leads to the formation of aerosol is more complex and is dependent on the class of amine reacted (Angelino et al., 2001; Murphy et al., 2007). Tertiary amines in particular react to form more aerosol mass than secondary and primary amines (Murphy et al., 2007). None of these studies looked at the chemistry of amines with the nitrate radical.

In the previous chapter, we reported results from a series of experiments in which trimethylamine was reacted with ozone, nitrate radical and nitric acid. These results showed that the reaction of trimethylamine with nitrate radical produced mostly secondary organic aerosol. Formation of aminium salts was minimal. The reaction also exhibited relatively fast kinetics and high aerosol yields. This chapter builds on that work in order to achieve a three-fold objective: i) to extend the study of trimethylamine to other tertiary amines, ii) to examine the products formed and iii) to devise a reaction mechanism that is consistent with the observations. The amines under investigation here are trimethylamine (TMA), triethylamine (TEA) and tributylamine (TBA).
Experimental

The experiments described in this section were conducted in the smog chamber described in the previous chapter. A proton transfer reaction mass spectrometer together with a high resolution mass spectrometer was used to characterize aerosol formed in the chamber. A brief overview of the two is presented.

A proton transfer reaction mass spectrometer (PTR-MS, Iconicon Analytik) located at CE-CERT was used to detect and analyze volatile organic compounds in real time and with high sensitivity. A detailed description of PTR-MS has been given by Lindinger and Hansel (1997) and only a summary of the key features will be given here. The instrument consists of four main components: an ion source, a drift tube, a mass analyzer (quadrupole), and an ion detector/amplifier. H$_3$O$^+$ ions are produced at high concentrations from pure water vapor within a hollow cathode ion source and pass via a Venturi-type inlet into the drift tube. The air sample to be analyzed is introduced into the drift tube and because of their low proton affinities, the major components of air undergo non-reactive collisions with H$_3$O$^+$ ions and therefore act as buffer gas. However, any collisions of H$_3$O$^+$ ions with the volatile organic compounds (VOCs) present in the gas flow possessing a greater proton affinity than water will result in a proton transfer reaction (Eq. R1).

$$ VOC (g) + H_3O^+ (g) \rightarrow VOCH^+ (g) + H_2O (g) \quad (R1) $$

The resultant ions are mass-selected using a quadrupole mass analyzer and measured as count rates by an electron multiplier detector. The online PTR-MS was used in scan
mode to monitor the ion traces from \( m/z \) 21 to \( m/z \) 200 with a dwell time of 0.2 s per mass.

A high resolution time of flight mass spectrometer (DeCarlo et al., 2006), also located at CE-CERT, was used to detect and characterize aerosol products. It is similar to the quadrupole AMS except that it uses a time-of-flight mass analyzer and an MCP detector. This instrument can be alternated between a shorter flight path (V-Mode) that gives higher ion throughput and therefore better sensitivity and the longer flight path (W-mode) that offers better separation but lower sensitivity. The strength of HR-ToF-AMS lies in its ability to offer a high resolving power of up to 4300 times for W-mode and about 2100 times for V-mode (at \( m/z \) 200) better than that of the quadrupole. This ability was useful in definitive identification of the product peaks. The HR-ToF-AMS was used to detect peaks in the mass range between \( m/z \) 10 to \( m/z \) 500.

Each experiment started with thorough cleaning of the bags as outlined in Carter et al. (2005). Background concentrations of NO\(_x\) and ozone were also determined to be at an acceptable low level (< 2 ppb for ozone and NO\(_x\)). The amines were introduced into the chamber by injecting a known volume of liquid amine into a small glass injection manifold or by introducing a known volume of the gas phase amine into a calibrated bulb based on calculated partial pressures. Pure nitrogen was then passed over the liquid or through the bulb, flushing the amine into the reactors. Injections of amines were verified using PTR-MS. Table 4-1 lists the initial conditions of all experiments in this chapter. After amine injection, ozone was introduced by passing 20 psig of pure air through two UV ozone generators and the reaction was left to proceed until the amount of wall-loss
corrected aerosol formed stabilized (usually 1-2 hrs). Then NO\textsubscript{x} was added to the reactors as NO using a calibrated bulb (usually \sim 1-2 hrs after ozone addition). The reaction was left to proceed until the amount of wall-loss corrected aerosol formed leveled off (usually 2-3 hrs after injection of NO\textsubscript{x}). The ozone and NO\textsubscript{2} in the chamber react to form nitrate radical as shown in Eq. R2. All the experiments were conducted in the dark to simulate night-time NO\textsubscript{3} radical chemistry.

\[ O_3 (g) + NO_2 (g) \rightarrow NO_3 (g) + O_2 (g) \]  \hspace{1cm} (R2)

**Table 4-1.** Initial conditions and results obtained from reaction of tertiary amines with ozone/NO\textsubscript{x}.

<table>
<thead>
<tr>
<th>Amine</th>
<th>[Amine] (ppb)</th>
<th>[NO\textsubscript{x}] (ppb)</th>
<th>[Ozone] (ppb)</th>
<th>[Aerosol\textsubscript{max}] (\mu m^3 cm^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trimethylamine</td>
<td>100</td>
<td>50</td>
<td>300</td>
<td>90</td>
</tr>
<tr>
<td>Triethylamine</td>
<td>100</td>
<td>40</td>
<td>245</td>
<td>40</td>
</tr>
<tr>
<td>Tributylamine</td>
<td>100</td>
<td>35</td>
<td>255</td>
<td>110</td>
</tr>
</tbody>
</table>
Results and Discussion

TMA Reaction

Smog chamber reactions of TMA with nitrate radical have been given in chapter 3. The discussion here will only dwell on details pertinent to the objectives of this chapter. Figure 4-1a shows a typical TMA reaction profile. In this experiment, some aerosol formed after injection of ozone. The aerosol concentration leveled off at about 30 µg/m³ (This was obtained from wall-loss corrected SMPS volume concentration using density of 1 g/cm³). Four hours after ozone injection, NO was introduced leading to more aerosol formation leveling off at about 90 µg/m³. TMA quasi parent ion peak (m/z 60) was monitored by the PTR-MS. This peak started decaying immediately ozone was injected. The decay continued as more TMA was converted into aerosol phase.

An average mass spectrum of the particulate products from the TMA reaction with the ozone/NOₓ system is shown in Fig. 4-1b. The ion peaks at m/z 44.052 (C₂H₆N⁺) and m/z 58.066 (C₃H₈N⁺) represent amine backbone fragments while m/z 58.030 (C₂H₄NO⁺), 76.040 (C₂H₆NO₂⁺), m/z 88.037 (C₃H₆NO₂⁺) and m/z 104.040 (C₃H₆NO₃⁺) represent fragments of amines that have been oxidized. (Table 4-2 contains a summary of other major ion fragments detected).

PTR-MS peaks at m/z 31 (formaldehyde), m/z 45 (acetaldehyde), m/z 47 (formic acid), m/z 59 (acetone/propanal) and m/z 61 (acetic acid/propanol) were present in all the three tertiary amines reacted. During the TMA reaction, the PTR-MS also detected m/z 74 (dimethyl formamide), m/z 88 (methylidiformamide), m/z 102 (triformamide), m/z 91 (dimethylnitramine) and m/z 75 (dimethylnitrosamine).
Fig. 4-1. a) Temporal profiles of $m/z$ 60 and aerosol volume concentration for the reaction of TMA with ozone/NO$_x$. b) Aerosol mass spectrum taken at the end of the experiment after the SMPS volume concentration leveled off.
Table 4-2. Major AMS ion peaks and assignments

<table>
<thead>
<tr>
<th></th>
<th>TMA</th>
<th></th>
<th>TEA</th>
<th></th>
<th>TBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>Formula</td>
<td>m/z</td>
<td>Formula</td>
<td>m/z</td>
<td>Formula</td>
</tr>
<tr>
<td>30.010</td>
<td>CH₂O⁺</td>
<td>30.000</td>
<td>NO⁺</td>
<td>44.027</td>
<td>C₂H₄O⁺</td>
</tr>
<tr>
<td>30.036</td>
<td>CH₄N⁺</td>
<td>30.036</td>
<td>CH₄N⁺</td>
<td>44.051</td>
<td>C₂H₆N⁺</td>
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<tr>
<td>43.982</td>
<td>CO₂⁺</td>
<td>44.024</td>
<td>C₂H₄O⁺</td>
<td>58.065</td>
<td>C₃H₈N⁺</td>
</tr>
<tr>
<td>44.052</td>
<td>C₂H₆N⁺</td>
<td>44.052</td>
<td>C₂H₆N⁺</td>
<td>72.080</td>
<td>C₃H₁₀N⁺</td>
</tr>
<tr>
<td>45.993</td>
<td>NO₂⁺</td>
<td>58.066</td>
<td>C₃H₈N⁺</td>
<td>86.092</td>
<td>C₅H₁₂N⁺</td>
</tr>
<tr>
<td>46.03</td>
<td>CH₄NO⁺</td>
<td>72.046</td>
<td>C₃H₆NO⁺</td>
<td>100.080</td>
<td>C₅H₁₀NO⁺</td>
</tr>
<tr>
<td>58.066</td>
<td>C₃H₆N⁺</td>
<td>72.082</td>
<td>C₄H₁₀N⁺</td>
<td>114.090</td>
<td>C₆H₁₂NO⁺</td>
</tr>
<tr>
<td>76.040</td>
<td>C₂H₆NO₂⁺</td>
<td>86.068</td>
<td>C₄H₈NO⁺</td>
<td>126.130</td>
<td>C₅H₁₆N⁺</td>
</tr>
<tr>
<td>88.040</td>
<td>C₃H₆NO₂⁺</td>
<td>86.095</td>
<td>C₅H₁₂N⁺</td>
<td>142.120</td>
<td>C₅H₁₆NO⁺</td>
</tr>
<tr>
<td>104.040</td>
<td>C₃H₆NO₃⁺</td>
<td>102.050</td>
<td>C₄H₈NO₂⁺</td>
<td>158.120</td>
<td>C₅H₁₆NO₂⁺</td>
</tr>
<tr>
<td>191.070</td>
<td>C₆H₁₁N₂O₅⁺</td>
<td>130.080</td>
<td>C₆H₁₂NO₂⁺</td>
<td>174.110</td>
<td>C₅H₁₆NO₃⁺</td>
</tr>
<tr>
<td>207.060</td>
<td>C₆H₁₁N₂O₆⁺</td>
<td>146.070</td>
<td>C₆H₁₂NO₃⁺</td>
<td>214.180</td>
<td>C₁₂H₂₄NO₂⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>230.170</td>
</tr>
</tbody>
</table>

As expected, dimethylnitramine and dimethylnitrosamine were detected only after injection of NOₓ. The ion peak detected at m/z 44 was specific to TMA reaction and it likely represents methyl-methyleneimine (CH₂=NCH₃). Since imines have double bonds, they can potentially be attacked by ozone to form other products, but at least one study has indicated that this reaction is too slow to be of any significance (Mori et al., 1988). Table 4-3 displays the high intensity peaks that were detected with the PTR-MS and the assigned VOCs.
Table 4-3. Major PTR-MS peaks and assignments

<table>
<thead>
<tr>
<th>TMA</th>
<th>TEA</th>
<th>TBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/z</td>
<td>VOC</td>
<td>m/z</td>
</tr>
<tr>
<td>44</td>
<td>Methylimine</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} )</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>Trimethylamine</td>
<td>74</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{CH}_3)</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{NH} \equiv \text{O} )</td>
</tr>
<tr>
<td>62</td>
<td>Nitromethane</td>
<td>76</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
</tr>
<tr>
<td>74</td>
<td>Dimethylformamide</td>
<td>102</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{CH}_3)</td>
</tr>
<tr>
<td>75</td>
<td>Dimethyl- Nitrosamine</td>
<td>103</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{N} \equiv \text{O} )</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
</tr>
<tr>
<td>88</td>
<td>Methyl-Diformamide</td>
<td>116</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
</tr>
<tr>
<td>90</td>
<td>Hydroxymethyl- methylformamide</td>
<td>119</td>
</tr>
<tr>
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<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
</tr>
<tr>
<td>91</td>
<td>Dimethyl- Nitramine</td>
<td>200</td>
</tr>
<tr>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
<td></td>
<td>(\text{C}_2\text{H}_5\text{N} \equiv \text{O} )</td>
</tr>
<tr>
<td>102</td>
<td>Triformamide</td>
<td></td>
</tr>
</tbody>
</table>
We examined spectra for evidence of amine-N-oxide, a possible product according to Angelino et al. (2001). Trimethylamine-N-oxide (TMAO) parent-ion peak is \( m/z \) 75. The ion peak at \( m/z \) 75 was detected albeit at low intensity. The HR-ToF-AMS spectrum (Fig. 4-2a) indicates it consists of two peaks, \( m/z \) 75.029 (\( \text{C}_2\text{H}_5\text{NO}_2^+ \)) and \( m/z \) 75.065 (\( \text{C}_3\text{H}_9\text{NO}^+ \)). As shown in Fig. 4-2b, after injection of NO\(_x\) only \( m/z \) 75.029 was detected. This indicates that TMAO was present after the reaction with ozone, but was reduced after NO\(_x\) injection. There was no protonated TMAO (\( m/z \) 76.073) detected in the mass spectra during either injection. The plausible explanation for this observation is that ozone indeed reacts with TMA to form TMAO, but it may be vulnerable to radical chemistry itself to form other products.

**Fig. 4-2.** Expanded \( m/z \) 75 and \( m/z \) 76 peaks from the HR-ToF-AMS. a) TMA-O\(_3\) reaction system. b) TMA-O\(_3\)-NO\(_x\) reaction system.
**TEA Reaction**

The reaction of TEA with ozone/NO°C followed a pattern similar to that of TMA. After ozone injection, some aerosol was formed leveling off at about 20 µg/m³. Two hours later, NO was injected resulting in formation of more aerosol that leveled off at about 40 µg/m³ (Fig. 4-3a). The amount of aerosol from TEA reaction was less than that of TMA even though TEA has higher molecular weight and should theoretically form more aerosol. Immediately after NO injection, there was sudden buildup of aerosol that quickly dropped before leveling off. Injection of TEA was confirmed with PTR-MS by monitoring the quasi parent ion peak ($m/z$ 102) that gradually decayed during the course of the experiment as more aerosol was being formed. Other volatile products detected specific to the TEA reaction include amides: diethylacetamide ($m/z$ 119) and ethylformamide ($m/z$ 74); nitro/nitroso species: diethylnitramine ($m/z$ 116) and diethylnitrosamine ($m/z$ 103) and an imine: ethyl-ethyleneimine ($m/z$ 72).

The AMS spectrum for TEA reaction is shown in Fig. 4-3b. The low mass peaks for these reactions include $m/z$ 44.052 (C₂H₆N⁺), $m/z$ 58.065 (C₃H₈N⁺), $m/z$ 72.082 (C₄H₁₀N⁺) and $m/z$ 86.095 (C₅H₁₂N⁺) that represent fragments from the amine backbone. Other ions detected are $m/z$ 72.046 (C₃H₆NO⁺), $m/z$ 86.068 (C₄H₈NO⁺), $m/z$ 102.05 (C₅H₈NO₂⁺) and $m/z$ 146.07. (C₆H₁₂NO₃⁺) In each of these cases, one, two, or three oxygen atoms have been added representing oxidized amine fragments. There were fewer high mass peaks in the TEA reaction compared to that of TMA.
Shortly after the NO injection, the nitrate fragments ($\text{NO}^+/\text{NO}_2^+$) were detected as shown in Fig. 4-4. These fragments are usually indicative of the presence of nitrate. The salt burst was short-lived and did not appear in the other two amines investigated. It is likely that this observation was as a result of sudden build up in nitric acid in the chamber.
near the injection/sampling port. This nitric acid could have formed at the injection port due to high concentration of NO\textsubscript{x} that reacted with OH radical. Apart from this instantaneous period, nitrate salt formation was generally minimal as depicted by the low intensity of NO\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{+} peaks at \textit{m/z} 30 and \textit{m/z} 46, respectively.

**Fig. 4-4.** Expanded product peaks for the TEA reaction. a) \textit{m/z} 30 after ozone injection, b) \textit{m/z} 30 shortly after NO\textsubscript{x} injection, c) \textit{m/z} 46 after ozone injection, d) \textit{m/z} 46 shortly after NO\textsubscript{x} injection.
**TBA Reaction**

Figure 4-5a presents results of the TBA reaction with ozone/NO$_x$. The amount of aerosol formed after ozone injection (at ~ 60 $\mu$g/m$^3$) was more than the total amount of aerosol formed during the TEA-ozone/NO$_x$ reaction. This was expected because TBA is a twelve-carbon compound and the oxidation products are expected to have lower vapor pressure. The maximum aerosol recorded for the TBA reaction was ~160 $\mu$g/m$^3$ after injection of NO approximately 3 hours after ozone injection. PTR-MS quasi parent peaks of $m/z$ 60 (TMA) and $m/z$ 102 (TEA) showed clear decay in the course of the experiment. This was not the case with TBA quasi parent peak ($m/z$ 186) which was not detected even though TBA has the highest proton affinity of the three tertiary amines (Green-Church et al., 2000). A possible explanation could be that the ion transmission efficiency was lower for TBA parent ion than the other two amines. Volatile products detected by the PTR-MS for the TBA reaction were similar to those formed by TMA and TEA and include an amide (dibutylbutanamide; $m/z$ 200), a nitro-compound (dibutylnitramine; $m/z$ 175), a nitroso-compound (dibutylnitrosamine; $m/z$ 159) and an imine (butyl-butylenimine; $m/z$ 128).

Figure 4-5b shows the AMS mass spectrum for the TBA reaction where high intensity ion peaks were detected at $m/z$ 44.052 ($C_2H_6N^+$), $m/z$ 58.065 ($C_3H_8N^+$), $m/z$ 72.082 ($C_4H_{10}N^+$), $m/z$ 86.095 ($C_5H_{12}N^+$) and $m/z$ 126 ($C_8H_{16}N^+$). The oxygenated fragments from TBA reaction were $m/z$ 100 ($C_5H_{10}NO^+$), $m/z$ 142 ($C_8H_{16}NO^+$), $m/z$ 174 ($C_8H_{16}NO_3^+$) and $m/z$ 230 ($C_{12}H_{24}NO_3^+$).
Fig. 4-5. a) Temporal profiles of $m/z$ 186 and aerosol volume concentration for the reaction of TBA with ozone/NO$_x$. b) Aerosol mass spectrum taken at the end of the experiment after the SMPS volume concentration leveled off.

Reaction Mechanism

Patterns in both gas phase and aerosol phase products emerged from all three tertiary amines reacted. Homologous volatile products include amides, nitro/nitroso compounds and imines. Formation of aminium salt with nitric acid was minimal, based on the low
intensities of nitrate ions \((m/z\) 30 and 46). The high mass fragments \(\text{C}_3\text{H}_6\text{NO}_3^+\) \((m/z\) 104), \(\text{C}_6\text{H}_{12}\text{NO}_3^+\) \((m/z\) 146) and \(\text{C}_{12}\text{H}_{24}\text{NO}_3^+\) \((m/z\) 230) from TMA, TEA and TBA reactions are similar. These high mass fragments indicate that each tertiary amine gains three oxygen atoms during the reaction while losing three hydrogen atoms. Because molecules containing one nitrogen atom in the structure must have an odd molecular mass, the ion peak at \(m/z\) 104 for TMA \((\text{C}_3\text{H}_6\text{NO}_3^+)\) is a fragment ion of a larger molecule. Further, the degree of unsaturation suggests the structure contains only one double bond. This ion is replicated for TEA at \(m/z\) 146 \((\text{C}_6\text{H}_{12}\text{NO}_3^+)\) and for TBA at \(m/z\) 230 \((\text{C}_{12}\text{H}_{24}\text{NO}_3^+)\). The structure for all three tertiary amines is consistent with the formation of a di-hydroxylated amides. This structure can account for all high mass fragments present in the spectra for all three compounds with the exception of the TMA reaction where it appeared to be forming dimers, possibly oligomers as outlined in chapter 3.

With the high resolution aerosol mass spectra and gas phase species detected by PTR-MS, we propose a reaction mechanism for the ozone/\(\text{NO}_x\) interaction with tertiary amines as shown in Fig. 4-6. Some of the products detected are shown with bold numbers 1-11 in Fig. 4-6.

The reaction with the nitrate radical starts with an initial abstraction step of the hydrogen atom from one of the alkyl groups in the amine. The resulting amine alkyl radical then reacts solely with \(\text{O}_2\) to form an aminyl alkylperoxy radical, which reacts with \(\text{NO}\) to form an aminyl alkoxy radical. The aminyl alkoxy radical then either reacts with \(\text{O}_2\) to form dimethylformamide (1) or decomposes to form formaldehyde (2) and an aminyl alkyl radical. The resulting aminyl alkyl radical can react with \(\text{NO}\) or \(\text{NO}_2\) to form
dimethylnitrosamine (3) and dimethylnitramine (4) respectively or it can lose a proton to form methyl-methyleneimine (5). This procedure, starting with the initial abstraction of proton from the alkyl group can repeat itself until methyldiformamide (6) and triformamide(7) are formed.

For aerosol formation, we propose that the reaction proceeds via rearrangement of the aminyl alkoxy radical through 1,4 H-shift to form a hydroxyaminy1 alkyl radical that then reacts with oxygen, NO and oxygen again to form hydroxymethyl-methylformamide (8). This procedure can be repeated until formyl-hydroxymethyl-formamide (9) and N, N-bis(hydroxymethyl) formamide (10) are formed. The vapor pressures of the hydroxylated products are calculated to be much lower than the corresponding aldehydes. For example, the theoretical estimation of the vapor pressure of dihydroxymethyl-formamide is \( \sim 6.38 \times 10^{-8} \) Torr, at 25°C, and would therefore be consistent with a condensed phase species. (Scifinder Scholar, 2008). The major high mass AMS peaks for TMA reaction such as \( \text{C}_3\text{H}_6\text{NO}_3^+ \) (m/z 104) and \( \text{C}_3\text{H}_6\text{NO}_2^+ \) (m/z 88) can well be explained from loss of proton and OH respectively from N, N-bis(hydroxymethyl) formamide. Formation of aerosol via the ozone only route has been previously reported by Tuazon et al. (1994). In this mechanism for example, TMA is oxidized to TMAO (11) as hypothesized by Angelino et al. (2001). TMA products may undergo further reactions to form higher molecular weight products (Silva et al., 2008) through one of the various mechanisms reported by Jang et al. (2002). This may explain AMS peaks such as m/z 207 (two \( \text{C}_3\text{H}_6\text{NO}_3^+ \) with a loss of proton) and m/z 191 (two \( \text{C}_3\text{H}_6\text{NO}_3^+ \) with a loss of OH).
Fig. 4-6. Proposed mechanism for the reaction of TMA with nitrate radical. TMA oxidation by ozone (Tuazon et al, 1994) is also shown.
Conclusions

Experiments in this study explore the chemistry of tertiary amines with ozone/NO\textsubscript{x}. The reaction between ozone and NO\textsubscript{x} yields nitrate radical that is an important night-time oxidant in the atmosphere. Of particular interest are aerosol yields and the nature of oxidation products, whether secondary organic aerosol or aminium salts. As expected, TBA formed the most aerosol on volume basis. However, TMA formed more aerosol than TEA, contrary to the general rule that oxidation products of higher molecular weight species produce more aerosols. Aerosol composition was mainly non-salt secondary organic aerosol. In particular, hydroxylated amides have been identified as major constituents. In addition, TMA appears to form dimers (perhaps oligomers) and this may explain why TMA yielded more aerosol volume than TEA. In addition to identifying aerosol products, gas phase products were examined as well. A number of species were identified including homologous amides, nitramines, and imines. These product studies have led us to propose a mechanism for the reaction of tertiary amines that proceeds via abstraction of hydrogen, then RO\textsubscript{2} chemistry and H-shifts. These results suggest that night-time oxidation of tertiary amines could be significant contributors to ambient particles and should be considered in atmospheric chemistry models. Moreover, there is need for extensive analysis of ambient data from past field campaigns, where amine signatures have been qualitatively identified. This will help in assessing the importance of nitrate oxidative chemistry especially in areas where these species may be emitted in high concentrations.
References


CHAPTER 5
METHOD FOR DETERMINATION OF METHYLAMINES AND TRIMETHYLAMINE-N-OXIDE IN AIR SAMPLES BY NON-SUPPRESSED ION CHROMATOGRAPHY WITH CONDUCTIVITY DETECTION

Abstract

An ion chromatography method with non-suppressed conductivity detection was developed for the simultaneous determination of methylamines (methylamine, dimethylamine, trimethylamine) and trimethylamine-N-oxide (TMAO) in air samples. The analytes were well separated by means of cation-exchange chromatography using a 3 mM methanesulfonic acid solution as eluent and an IonPac SCS1 column (250mm×4mm i.d.) as the separation column. The effects of the different chromatographic parameters on the separation were also investigated. Detection limits of methylamine, dimethylamine, trimethylamine and trimethylamine-N-oxide were 43, 46, 76 and 72 ppb, respectively. The method is suitable for determining if methylamines and TMAO are significant component of organic aerosol formed from reactions of trimethylamine and ozone and thus help in understanding the reaction pathways of amines.

Introduction

It is clear that organic nitrogen is ubiquitous yet still poorly characterized component of atmospheric aerosol (Cornell et al., 1995, 2001; Russell et al., 1998; Seitzinger and Sanders, 1999; Neff et al., 2002; Mace et al., 2003). With growing concerns of aerosol effects on health, climate and modification of nitrogen cycle, it is crucial to identify sources as well as understand the composition of atmospheric aerosol
including the organic nitrogen component (Jacobson et al., 2000; Cornell et al., 2001; Neff et al., 2002). Previous studies on organic nitrogen in the atmosphere have concentrated on dissolved organic nitrogen (e.g. Calderon et al., 2007). Most of these were bulk studies where for example, the total water soluble organic nitrogen was determined. Compound specific studies of organic nitrogen aerosol are rare (Milne and Zika, 1993; Cornell et al., 2003; Zhang and Anastasio, 2003). Given the diversity of the organic nitrogen compounds, it has been difficult to define source-and-sink budgets and describe their atmospheric behavior. This knowledge demands both the quantitative determination of bulk organic nitrogen aerosol and the characterization of individual compounds (Cornell et al., 2003).

Agricultural practices are known to input large amounts of nitrogenous species into the atmosphere (Schade and Crutzen, 1995). Recent work has shown that the concentration of some of the gas phase organic nitrogen species such as aliphatic amines may be as high as that of ammonia in some areas (Rabaud et al., 2003). Most studies have however focused on the inorganic nitrogen chemistry especially that of ammonia in aerosol formation, but the relative importance of organic nitrogen species is now recognized (Cornell et al., 2003). These organic species may react using a number of pathways to form gas phase products as well as aerosol (Murphy et al., 2007).

Trimethylamine oxide (TMAO) is a product that has been hypothesized as an aerosol product by Angelino et al. (2001) through oxidation of trimethylamine by ozone. TMAO is also a natural osmolyte found in some marine creatures such as fish (Athawale et al., 2005). When fish is rotten, TMAO gets converted to TMA that gives the
characteristic “fishy” smell. As a result, analysis methods for the determination of TMA and TMAO in seafood and other matrices have previously been developed (e.g. Hatton, 1999).

Here we adapt a method from seafood analysis in order to detect and quantify TMAO and methylamines in air samples. This method uses non-suppressed ion chromatography with conductivity detection. The composition of mobile phase was optimized and efficient separation between the analytes was achieved. An efficient and simple method is needed in order to determine whether TMAO is quantitatively significant product from reaction of trimethylamine with ozone.

Experimental

Reagents, Reference Substances and Samples

All the reagents used in this study were of analytical-reagent grade. Water was purified using a Milli-Q system (Millipore, Bedford, MA, USA). Methylamine, diethylamine and trimethylamine (analytical grade) were purchased from Acros Organics USA (Morris Plains, NJ). TMAO and methanesulfonic acid, (MSA, analytical grade) were obtained from Sigma-Aldrich (St Louis, MO). All reference substances were dissolved into water to make stock solution that contained all ions of interest. The stock solution contained 3000 ppm (TMAO and TMA) and 1000 ppm (MA and DMA). Samples were extracted into deionized (DI) water after sonicating for 30 minutes. The sample was injected into the ion chromatograph without further dilution. The stock and sample solutions was stored in polyethylene containers and refrigerated.
**Instrumentation**

The schematic diagram of the apparatus employed in this study is illustrated in Fig. 5-1. Chromatographic analysis were performed on a ICS-1000 (Dionex, Sunnyvale, CA, USA) ion chromatograph equipped with a dual-piston pump, a degas assembly, a digital conductivity detection and an injector with a 25 µL sample loop. The conductivity detector with a 6DS6 heated conductivity cell which the cell heater was set to 35 °C and temperature compensation was set to 1.7% per °C was placed after the IC column in the non-suppressed mode. Data collection and handling were carried out by Dionex Chromeleon 6.8 software.

![Schematic set-up of ion chromatograph with non suppressed conductivity detection](image)

**Fig. 5-1.** Schematic set-up of ion chromatograph with non suppressed conductivity detection
**Chromatographic Conditions**

The ion chromatography system was composed of a Dionex IonPac SCSG1 guard column (50mm×4mm i.d.) and a Dionex IonPac SCS1 analytical column (250mm×4mm i.d.). The SCS1 column was employed because of its advantage in the analysis of the amines as well as common inorganic cations with non-suppressed conductivity detection. The optimized eluent solution contained 3 mM MSA. Separation was carried out under isocratic conditions at a flow-rate of 1 mL/min and at room temperature of ~20°C.

**Results and Discussion**

**Optimizing the Separation**

The influence of the concentration of MSA in the mobile phase was studied from the point of view of the retention times, resolution and detection limit. MSA has been selected as the eluting acid in this study because of its relatively low conductivity. Different concentrations of MSA from 2.5 to 4.5 mM have been studied to determine the optimum concentration. As expected, retention times decreased with an increase in MSA concentration, with 3 mM chosen as optimum, based on a compromise between the resolution and background conductivity. Under the optimized experimental conditions, the chromatogram of a standard solution is shown in Fig. 5-2, in which the sample including the analytes is well separated in less than 45 minutes.
**Method Validation**

Under optimized experimental conditions, all four analytes showed good linearities between the concentrations and peak height responses. The detection limits, defined as the signal three times the noise level, were also calculated. The precisions were evaluated by performing 4 replicate analysis of a standard solution where the concentrations of the four analytes were 1.6 ppm (MA and DMA) and 4.8 ppm (TMA and TMAO). All the results are listed in Table 5-1.

![Chromatogram](image.png)

**Fig. 5-2.** A chromatogram of the standard solutions of methylamines and trimethylamine-N-oxide obtained under optimized conditions
Table 5-1. Summarized data for the detection limits (LODs), correlation coefficients, and retention times ($t_R$) of methylamines and trimethylamine-N-oxide obtained under the optimum operating conditions as in Fig. 5-2.

<table>
<thead>
<tr>
<th>Analytes</th>
<th>LOD (S/N=3) ppb</th>
<th>Correlation Coefficients</th>
<th>$t_R$/min</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MA</td>
<td>43</td>
<td>0.999</td>
<td>18.8</td>
<td>1.8</td>
</tr>
<tr>
<td>DMA</td>
<td>46</td>
<td>0.999</td>
<td>22.5</td>
<td>2.4</td>
</tr>
<tr>
<td>TMA</td>
<td>76</td>
<td>0.999</td>
<td>29.6</td>
<td>1.5</td>
</tr>
<tr>
<td>TMAO</td>
<td>72</td>
<td>0.999</td>
<td>34.7</td>
<td>2.1</td>
</tr>
</tbody>
</table>

Lab Sample Determination

In order to illustrate an application of the developed method, a lab generated sample was analyzed. The sample was obtained by atomizing a solution containing methylamines and TMAO into a pre-weighed filter and then extracted with DI water before being injected into the ion chromatograph. Fig. 5-3 is the chromatogram of a lab generated aerosol sample. It can be seen that all the peaks were detected and quantified. Table 5-2 gives the summary of the results from the lab generated aerosol sample. Sample recoveries of between 78.8% and 88.3% were achieved, a good recovery given that amines tend to be sticky and difficult to extract.
**Fig. 5-3.** Chromatogram of a lab generated sample. The conditions are the same as in Fig. 5-2. Peaks: (1) methylamine (2) dimethylamine (3) trimethylamine-N-oxide (4) trimethylamine

**Table 5-2.** The concentrations and recovery data of methylamines and trimethylamine-N-oxide obtained from the laboratory generated aerosol sample

<table>
<thead>
<tr>
<th>Analytes</th>
<th>Measured ppm</th>
<th>Actual ppm</th>
<th>Recovery %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylamine</td>
<td>16.1</td>
<td>20</td>
<td>80.5</td>
</tr>
<tr>
<td>Dimethylamine</td>
<td>16.92</td>
<td>20</td>
<td>84.6</td>
</tr>
<tr>
<td>Trimethylamine</td>
<td>47.28</td>
<td>60</td>
<td>78.8</td>
</tr>
<tr>
<td>Trimethylamine N-oxide</td>
<td>52.98</td>
<td>60</td>
<td>88.3</td>
</tr>
</tbody>
</table>
Conclusions

Ozonolysis of tertiary amines in the atmosphere likely results in the formation of tertiary amine oxides (Angelino et al., 2001). In light of smog chamber experiments described in Chapters 3 and 4, ozonolysis of tertiary amines produces a significant amount of aerosol, an unknown fraction of which may be tertiary amine oxides. Identifying and quantifying these species using existing mass spectrometric techniques may be challenging. A method that can identify and quantify tertiary amine oxides in aerosol samples is therefore required. In this work, a method for simultaneous determination of methylamines and TMAO has been developed using ion-exchange chromatography with a non-suppressed detection. The method described here is simple and has lower detection limits suitable for analysis of aerosols from laboratory reactions as well as those collected from ambient air. This method has been tested using lab-generated aerosol samples and it is reproducible and quantitative. This method will especially prove crucial in better understanding of the mechanism proposed in Chapter 3.

References


Zhang, Q. and Anastasio, C.: Free and combined amino compounds in atmospheric fine particles (PM₂.₅) and fog waters from Northern California, Atmos. Environ., 37(16), 2247-2258, 2003.
CHAPTER 6

SUMMARY AND FUTURE DIRECTIONS

The challenge of characterizing atmospheric aerosols requires instruments that can measure as many properties as possible in real-time. Currently, a combination of instruments is used to perform this task, each with its own individual issues. A lot of assumptions are thus made when comparing data from the various instruments. In recent years, real-time aerosol mass spectrometry has attempted to close that gap. Not only does it provide chemical and size information, but it is also quantitative and has a fast time resolution.

Scientific Findings from Field Measurements

The AMS was used in studies in Cache Valley in Northern Utah that suffers winter pollution from fine particles. The findings include the presence of reduced organic nitrogen aerosol in the spectra. Whereas a number of studies have detected similar peaks, so far this was the only study that attempted to quantify them. It is not clear where the precursor organic nitrogen comes from, but Cache Valley is known for producing large amount of ammonia from the agricultural activities. Amines, which are derivatives of ammonia, can also come from these sources. Some studies have indicated that the concentration of gas phase amines from these sources may be as high as that of ammonia. Size distribution and principal component analysis indicate that particles in Cache Valley arise mainly from secondary sources from atmospheric reactions of precursor gases. A small fraction may be emitted directly into the atmosphere, the likely sources being vehicle emissions and winter-time residential heating. Since no source profiles exist in
Logan, it is difficult to gauge using mass spectrometry alone, the relative contributions from each source.

A source study that was conducted in Ames, IA at a swine facility indicates that larger particles were the major components of PM, likely from dust and debris from these facilities. The AMS measurement indicated that the main source of submicron aerosols here was organic aerosol and likely background emission. No evidence of amines in particles from the data collected at this site.

**Scientific Findings from Laboratory Studies**

Lab calibration experiments indicate that ionization efficiencies of amine compounds may be significantly different depending on nature of the compound. Salts have higher response factors than neutral species. This means that converting the observed AMS signals into mass loading may produce results that may differ by as much as an order of magnitude. Care should therefore be exercised when quantifying amines into mass concentration.

Experiments conducted in a smog chamber indicate that both salts and secondary organic aerosol species may form from amine reactions. However, the reaction of amines with acids was slower. On the other hand, products formed from amine reactions tend to be mostly secondary organic aerosol. If this was true for the Cache Valley aerosol, then organic nitrogen aerosols may contribute up to 10 µg/m$^3$ during the inversions. This translates to ~30% of the total aerosol (PM$_{2.5}$) during the night-time.

Based on the observed products and isotopic experiments, it is likely that the reaction of amines proceeds via abstraction of hydrogen from the amine followed by RO$_2$
chemistry. Products include both volatile and condensed phase species. The chemical composition of the secondary organic aerosol formed from tertiary amines appears to be complex and mass spectrometry alone may not achieve the task of identifying them. Some of the products formed may include hydroxylated amides. There is possibility that some of the compounds formed may undergo oligomerization to form low volatility products from otherwise volatile constituents. One other product that possibly forms from the reaction of trimethylamine with ozone is trimethylamine oxide. The parent ion for this compound is small and there may be interferences from other ion fragments. A method that utilizes ion chromatography with non-suppressed conductivity appears to be able to not only detect this compound, but also to quantify it.

**On-going Work and Future Directions**

The work that is currently on-going includes studying the chemistry of the different classes of amines. Preliminary results from some of these studies indicate that they differ significantly from the chemistry of tertiary amines. For example, while the products of the tertiary amines indicate oxidized products (up to 3 oxygen atoms in some mass ion fragments), the secondary amine products show that they are mainly molecular weight building (accretion) reactions with only C, H and N in the ion fragments.

In order to better understand the formation mechanism for the reaction of tertiary amines, there is need to identify the products formed from their smog chamber reactions with ozone. For trimethylamine, that product has been proposed to be TMAO. The method reported in Chapter 5 will be used for that purpose. Preliminary results indicate that TMAO may not be a major product.
Future work includes a detailed study of the role of water in amine chemistry. This was initially attempted, but there was no change in aerosol yield/spectra. This will help to bridge the gap between ambient studies where the relative humidity during the measurements was high. Other work that may be needed in future is to study the kinetics of the reaction of amines with various oxidants. The proposed reaction mechanism in this thesis suggests that NO₃ radical reacts by abstracting hydrogen from the amines, a task that may be accomplished by OH radical. It is not quite clear why the total amine signal peaked during the night-time. It could be due to more emission of precursor gases during the night-time or it could be due to the relative reaction rates of amines with these radicals. This needs further investigation.
APPENDICES
Appendix A. Ames, Iowa Source Study
Particle composition and size distributions in and around a deep-pit swine operation, Ames, IA

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Abstract The contribution of emissions from agricultural facilities is rapidly becoming a major concern for local and regional air quality. Characterization of particle properties such as physical size distribution and chemical composition can be valuable in understanding the processes contributing to emissions and ultimate fate of particulate matter from agricultural facilities. A measurement campaign was conducted at an Iowa, deep-pit, three-barn swine finishing facility to characterize near-source ambient particulate matter. Size-specific mass concentrations were determined using minivol samplers, with additional size distribution information obtained using optical particle counters. Particulate composition was determined via ion chromatographic analysis of the collected filters. A thermal-CO₂ elemental/organic carbon analyzer measured particulate carbon. The chemical composition and size distribution of sub-micron particles were determined via real-time aerosol mass spectrometry. Primary particulate was not found to be a major emission from the examined facility, with filter-based impactor samples showing average near-source increases (~15–50 m) in ambient PM₁₀ of 5.8±2.9 μg m⁻³ above background levels. PM₂⁻5 also showed contribution attributable to the facility (1.7±1.1 μg m⁻³). Optical particle counter analysis of the numerical size distributions showed bimodal distributions for both the upwind and downwind conditions, with maxima around 2.5 μm and below the minimum quantified diameter of 0.3 μm. The distributions showed increased numbers of coarse particles (PM₁₀) during periods when wind transport came from the barns, but the differences were not statistically significant at the 95% confidence level. The PM₁₀ aerosols showed statistically increased concentrations of sulfate, nitrate, ammonium, calcium, organic carbon, and elemental carbon when the samplers were downwind from the pig barns. Organic carbon was the major constituent of the barn-impacted particulate matter in both sub-micron (54%) and coarse size (20%) ranges. The AMS PM₁ chemical speciation showed similar species increases, with the exception of NO₃⁻ and Ca²⁺, the latter not quantified by the AMS.

Keywords Swine • Particles • PM₁₀ • PM₂⁻5 • Composition • Size distribution
1 Introduction

Agricultural operations are known to be sources of many types of particles and gases that can ultimately exhibit an influence on local and regional air quality. Emissions potentially impacting air quality from agricultural sources have become a concern for regulatory agencies such as the United States Department of Agriculture (USDA) and the United States Environmental Protection Agency (EPA; USDA 2006; U.S. EPA 2005a). In particular, particulate emissions and gas-phase precursors are of interest because of the implied health effects of particulate matter from epidemiological studies (e.g. Dockery 1993). Agricultural facilities are generally treated as area sources in emissions inventories, however emissions can vary depending on practices used from facility to facility. Particulate influences from agricultural sources can include both primary particles (direct dust-type or combustion emissions) and secondary particles (formed photochemically from gaseous precursors such as ammonia).

Several deficiencies exist for understanding agricultural sources that must be addressed before effective regulations and remediation practices can be implemented (Aneja et al. 2006; USDA 2006). The areas of deficiency include accurate particulate and gaseous emission factors relevant to operational practices, validation of accurate and precise instrumentation and measurement protocols, and establishment of educational and outreach programs to effectively transfer the most current information to all stake holders, including facility operators. Within the past few years, several studies have been implemented which focus on the development of relevant emission factors for confined animal feeding operations (CAFOs), most commonly targeting total suspended particulate (TSP), particulate matter less than or equal to 10 microns (μm) in diameter (PM₁₀), and gas-phase ammonia (NH₃; Wailes et al. 1997; Takai et al. 1998; Schmidt et al. 2002; Heber et al. 2005; Hoff et al. 2005 and others). Martin et al. (2006a, b) reported particulate matter less than or equal to 2.5 μm in diameter (PM₂.₅) emissions for swine and dairy operations.

Most of the currently available particulate emission algorithms for agricultural facilities focus only on total emissions, with little emphasis on particle composition and size distribution beyond base categorization (e.g. PM₁₀). This may be due to the domination of coarse (>5 μm) particulate emissions from typical agricultural facilities (Auermann et al. 2006). However, near-source particles may undergo rapid physical and compositional changes which affect their size distribution (coagulation and nucleation) and base chemistry (secondary species formation) as they transport downwind from the source (Lammel et al. 2004). Physical and chemical properties of the anthropogenically produced aerosols near-source and in ambient environments have been widely studied (Rogge et al. 1993; Hughes et al. 1999; Turnbull and Harrison 2000; Alfaro and Laurent 2001; and others). Although some particulate size and mass distributions and their variabilities have been investigated for various livestock facilities like swine, poultry, dairy, etc. (e.g. Crichlow et al. 1980; Nilsson 1982; Müller and Wieser 1987; Speizer et al. 1988; Barber et al. 1991), these studies were primarily limited to inside facilities and their behavior upon exhaust into the ambient environment has not been sufficiently investigated. Lammel et al. (2004) quantified numerical size distribution of the particles 100–400 m from a German diverse livestock facility (pigs, cows and poultry) and found the tested facility strongly contributed an increased number of particles in the upper two observed size ranges (1–4 μm and 4–20 μm), 1.7×–2.1× and 2.0×–6.4× above background, respectively. Lammel et al. (2004) reported that approximately 20% of the near-farm particulate material consisted of organic carbon (OC), but they were not certain statistically what fraction of OC originated from the facility.
Characterization of the particle properties such as physical size distribution and chemical composition can be valuable in understanding the processes contributing to emissions of particulate matter from agricultural facilities. The study described was designed to characterize concentrations of particulate matter in the immediate vicinity of a deep-pit swine facility. In addition, characterization of particle mass and number distributions was obtained to determine relative contribution of the swine facility to fine and coarse particulates. The chemical composition of the detected particulate matter was also characterized.

A secondary purpose for the data acquired will be for validation and calibration of a Light Detection and Ranging (LiDAR) system developed by Utah State University’s (USU’s) Space Dynamics Laboratory (SDL). SDL’s “AGLITE” LiDAR system, which has been developed for the measurement of particle emissions from agricultural facilities (Wilkerson et al. 2006), is an example of remote sensing instrumentation being developed to determine particulate emissions on finer temporal and wider spatial scales across an entire facility. Data for particle mass concentration and number density are used to calibrate the measurement of the LiDAR system. While the LiDAR can obtain real-time information about particle plumes from different locations within an area source, calibration of the signals to real mass concentrations obtained from point samplers is necessary. The use of the data described here for the calibration of the LiDAR is described in a separate report. (Zavyalov et al. 2006).

2 Methodology

2.1 Site description

The study described herein occurred from August 24 to September 8, 2005. The sampling site was a deep-pit, swine finishing operation located near Ames, Iowa, USA. The facility consisted of three parallel, east–west oriented barns. Each barn was approximately 80 meters (m) long by 14 m wide, and housed around 1,250 pigs, each with an average animal weight of about 45.5 kilograms (kg). The ventilation for each barn was primarily via passive air exchange by means of two large 79 m by 1.5 m curtain-controlled window openings on the north and south sides of each building. A graveled county road ran parallel to the south property line about 46 m from the southern most barn (Barn 1). The site layout and receptor/sampling locations are shown in Fig. 1.

The farm was surrounded by cultivated corn fields on the north and west sides and soybean fields on the east and south sides. Fields immediately adjacent to the facility were planted during the study period, with no harvesting or other activities taking place. Five years of historic climatological data were examined to determine the prevailing wind direction during the calendar sampling period and it was found that the expected wind was predominantly from the south (U.S. EPA 2005b). Samplers were placed at locations downwind of the facility given this wind assumption. A sampler in the beanfield was placed due east of the barns to serve as a representative background. On-site meteorological data were collected using a VantagePro 2 weather system (Davis Instruments, Inc.). The meteorological system recorded temperature, pressure, wind direction, wind speed, total solar radiation, UV index, precipitation and relative humidity. An instrument trailer containing real-time particle and gas instrumentation, as well the meteorological data acquisition system, was setup 39 m north of the northernmost barn (Barn 3, refer to Fig. 1) and also served as the main downwind sampling location/receptor based on historical wind data.
2.2 Particle collection and analysis

Size-fractionated particulate mass concentration data (PM$_{2.5}$ and PM$_{10}$) at the sample locations were collected on filters using ten MiniVol portable air samplers (AirMetrics, Inc.). The MiniVols’ inlets were assembled to sample PM$_{2.5}$ for the first eight days (August 24 to September 1, 2005) and PM$_{10}$ for the rest of the test period (September 2–8, 2005). Visual observations of relatively light collections on the PM$_{2.5}$ background and facility-impacted filters motivated the switch to the PM$_{10}$ impactor heads. The samplers’ rotameters were calibrated prior to field deployment and operated at actual flow rates of 5.0 liters per minute (L min$^{-1}$), with a nominal 23-h sampling time. The particles were collected on pre-weighted, pre-conditioned 47 millimeter (mm) Teflon filters according to federal protocols (40 CFR 50.), which were transported back to USU’s Utah Water Research Laboratory (UWRL) for analysis. Conditioning was at room temperature in a desiccator (~20–40% RH). The filter weights both pre- and post-sampling were measured using a Mettler MTS microbalance (Mettler Instrument Corp.) to the nearest microgram (µg) and the reported filter weights were the mean of three separate daily weights within ±2.5 µg. This uncertainty is roughly equivalent to a minimum system detection level (MDL) of 0.36 micrograms per cubic meter (µg m$^{-3}$).

Chemical characterization of the collected ambient particulate matter involved both real-time and post-test laboratory analyses. Ion chromatography (IC) was used to determine the concentrations of dominant anions and cations from the collected filters. After the filter weights were finalized, the filter ions were extracted with a total of 30 milliliters (mL) of 0.2 µm filtered, double-distilled, deionized water (DDW). The Teflon filters were sequentially sonicated with 10 mL of DDW for 10 min three times each. The 30 mL total eluted solution was split into two 15 mL aliquots: one for anion analysis and one for cation.
analysis. The solutions for cation analysis were additionally spiked with 10 microliters (μL) of 0.5 molar (M) HCl to prevent the ammonium (NH₄⁺) from volatilizing as ammonia (NH₃). The IC system (Dionex, Inc.) consisted of the following equipment: an AS 40 automated sampler, a CD 20 conductivity detector, a GP 40 gradient pump, an ASRS-Ultra II membrane suppressor for anions and a CSRS-Ultra II membrane suppressor for cations, LC 25 chromatography oven, and an IonPac® AS4A-SC (4 mm) anion column or an IonPac® CS12A cation column, depending on the ionic species of interest. For anion analysis, a 195-μL injection loop was used in the IC, while for cations analysis, an 80-μL injection loop was used. The IC eluent used for anions analysis was a 30 millimolar (mM) sodium hydroxide (NaOH) solution. The eluent used for cation analysis was a 0.15 M sulfuric acid (H₂SO₄) solution. Standard solutions were prepared from ACS reagent grade salts (Fisher-Scientific) and calibration curves were prepared using concentrations of 0.1, 0.5, 1, 5, and 10 milligrams per liter (mg L⁻¹) or parts per million (ppm). Blank and continuing calibration verification standards (CCV) were tested approximately every 10 samples. Ten percent of the samples were randomly chosen for duplicate analysis to ensure reproducibility.

A Series 5400 Ambient Particulate Carbon Monitor (Rupprecht & Patashnick Co., Inc.) was assembled in the instrument trailer to characterize organic and inorganic (elemental) particulate carbon (OC and EC, respectively) downwind from the facility. The 5400 is a semi-real-time system which provides data at user defined time intervals (every 3 h for these studies) for organic carbon and total carbon (TC) concentrations (μg m⁻³). The instrument determines carbon concentrations by thermal-carbon dioxide (CO₂) analysis (R&P 2004). As recommended by the operating manual (R&P 2004), the system dwell times and temperatures were set for 600 s at 275°C and for 360 s at 750°C for OC and TC determination, respectively. The EC fraction is determined as the difference between the TC and OC concentrations. Flow and CO₂ response calibrations were performed prior to field deployment and zero air and CO₂ span audits were performed on-site every third day using commercially-purchased calibration gases (Scott Specialty Gases, Inc.). The instrument was set to operate at 16.7 L min⁻¹ and the size fractionation head (PM₁₀ or PM₂.₅) was set in conjunction with MiniVols’ inlets. Because the method measures only the carbon part of the organic fraction, one must compensate for oxygen-containing and other functional groups. The CO₂ based concentrations were multiplied by a correction factor, R_organic, of 2.1 recommended for non-urban organic aerosols (Malm and Hand 2005).

Ambient particulate size analyses were also performed using six Model 9722 Ambient Aerosol Particulate Profilers (MetOne, Inc.) at several of the same locations as the filter-based samplers. The 9722 are real-time, optical particle counters (OPCs) which simultaneously measure particle number concentrations using laser diode technology into eight user-defined size ranges between 0.3 μm and 10 μm over 20 second time periods. The system samples at a nominal flow rate of 1 L min⁻¹; however, the systems’ flow paths are plumbed such that they operate with a 2:1 dilution rate to allow for sampling of high concentration particulate fields. The lower cut off size for the sampling ranges were set to 0.3, 0.5, 0.7, 1, 2, 2.5, 5 and 10 μm. The systems’ were factory calibrated immediately prior to field use. Data were archived to central data acquisition system via individual radio frequency channels.

An aerosol mass spectrometer (AMS; Aerodyne, Inc.) was also stationed inside the instrument trailer to quantify and characterize sub-micron organic and inorganic ions. The AMS is made up of three differentially pumped chambers: the sampling chamber, the sizing chamber, and the analysis chamber. The sample is brought into the instrument by the difference in pressure through an aerodynamic focusing lens (Liu et al. 1995). Particles in
the range of 50–700 nanometers (nm) are focused with almost 100% efficiency with particles above and below that size range focused with less efficiency. As the AMS system essentially characterizes particulate matter less than or equal to 1.0 μm, it approximates a PM$_1$ measurement. However, this is dependent on composition as some components, especially metals and elemental carbon are not detected by this method. In addition, the AMS detects the full organic matter (OM) composition rather than simply the carbon fraction. The particles within the chambers are accelerated through supersonic expansion to a velocity proportional to their size. Particles continue onto an oven where the non-refractory components are flash vaporized at 600–700°C. The vapors are then subjected to a beam of electrons at 70 electron volts (eV) for ionization before being scanned by a quadrupole mass spectrometer and detected with an electron multiplier. The instrument can be operated in two modes: (1) the “mass spec” (MS) mode, which obtains chemical speciation for the ensemble particle sample and (2) the “time-of-flight” (ToF) mode which obtains particle size distributions associated with specific chemical species. A more detailed explanation of the principles and capabilities of the AMS can be found in Jayne et al. (2000) and Jimenez et al. (2003).

The AMS was operated on-site continuously from August 29 to September 4, 2005. Particulate samples were withdrawn from the ambient air through 0.25-in., outer diameter (o.d.) copper tubing at a flow rate of about 1.2 cubic centimeters per second (cm$^3$ s$^{-1}$). The AMS time averaging interval was set to 1 hour due to the low concentrations of the submicron particles expected at the site. During this time, the AMS alternated between MS and ToF modes of acquisition. Ionization efficiency and size calibrations were performed on-site using ammonium nitrate (NH$_4$NO$_3$) and commercially-purchased polystyrene latex (PSL) spheres. The former were used in the computation of the mass concentration calibrations, while the latter were for size distribution quantification.

3 Results and discussion

3.1 Observed meteorology

Figure 2 shows the hourly averaged wind directions for the entire study period as measured by the Vantage Pro on the top of the instrument trailer (5 m height). As can be seen, the wind blew from the optimum direction in relationship to the established sampling array, the southern quadrant (135–225°), only about 37% of the time. Furthermore, calm or non-detectable winds were observed 14% of the time. The wind directions were most variable during the early (PM$_{2.5}$) portions of the study period, but as can be seen, were rarely from the desired southern quadrant. Similarly, the first two days of the PM$_{10}$ studies were characterized by primarily northern winds. Southern winds became more typical during the final few days of the study. Therefore, the data were divided into three analysis periods based on sample type and prevailing wind direction: (1) PM$_{2.5}$ variable winds (north & south), August 24–31, 2005, (2) PM$_{10}$ upwind (north winds), September 1–2, 2005, and (3) PM$_{10}$ downwind (south winds), September 3–8, 2005. Unless otherwise noted, the Beanfield sampling location (refer to Fig. 1) was found to be most consistently crosswind to the presumed particulate source (the barns) and considered as the ambient background location.

Atmospheric pressures were stable for most of the campaign. A 4.1 mm pressure drop was observed over five hours on August 25–26, 2005 and a 3 mm pressure increase was observed over a one hour period on September 5, 2005. Ambient temperature averaged 21.1
degrees Celsius (°C), the highest hourly temperature observed was 30.5°C, and the lowest hourly temperature observed was 10.1°C. The average barometric pressure was 738.3 mm mercury (mm Hg), with maximum and minimum hourly values of 743.7 and 732.3 mm Hg, respectively.

3.2 Particle emissions

Figure 3 shows the average facility-derived PM$_{2.5}$ and PM$_{10}$ concentrations measured by the MiniVol samplers located throughout the study area. The facility-derived particulate concentration refers to a selected receptor’s concentration minus the observed local background concentration. The PM$_{2.5}$ background concentrations during the early phases of the study (August 24–31, n=8) averaged 13.5±3.6 μg m$^{-3}$ and PM$_{10}$ background concentrations averaged 36.4 μg m$^{-3}$ and 37.9±6.3 μg m$^{-3}$ for the upwind (September 1–2, n=2) and downwind (September 3–8, n=6) periods, respectively. Unless otherwise noted, all uncertainties reported represent the 95% confidence interval (95% CI) about the average. Furthermore, it should be noted that during the PM$_{10}$ upwind period, samples were only collected on two days, as such, confidence intervals could not be calculated for that period.

As can be derived from Fig. 3, the facility-derived (downwind-background) PM$_{2.5}$ concentrations were only slightly above the typical background values. The average PM$_{2.5}$ concentration attributable to the facility averaged only 1.7±1.1 μg m$^{-3}$, indicating relatively little emissions of PM$_{2.5}$-sized particles from deep-pit swine finishing operations. Even though the wind directions during the PM$_{2.5}$ measurement phase of the described study were variable, the receptors placed between the barns averaged only 1.8±0.8 μg m$^{-3}$ and 1.6±0.8 μg m$^{-3}$ above background, respectively. Similarly, the PM$_{10}$ concentrations at most of the receptor locations on the north or upwind days showed little difference above background concentrations. Not unexpectedly, the sampler between Barns 1 and 2 did show an increased concentration an average of 9.2 μg m$^{-3}$ above background levels (over two daily periods).

However, on days when the winds were predominantly southern (September 3–8) most of the receptors were downwind of the facilities. The PM$_{10}$ attributable to the local swine
Fig. 3 Facility-derived PM$_{2.5}$ and PM$_{10}$ concentrations measured by MiniVol samplers around the deep-pit swine operation (error bars represent the 95% confidence interval about the mean). Missing data indicate periods when no samples collected due to sampler availability or system error.

operation became more significant: 5.8±2.9 µg m$^{-3}$ above background averaged across all of the receptor locations. As can be seen from Figs. 1 and 3, the facility-derived PM$_{10}$ decreased as the distance from the barns increased. The near-source, ground-level PM$_{10}$ attributable to the barns (Barns 1–2, Tower 3.9 m, Central, and Trailer receptors) averaged 10.3±5.0 µg m$^{-3}$. The highest and most significant concentrations above background were observed at the inter-barn locations (25.1±13.2 µg m$^{-3}$).

The AMS found PM$_{1}$ mass concentrations of 0.91±0.14 µg m$^{-3}$ and 1.02±0.19 µg m$^{-3}$, for the previously discussed PM$_{2.5}$ and upwind PM$_{10}$ periods, indicating a statistically consistent background concentration of the submicron (≤1 µm) particulate matter. The average AMS PM$_{1}$ mass concentration during the downwind study period was 2.47±0.28 µg m$^{-3}$, indicating a small contribution of PM$_{1}$ material from the observed facility. Comparing these values with the averaged filter-based ambient PM$_{2.5}$ and PM$_{10}$ concentrations measured at the sampling trailer, the PM$_{1}$ made up 6.6% and 4.1% of the upwind or background PM$_{2.5}$ and PM$_{10}$, respectively. During the facility-impacted (downwind) measurements, the ultra-fine particle concentrations increased (Fig. 4) as did the larger particle sizes. However, the PM$_{1}$ fractionally made up around the same percentage (5.9%) of the PM$_{10}$ mass as during the upwind periods.

3.3 Particle composition

The chemical compositions of the PM$_{2.5}$ and PM$_{10}$ as determined from the filter-based AirMetrics’ sampler located at the air quality trailer are shown in Table 1. Approximately 48% and 33%, of the upwind (PM$_{2.5}$ and PM$_{10}$) and downwind (PM$_{10}$) filter mass, respectively, were unidentified using the employed analytical techniques. Although not enough samples were collected for statistical analysis of the upwind PM$_{10}$ data, of the identified species only calcium (Ca$^{2+}$) concentrations appeared to be different between the upwind PM$_{2.5}$ and PM$_{10}$ samples. Shacklette and Boerngen (1984) identified the crustal
surfaces of north-central Iowa as abundant in calcium. Particulate-bound concentrations of fluoride (F⁻), chloride (Cl⁻), sodium (Na⁺), and magnesium (Mg²⁺) showed no statistical difference between upwind and downwind (source-impacted) conditions, indicating these species are likely associated with local or regional background particulate. It is of further interest to note the observed abundance of fluoride in the background particulate mass (1.04±0.31 µg m⁻³, over all trailer samples). Shacklette and Boerngen (1984) showed regional Iowa soil elevated in fluoride concentrations which could explain the relatively high fluoride levels. Sulfate (SO₄²⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), calcium, organic carbon (OC), and elemental carbon (EC) all showed statistical (95% CI) concentration increases when impacted by the swine facilities. The OC was consistently the largest single, identified component of the PM₁₀ concentrations measured at the sampling trailer (≈20%). The OC component increased by a factor of approximately three from 2.53±0.48 to 7.56±2.65 µg m⁻³ between periods when the sampling trailer was upwind and downwind of the barns. The EC component showed approximately a four fold increase between non-impacted and impacted conditions: 0.40±0.13 to 1.76±0.76 µg m⁻³, respectively. However, the EC contribution accounted for only ≈3–5% of the particle mass.

The AMS-measured PM₁ composition is shown in Table 2. Due to equipment malfunctions the AMS data contained gaps at the beginning and end of the period while the MiniVol instruments sampled. The PM₁ system found measurable concentrations of SO₄²⁻, NO₃⁻, NH₄⁺, and OM. All but NO₃ show statistically significant concentration increases when the trailer was downwind versus upwind of the swine barns (≈2–3%). As with the PM₁₀, the OC was the largest component of the PM₁ and showed similar behavior depending on the wind direction (see Fig. 5). As can be seen, the PM₁ OM concentration was on an order of magnitude less than the PM₁₀ OC concentrations.

In order to examine one possible reason for the unknown mass concentrations previously mentioned, an ion mass balance was performed for the analyzed AMS and trailer aerosols (Fig. 6). The total cations measured were found to be in excess for all observed samples, regardless of wind direction or particle size classification. However, as can be seen, the deficit was only statistically significant (95% CI) for the downwind, barns-impacted conditions. Recall, there were an insufficient number of PM₁₀ upwind samples to determine confidence intervals. It is suspected that much of the ion deficit could be the result of carbonate (CO₃⁻), which was not resolved with the employed analytical techniques. The presence of abundant particle-based Ca²⁺ and Mg²⁺ further suggests the presence of carbonates, which are often associated with soil-derived particles (Krivacsy and Molnar 1998; Oscay et al. 2006). An additional possibility for the mass deficit could be the result of unquantified crustal materials. During the field campaign, the LiDAR measurements of
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<th>Na^+</th>
<th>NH4^+</th>
<th>K^+</th>
<th>Mg^{2+}</th>
<th>Ca^{2+}</th>
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<td>0.25±0.03</td>
<td>0.69±0.60</td>
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<td>BDL</td>
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<td>0.15</td>
<td>0.36</td>
<td>0.39</td>
<td>0.38</td>
<td>BDL</td>
<td>0.25</td>
<td>2.67</td>
<td>2.75</td>
<td>0.58</td>
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<td>9/3-7/2006 PM_{10} Downwind</td>
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<td>0.74±0.25</td>
<td>0.48±0.12</td>
<td>1.49±0.49</td>
<td>BDL</td>
<td>0.35±0.04</td>
<td>3.74±0.73</td>
<td>7.56±2.65</td>
<td>1.76±0.76</td>
<td>40.5±6.7</td>
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Table 1 Average filter-based ambient particulate-phase ionic and EC/OC concentrations as measured at the air quality trailer (BDL = below detection limit)
Table 2  Average particle-phase ionic and organic carbon concentrations measured by the AMS (PM$_1$)

<table>
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<th>NO$_3$</th>
<th>NH$_4^+$</th>
<th>OC</th>
<th>Total AMS PM$_1$</th>
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<td>8/29–31/2006</td>
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<td>0.04±0.01</td>
<td>0.06±0.02</td>
<td>0.38±0.07</td>
<td>0.91±0.14</td>
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<tr>
<td>9/1–2/2006 (upwind)</td>
<td>0.03±0.01</td>
<td>0.02±0.01</td>
<td>0.03±0.01</td>
<td>0.61±0.14</td>
<td>1.02±0.19</td>
</tr>
<tr>
<td>9/3–5/06 (downwind)</td>
<td>0.12±0.02</td>
<td>0.04±0.01</td>
<td>0.12±0.03</td>
<td>1.34±0.11</td>
<td>2.47±0.28</td>
</tr>
</tbody>
</table>

Zavyalov et al. (2006) observed several instances of plumes from the nearby gravel road dispersing over the various sample locations. This happened on 2 days and due to calm winds, affected all of the samplers.

3.4 Particle distributions

The numerical particle size distributions at the trailer location, as measured by the MetOne OPCs, for upwind and downwind periods can be seen in Fig. 7. As can be seen, both the background and barns-impacted distributions showed strong bimodal distributions. The observed bimodal curve is similar in shape and modal locations as those reported by Schneider et al. (2001) for upwind and inside an experimental piggery. However, the number concentrations reported here were more in line with Schneider’s reported upwind values, especially for particles less than approximately 1.0 μm in diameter. A large particle mode appeared centered around 2.5 μm and a fine (accumulation) mode was evident somewhere below the OPCs’ minimum quantified diameter (~0.3 μm). The barns-impacted (downwind) average number distribution showed a trend for increased numbers of supermicron particles (>1 μm) compared to the non-impacted (upwind) number distributions, but as shown in Fig. 7, the difference was not statistically significant at the 95% confidence level. As shown, this was due to the relatively large uncertainties associated with the background distributions. The average count mean diameters (CMDs)
for the south and north wind periods were found to be similar, yet statistically different at 0.46±0.01 μm and 0.43±0.01 μm, respectively.

Size fractionated mass distributions were obtained from the particle counts using the average density of the particles derived by combining the number and AirMetrics’ mass concentrations and assuming uniform density throughout the entire size range following the procedure outlined by Hinds (1999). The calculated particulate density of 2.15 grams per cubic centimeter (g cm⁻³) agrees well with densities from atmospheric aerosol databases (Jursa 1985; Hess et al. 1998). As with the number distributions, bimodal distributions were observed and the downwind and upwind periods did not show statistically different mass distributions (Fig. 8). However, the larger particle size range (coarse mode) did show higher average concentrations. As can also be seen in Fig. 8, the modal diameters are not apparent, but a minimum mass diameter was observed around 0.8 μm. The mass mean diameters (MMDs) for the south and north wind periods were found to be 5.14±0.11 μm and 4.52±0.16 μm, respectively. The increase in MMD during south wind periods is consistent with observed particulate impacts from the swine facilities.

The mass distributions of the individual chemical species measured by the AMS are shown in Fig. 9 with respect to vacuum aerodynamic diameter (Dva). This is the aerodynamic diameter measured under the free-molecular regime. During the upwind
periods sulfate was found to be the dominant mass species, followed by OM. During downwind periods OM was the only dominant species detected by the AMS.

4 Summary

Primary particulate matter was a minor pollutant emitted from the examined swine finishing facility, adding ~15% to the prevailing background levels of PM$_{10}$ and ~12% to the background PM$_{2.5}$. Filter-based, AirMetrics’ MiniVol impactor samples found that the general area around the facility showed an increase in PM$_{10}$ of 5.8±2.9 μg m$^{-3}$ above background levels (≈37 μg m$^{-3}$), although in the area between the barns the PM$_{10}$ was found to be 25.1±13.2 μg m$^{-3}$ above background. Local PM$_{2.5}$ attributable to the facility was found to be increased by an average of 1.7±1.1 μg m$^{-3}$, relative to background PM$_{2.5}$ concentrations (≈14 μg m$^{-3}$). Interestingly, the areas between the barns showed essentially the same above background concentrations as the receptors located further from the barns. An aerosol mass
spectrumometer measured ambient PM$_1$ at a single location, the air quality trailer, located approximately 39 m north of the northern most barn (refer to Fig. 1) and reported upwind (non-facility impacted) and downwind PM$_1$ concentrations of 1.0±0.2 µg m$^{-3}$ and of 2.5±
0.3 µg m$^{-3}$, respectively. Optical particle counter (OPC) analysis of the numerical size
distributions showed a strong bimodal distribution with maxima around 2.5 µm and
somewhere below the OPCs' minimum quantified diameter (<0.3 µm). The average
distributions showed increased numbers of coarse particles during barns-impacted periods,
but the differences did not become statistically significant until the 68% confidence level
(approximately one standard deviation).

Chemical composition of the aerosols at the air quality trailer was quantified by ion
chromatographic analysis of the impactor filters, with the use of a semi-real time EC/OC
analyzer (configured to match the size fractionation of the MiniVol impactors), and via the
AMS. For the PM$_{10}$, sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), ammonium (NH$_4^+$), calcium (Ca$^{2+}$),
organic carbon (OC), and elemental carbon (EC) all showed statistically significant
concentration increases when the wind direction was from the pig barns to the samplers
(south winds). Particulate magnesium (Mg$^{2+}$), potassium (K$^+$), sodium (Na$^+$), fluoride, (F$^-$),
and chloride (Cl$^-$) showed no statistical difference based on wind direction. An excess of
cations to anions was observed which may be attributed to the fact that carbonate (CO$_3^{2-}$) was
not detected with the utilized analytical scheme. The AMS PM$_1$ chemical speciation showed
similar species increases as with the filter-based measurements, with the exception of
NO$_3^-$, which was not significantly different between the upwind and downwind samples
and Ca$^{2+}$ which is not quantified by the AMS. Organic carbon was the major constituent of
the barn-impacted particulate matter in both sub-micron and coarse size ranges, accounting
for approximately 54% and 20% of the observed mass, respectively.

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recommendations expressed in this publication are those of the authors and do not necessarily reflect the
view of the U.S. Department of Agriculture.

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September 18, 2008

Dear Derek Price,

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I hereby give my permission to Mark E. Erupe to reprint the manuscript entitled “Trimethylamine as a precursor to secondary organic aerosol in the atmosphere via nitrate radical reaction” co-authored by Philip J. Silva, Derek Price, John Elias, Quentin Malloy, Li Qi, Bethany Warren and David R. Cocker III, in his dissertation.

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Date: 11/19/08
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CURRICULUM VITAE

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SPECIAL TRAINING:

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CONFERENCE PRESENTATIONS:

2. SOA Formation from Reactions of Tertiary Amines with Nitrate Radical, ACS Regional Meeting, Provo, UT, (2008) [Talk]
3. Trimethylamine Amine as Precursor to SOA Formation via Nitrate Radical Reaction, AAAR Annual Conference, Reno, NV, (2007) [Poster]
5. Amines in Fine Particles: Myth, Trace Species, or Major Components? AAAR Annual Conference, Austin, TX, (2005) [Talk]
PUBLICATIONS:


