Characterization of ambient aerosols and their evolution under various atmospheric conditions in the Northeast U.S

Jie Zhang
University at Albany, State University of New York, jzhang35@albany.edu

The University at Albany community has made this article openly available. Please share how this access benefits you.

Follow this and additional works at: https://scholarsarchive.library.albany.edu/legacy-etd

Part of the Atmospheric Sciences Commons, and the Other Chemistry Commons

Recommended Citation

This Dissertation is brought to you for free and open access by the The Graduate School at Scholars Archive. It has been accepted for inclusion in Legacy Theses & Dissertations (2009 - 2024) by an authorized administrator of Scholars Archive. Please see Terms of Use. For more information, please contact scholarsarchive@albany.edu.
Characterization of ambient aerosols and their evolution under various atmospheric conditions in the Northeast U.S.

by

Jie Zhang

A Dissertation
Submitted to the University at Albany, State University of New York
in Partial Fulfillment of
the Requirements for the Degree of
Doctor of Philosophy

College of Arts and Sciences
Department of Atmospheric and Environmental Sciences

2019
Abstract

The University at Albany Atmospheric Sciences Research Center (ASRC) mobile laboratory, which includes a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), a Scanning Mobility Particle Sizer (SMPS), and several gas sensors, etc., has been used to characterize atmospheric aerosols and air quality at different locations in the Northeastern US (including urban, forest, and mountain areas) and the aerosol evolutions under a variety of atmospheric conditions (including extreme weather, fog, and cloud, etc.). In this dissertation, I present the findings of the several field measurements using the ASRC mobile lab, focusing on the influences of extreme events (including high O$_3$, heat wave, and firework displays) on urban aerosol properties, fog processing on rural forest formed secondary organic aerosol, and cloud processing of the mountain area aerosol.

For the urban area, we first investigated the influence of sea breeze on ozone and air quality using on-road measurements. Dramatic O$_3$ spatial variations with a $\Delta$O$_3$ $\Delta$y$^{-1}$ in excess of 10 ppb km$^{-1}$ were captured by the instruments, and high O$_3$ and aerosol mass concentrations with high oxidation states were clearly influenced by the sea breeze plume. We also studied the aerosol evolution during an extreme heatwave period, and the results show two pollution patterns - one related directly to photo-oxidation of anthropogenic VOC and the other one related to further reaction through the oxidation of DMS throughout the ocean surface boundary layer. In a separate study, the impact of fireworks (FW) events on air quality was determined though measurements of aerosol particles from FW displays during the Independence Day (July 4, 2017) holiday period at Albany, NY, USA. The results showed the intense emission of FW particles from the Independence Day celebration (including K salt and FW related organics) contributed about 77%
(36.3 μg m$^{-3}$) of total PM1 (47.0 μg m$^{-3}$) measured at the uptown site during Independence Day FW significantly influenced period (07/04 23:00-07/05 03:00). This highlights the significant episodic influence of FW burning on fine aerosol mass concentration and chemical characteristics while large numbers of people are clustered together and breathing the outdoor air.

Moving to the rural forested location, the effect of foggy conditions and fog processing on the characteristics of secondary aerosol was studied at Pinnacle State Park, NY. Our study identified two fresh biogenic secondary organic aerosol factors (BSOA: BSOA-1 and BSOA-2); BSOA-1 was likely formed through the reaction of biogenic volatile organic precursors with NO$_3$ and converted to BSOA-2 through fragmentation or further oxidation. During fog processing, the more oxidized oxygenated organic aerosol (MO-OOA) showed the highest uptake into fog droplets, or scavenging efficiency (90%), followed by SO$_4^{2-}$ (50%), the less oxidized OOA (LO-OOA) (45%), and BSOA (BSOA-1+BSOA-2, 24%). The high positive correlation between relative humidity (RH)/or aerosol liquid water (ALW) and BSOA mass concentration suggests the importance of aqueous-phase processing on BSOA formation, and an increase in the ALW ratio of 0.1 corresponded to an average increase of about 0.2 μg m$^{-3}$ in the BSOA factor.

Finally, a pilot study took place at Whiteface Mountain (WFM) in the Adirondacks of upstate NY during the summer of 2017 to evaluate the chemical processing of aerosol below and within clouds. Below-cloud and cloud interstitial submicron aerosols were characterized in real-time using the ASRC mobile lab. The observations also show chemical differences between the below-cloud layer, the transition layer (just below-cloud), and the in-cloud layer. The aerosol properties, such as mass concentration, size distribution, oxidation state and hygroscopicity parameter for each layer are discussed in detail.
Acknowledgements

In the past four years, numerous individuals have supported and guided me to pursue my Ph.D., and this course is a truly life-changing one and would affect my whole life. Without them, none of these is possible.

First of all, I would give very big thank you to my supervisor Dr. James Schwab for all the support and encouragement you gave me. Thank you for your patience when I first came to ASRC and only spoke little English, and guiding me to improve it and developing the scientific mind for my study. Thank you for your encouraging when I was frustrating for the not-working instruments, and teaching me to fix them hand by hand. Thank you for supporting my experiment design and training me to join field campaign individually without any feeling of incompetence like before. Special thanks for your guidance of my publications. The thousands of comments you gave me for my original writing cost you so much time, and always guide me to learn more. And I will never forget the countless revisions we have had before submitting the manuscript, and the encouragement you gave me when I met the critical and negative reviewers. Your knowledge of science and all excellent personality would inspire me to be a better scientist in the future.

Second of all, I want to extend sincere thanks to my other committee members: Dr. Robert Keesee, Dr. Qilong Min, Dr. Sara Lance. It is my great pleasure to have you on my committee and I am very grateful for all the meetings we have had. Thank you for Dr. Keesee guiding me get a deep understanding about the mass spectrometry technologies, for Dr. Min giving me so much kindly suggestion during the build-up of my research, for Dr. Lance providing me countless help in the papers, in fixing the AMS, and in the CPOC field measurements. Certainly, I cannot thank you all enough for reading and providing feedback on my dissertation.
Many thanks also to other group members- Matthew Ninneman, Joseph Marto, Hesham Hassan, William May, Richard Brandt, Janie Schwab, for your help with all the experiments throughout the entire four years. I am also grateful to my other co-authors-Dr. Jeffrey Freedman, Dr. Yele Sun, Dr. Junfeng Wang, Brian Crandall, and all other people in the Atmospheric Sciences Research Center, and Department of Atmospheric and Environmental Sciences at the University at Albany.

Thanks are also due to the New York State Energy Research and Development Authority (NYSERDA) (contract number 48971), and Northeast States for Coordinated Air Use Management (NESCAUM) for their financial support.

Last but not least, I would like to dedicate this dissertation to my family and friends. Without your endless love, supporting, and patience, the dissertation could not be finished. I would specially thank my wife Ping, for being my best company and inspiring me from her previous expertise. I would also thank my son Oliver, for being my best gift during pursuing my Ph.D. Thank you again for making me who I am today.
# Contents

Abstract .................................................................................................................................................. ii

Acknowledgements ................................................................................................................................. iv

Lists of Figures ......................................................................................................................................... xi

Lists of Tables ........................................................................................................................................... xxiv

Chapter 1: Introduction ............................................................................................................................. 1

  1.1 Introduction and Motivation .............................................................................................................. 2

  1.2 Literature Review ............................................................................................................................ 3

    1.2.1 Urban aerosol properties ........................................................................................................ 3

    1.2.2 Interaction between fog and aerosol under fog conditions ...................................................... 5

    1.2.3 Interaction between cloud and aerosol under cloud conditions .............................................. 6

  1.3 Objective and Structure of this Dissertation ................................................................................... 7

  1.4 References ...................................................................................................................................... 9

Chapter 2: Experiment description ........................................................................................................ 19

  2.1 Instruments ....................................................................................................................................... 20

  2.2 Measurement locations and period .................................................................................................. 25

  2.3 References ....................................................................................................................................... 27

Chapter 3: Urban measured aerosol properties ..................................................................................... 29

  3.1 The interaction of the sea breeze and air quality in Long Island .................................................... 29

    3.1.1. Introduction .......................................................................................................................... 30

    3.1.2. Methodology ....................................................................................................................... 32
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.3.1 Introduction</td>
<td>113</td>
</tr>
<tr>
<td>3.3.2 Experimental Section</td>
<td>115</td>
</tr>
<tr>
<td>3.3.2.1 Measurement site and sampling instruments</td>
<td>115</td>
</tr>
<tr>
<td>3.3.2.2 Meteorological parameters</td>
<td>116</td>
</tr>
<tr>
<td>3.3.2.3 Data analysis methods</td>
<td>117</td>
</tr>
<tr>
<td>3.3.3 Results and discussion</td>
<td>119</td>
</tr>
<tr>
<td>3.3.3.1 Identification of firework events and aerosol composition</td>
<td>120</td>
</tr>
<tr>
<td>3.3.3.2 Source apportionment</td>
<td>124</td>
</tr>
<tr>
<td>3.3.3.3 Pollution processing and meteorological conditions</td>
<td>128</td>
</tr>
<tr>
<td>3.3.4 Conclusion</td>
<td>130</td>
</tr>
<tr>
<td>3.3.5 References</td>
<td>132</td>
</tr>
<tr>
<td>3.3.6 Supplement</td>
<td>138</td>
</tr>
<tr>
<td>Chapter 4: The interaction between Aerosol and fog</td>
<td>163</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>164</td>
</tr>
<tr>
<td>4.2 Methods</td>
<td>166</td>
</tr>
<tr>
<td>4.2.1 Sampling location and periods</td>
<td>166</td>
</tr>
<tr>
<td>4.2.2 Aerosol measurements</td>
<td>166</td>
</tr>
<tr>
<td>4.2.3 Data analysis</td>
<td>167</td>
</tr>
<tr>
<td>4.3 Results and discussion</td>
<td>168</td>
</tr>
<tr>
<td>4.3.1 OA source apportionment</td>
<td>168</td>
</tr>
</tbody>
</table>
4.3.2 Fog periods ........................................................................................................... 170

4.3.3 Relationship between BSOA and ALW .............................................................. 173

4.4 Conclusion .............................................................................................................. 175

4.5 References ............................................................................................................. 177

4.6 Supplement ........................................................................................................... 185

Chapter 5: The interaction between Aerosol and Clouds$^2$ ............................................ 204

5.1 Introduction ........................................................................................................... 205

5.2 Experimental procedures .................................................................................... 209

5.2.1 Sampling location and period ......................................................................... 209

5.2.2 Aerosol measurements .................................................................................... 209

5.2.3 Data analysis .................................................................................................... 211

5.3 Results and Discussion ....................................................................................... 213

5.3.1 Cloud layer classification ............................................................................... 215

5.3.2 Aerosol properties comparison ....................................................................... 217

5.4 Conclusion ........................................................................................................... 230

5.5 Reference ............................................................................................................. 230

5.6 Supplement ........................................................................................................... 242

Chapter 6: Concluding Remarks .................................................................................. 258

Appendix ..................................................................................................................... 263
The contents of this chapter are copied from (Zhang et al. 2019a) with permission from *ACS Earth and Space Chemistry* (APPENDIX). Link: https://pubs.acs.org/doi/10.1021/acsearthspacechem.9b00046

The contents of this chapter are copied from (Zhang et al. 2019b) with permission from *ACS Earth and Space Chemistry* (APPENDIX). Link: https://pubs.acs.org/doi/10.1021/acsearthspacechem.9b00117

I hereby state that the two of my previous published articles are reprinted in this dissertation as a whole with the exact wording. These studies are included because they are part of the programmatic line of research that comprised the dissertation and that including them provides a coherent and appropriately sequenced investigation. Lastly, I, the dissertation author, am the lead researcher for these works and the formal copies of permissions from the publications are shown in Appendix.
Lists of Figures

Figure 2.1. The Schematic of the Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS)-----20

Figure 2.1. The locations of the designed measurements in New York State-----------------24

Figure 3.1.1. (a) The observed 8-hour average O₃ concentration on Long Island and the NYC metro area during the on-road measurement period (red dashed line indicates the 70 ppb NAAQS). (b) The average diurnal variation of O₃ at Queens College on Long Island from 06/24-06/29 ----36

Figure 3.1.2. The spatial distribution of the on-road O₃ concentration on (a) 06/30 (15:20-16:20), (b) 07/01 (15:10-19:00), and (c) 08/06 (11:40-18:20) --------------------------------------------------------38

Figure 3.1.3: (a) The time series of O₃ and aerosol compounds on 06/30; (b) Time series of sea salt aerosol signal on 06/30---------------------------------------------------------------39

Figure 3.1.4. The time series of O₃ and NO₂ during on-road measurements on (a) 07/01 and (b) 08/06----------------------------------------------------------------------------------------------------------------------42

Figure 3.1.5. The TROPOMI NO₂ column concentration spatial distribution on (a) 07/01, and (b) 08/06---------------------------------------------------------------------------------------------------------------------43

Figure 3.1.6. (a) Relative aerosol mass spectra at Sands Point, Herrick, and Port Washington on 08/06. (b) Differential fraction of mass spectra signal – defined as Port Washington mass spectra signal minus Sands Point mass spectra signal – on 08/06. --------------------------------45

Figure 3.1.7. The time series of on-road measured O₃ and NO₂ on 07/10 and 07/16-------------46

Figure 3.1.8. (a) The TROPOMI NO₂ column concentration for 07/10. (b) The TROPOMI NO₂ column concentration for 07/16. (c) 07/10 back trajectory for central Long Island (40.74° N, 73.61° W). (d) 07/16 back trajectory for White Plains (40.99° N, 73.78° W)----------------------------------------47
Figure 3.1.9. The relationship between O₃ and NO₂, Oₓ and NO₂ on 07/10 and 07/16

Figure 3.1.10. The spatial distribution of the on-road measured aerosol mass concentration on (a) 08/15 (12:00-19:00), and (b) 08/16 (14:40-19:00)

Figure 3.1.S1. The names and locations of the six New York State Mesonet (NYSM) profiler sites on Long Island

Figure 3.1.S2: The BSI forecasted O₃ concentration distribution for 06/30/2018, 07/01/2018 and 08/16/2018

Figure 3.1.S3. Lidar wind vertical profile for (a) Staten Island; (b) Wantagh; (c) East Hampton; (d) Bronx; (e) Queens; (f) Stony Brook on 06/30. The red arrows indicate the approximate sea breeze onset time

Figure 3.1.S4. The 24-hour HYSPLIT back trajectory for (a) southwestern Long Island (40.59° N, -73.97° W), (b) south-central Long Island (40.74° N, -73.10° W), (c) southeastern Long Island (40.89° N, -72.37° W), (d) northeastern Long Island (41.08° N, -72.44° W), (e) north-central Long Island (40.94° N, -73.13° W), (f) northwestern Long Island (40.81° N, -73.68° W) on 06/30. The back trajectory ended at 20 UTC (16:00 EDT)

Figure 3.1.S5. The mass spectra of the aerosol under high/low O₃ concentration

Figure 3.1.S6. The 24-hour HYSPLIT back trajectory for (a) northwestern Long Island (40.81° N, -73.68° W), (b) north-central Long Island (40.94° N, -73.13° W), (c) northeastern Long Island (41.08° N, -72.44° W), (d) southwestern Long Island (40.59° N, -73.97° W), (e) south-central Long Island (40.74° N, -73.10° W), (f) southeastern Long Island (40.89° N, -72.37° W) on 07/01. The back trajectory ended at 21 UTC (17:00 EDT)

Figure 3.1.S7. Lidar wind vertical profile for (a) Staten Island; (b) Wantagh; (c) East Hampton;
(d) Bronx; (e) Queens; (f) Stony Brook on 07/01. The red arrows indicate the approximate sea breeze onset time.

**Figure 3.1.S8.** The 24-hour HYSPLIT back trajectory for (a) northwestern Long Island (40.81° N, -73.68° W), (b) north-central Long Island (40.94° N, -73.13° W), (c) northeastern Long Island (41.08° N, -72.44° W), (d) southwestern Long Island (40.59° N, -73.97° W), (e) south-central Long Island (40.74° N, -73.10° W), (f) southeastern Long Island (40.89° N, -72.37° W) on 08/06. The back trajectory ended at 21 UTC (17:00 EDT).

**Figure 3.1.S9.** Lidar wind vertical profile for (a) Staten Island; (b) Wantagh; (c) East Hampton; (d) Bronx; (e) Queens; (f) Stony Brook on 08/06. The red arrows indicate the approximate sea breeze onset time.

**Figure 3.1.S10.** NASA EOSDIS Worldview visible satellite image for Long Island on 08/06. The line of cumulus clouds virtually parallel to the shoreline suggests that both a sea and a shore breeze circulation developed.

**Figure 3.1.S11.** The mass concentration/fraction of the aerosol during (a) the Sands Point high O$_3$ period, and (b) the Port Washington high O$_3$ period on 08/06 (unit: µg m$^{-3}$).

**Figure 3.1.S12.** The spatial distribution of the on-road O$_3$ concentration on (a) 07/10 (13:00-16:50), and (b) 07/16 (11:40-17:50).

**Figure 3.1.S13.** The spatial distribution of the on-road O$_3$ concentration on (a) 08/15 (12:00-19:00), and (b) 08/16 (14:40-19:00).

**Figure 3.1.S14.** NASA EOSDIS Worldview visible satellite image for North American on 08/16. The star indicates the location of Long Island.
Figure 3.1.S15. Lidar CNR vertical profile for (a) Queens, (b) Wantagh, (c) Stony Brook, and (d) East Hampton. The sites are ordered going from western to eastern Long Island. The red arrow indicates the start time of the subsiding plume-----------------------------71

Figure 3.1.S16. The time series of PM$_{2.5}$ mass concentration for three DEC sites (Queens College, Maspeth, and Eisenhower Park) on Long Island from 08/15 to 08/19-----------------------------72

Figure 3.2.1. The hour-averaged PM$_{2.5}$ mass concentration at the DEC sites in the NYC metropolitan area from 27 June-7 July, and the PM$_{1}$ mass concentration (light blue line) measured by the HR-ToF-AMS at the Flax Pond Marine Laboratory-----------------------------80

Figure 3.2.2. The time series of (a) total aerosol mass concentration, temperature, wind speed, wind direction, and relative humidity; (b) speciated aerosol mass concentration with the time scale for different periods included; (c) aerosol size distribution; (d) PMF organic factors and MSA mass concentrations for the 27 June-7 July study period-----------------------------82

Figure 3.2.3. The average aerosol mass concentration and mass fraction for each period---------83

Figure 3.2.4. (a) The time series of LO-OOA and anthropogenic VOC concentrations. LO-OOA was colored by RH. (b) The relationship between LO-OOA and the measured anthropogenic VOCs during the study period-----------------------------------------------86

Figure 3.2.S1. (a) The mass spectra of three PMF factors, and (b) the diurnal variability in their mass concentration---------------------------------------------------------------98

Figure 3.2.S2. The mass spectra of MSA from the lab calibration using a pure MSA dilution in water -----------------------------------------------99
Figure 3.2.S3. (a-c) The daily-averaged PM$_{2.5}$ mass concentration for the DEC sites in the NYC metropolitan area from January 2016-December 2018. The blue dashed line indicates the 35 µg m$^{-3}$ NAAQS for PM$_{2.5}$.

Figure 3.2.S4. (a-d) The hour-averaged meteorological factors observed by Mesonet sites, and (e) O$_3$ measured by the DEC sites.

Figure 3.2.S5. The time series of (a) aerosol mass fraction; (b) PTR-MS anthropogenic VOCs (A-VOC); (c) PTR-MS biogenic VOCs for the 27 June-7 July study period.

Figure 3.2.S6. (a) The average aerosol number distribution of each period as a function of aerosol diameter; (b) the average organic and SO$_4$ mode size of each period.

Figure 3.2.S7. The time series of total aerosol mass concentration and LO-OOA mass concentration during EPG and the linear fitting result when comparing the two variables.

Figure 3.2.S8. (a) The vertical profile of CNR and (b) the vertical wind speed from the Stony Brook New York State Mesonet site.

Figure 3.2.S9. The time series of anthropogenic VOCs and O$_3$.

Figure 3.2.S10. The relationship between (a) MO-OOA and SO$_4$ mass concentration, and (b) MO-OOA and MSA mass concentration.

Figure 3.2.S11. (a) The 24-hour back trajectories during the EP period, and (b)-(e) the MODIS detected Chl-a mass distribution.

Figure 3.2.S12. The time series of (a) DMS concentration (colored by wind direction), and (b)
PM$_{2.5}$ concentrations from the DEC sites in upstate NY and in the NYC metropolitan area, in addition to LO-OOA and MO-OOA.

**Figure 3.2.S13.** The HR-ToF-AMS measured average SO$_4$, m/z 44 (representing MO-OOA), and MSA mass size distribution during the EPM period.

**Figure 3.2.S14.** The time series of MO-OOA mass concentration and solar radiation values.

**Figure 3.3.1.** The time series of 1 h (a) mass concentrations of aerosol components (Organic, NO$_3$, NH$_4$, Cl, K, and SO$_4$) from AMS; and (b) mass fraction of each component from 06/27/2017 to 07/07/2017.

**Figure 3.3.2.** Components of the NR-PM$_1$ measured by HR-ToF-AMS during FW event (a), during July 4 daytime (b), before July 1 (c) and after July 5 (d) (The compounds with mass fractions lower than 1% were ignored) (unit: ug m$^{-3}$).

**Figure 3.3.3.** HR-ToF-AMS measured mass size distribution (vacuum aerodynamic diameter: D$_{va}$) for SO$_4$, NO$_3$, organics and K compounds during the FW significantly influenced period (July 4 23:00 to July 5 03:00) and during July 4 daytime (09:00 to 17:00).

**Figure 3.3.4.** The time series of 1 h mass concentration of the five organic aerosol factors determined by the PMF analysis from 06/27/2017 to 07/07/2017.

**Figure 3.3.5.** The time series of 1 h mass concentration of inorganic salt and organic compounds estimated based on the PMF and ion-balance calculations from 06/27/2017 to 07/07/2017.

**Figure 3.3.6.** The time series of (a) 10-mins averaged LiDAR data on Independence Day from July 4 20:00 to July 5 12:00 EDT; (b) 1-hour averaged mass concentration of FW-OOA, SO$_4$, NO$_3$, ...
and K during the same period-----------------------------------------------128

**Figure 3.3.S1.** Locations of measurement sites (from Google maps) -------------------------138

**Figure 3.3.S2.** High-resolution mass spectra from the HR-ToF-AMS (Top: the mass spectra during chopper open mode; Middle: the mass spectra during chopper closed mode; Bottom: the difference between open and closed periods). (a) The m/z 39 ($^{39}$K$^+$) ion peak at July 5 00:30; (b) the m/z 48 (SO$^-$) ion peak at July 5 00:30----------------------------------------------------------140

**Figure 3.3.S3.** High-resolution mass spectra of the measurements of HR-ToF-AMS for K under different heater bias voltage settings during lab calibrations with K$_2$SO$_4$ (Top: the mass spectra from chopper open periods; Middle: the mass spectra from chopper closed periods; Bottom: the difference mass spectra between the above two). (a) heater bias voltage set to 31 V; (b) heater bias voltage set to 30 V---------------------------------------------------------------143

**Figure 3.3.S4.** High-resolution mass spectra of the measurements of AMS (mass spectra from chopper open minus chopper closed). (a) the m/z 39 ($^{39}$K$^+$) ion peak at 07/04 12:01 EDT; (b) the m/z 39 ($^{39}$K$^+$) ion peak at July 4 23:00; (c) the m/z 39 ($^{39}$K$^+$) ion peak at July 5 00:30; (d) the 1-min averaged time series of chopper open, closed and open-closed $^{39}$K$^+$ mass concentration for the night of July 4-5. (e) the 1-min averaged time series of the isotope ratio of $^{41}$K$^+$ to $^{39}$K$^+$ for chopper open and close signals; (f) the m/z 41 ($^{41}$K$^+$) ion peak at July 5 00:30-----------------------------------------145

**Figure 3.3.S5.** The correlation between (a) the reported mass concentration by HR-ToF-AMS and by SMPS from June 27 2017 to July 7 2017 (including the FW periods); (b) the K needed to balance charge for inorganic compounds (SO$_4$, Cl, and NO$_3$) and the HR-ToF-AMS measured K
--------------------------------------------------------------------------149
Figure 3.3.S6. a): The PMF quality of fit parameter ($Q/Q_{expected}$) as a function of the number of factors; b): mass spectra of four identified OA component factors; c): the time series of mass concentration of each organic aerosol factor; d): mass concentration diurnal variation of each organic aerosol factor--

Figure 3.3.S7. The time series of mass concentrations of (a) BBOA+HOA (measured at ASRC site) and BC (measured at ACHD site); (b): LO-OOA and NO$_3$*5; (c) MO-OOA and SO$_4$ ;(d) MO-OOA and LO-OOA--

Figure 3.3.S8. The time series of 1 h mass concentration of the four organic aerosol factors determined by the PMF analysis, their sum and the total organic from 06/27/2017 to 07/07/2017--

Figure 3.3.S9. Time series of (a) aerosol hourly-averaged mass concentration measured by ASRC AMS (PM$_1$), PDR (PM$_{2.5}$), and ACHD T640 (PM$_{2.5}$) ($\mu$g m$^{-3}$); (b) NYSM meteorological parameters, with relative humidity (%), wind direction, and wind speed (m s$^{-1}$) --

Figure 3.3.S10. (a) The m/z 85 ($^{85}$Rb$^+$) ion peak at 07/05 00:30 pm; (b) the time series of Rb ion signal during the measurement period--

Figure 3.3.S11. (a): Aerosol number size distribution (mobility diameter) measured by SMPS from July 4 12:00 to July 5 12:00; (b) aerosol mass size distribution measured by SMPS for the same time period--

Figure 3.3.S12. The surface weather map for the Northeastern United States for July 4$^{th}$ 23:00 (red circle indicates the location of Albany, https://www.wpc.ncep.noaa.gov/html/sfc-zoom.php)--
Figure 3.3.S13. (a) AMS organic mass spectra of July 5 05:00-06:00 and July 5 07:00-08:00; (b) the spectra difference between these two periods-----------------------------------------------159

Figure 3.3.S14. SMPS-measured total mass size distribution (mobility diameter) during the FW event (July 4 23:00 to July 5 03:00), during July 4 daytime (09:00 to 17:00), and the second peak hour (July 5 07:00-08:00)------------------------------------------------------------------160

Figure 4.1. The scatter plot between BSOA-1 with NO$_3$$_{org}$-----------------------------------------------169

Figure 4.2. The mass concentrations of aerosol compounds for each of the fog processing periods averaged over the four nights. The exact time periods are shown in Figure 4.S6 and listed in Table 4.S3. -----------------------------------------------171

Figure 4.3. (a) The correlation scatterplot of RH and the BSOA mass concentration for the night 19-20. All points are colored by temperature and sized by ALW. (b) The correlation of ALW mass fraction and the BSOA mass concentration for each night from Sep 19 to Sep 23----------------------174

Figure 4.S1. Time series of (a) aerosol chemical compound five minute-averaged mass concentrations; (b) PSP meteorological parameters, with relative humidity (%), wind direction, wind speed (m s$^{-1}$), and temperature (°C); and (c) PSP trace gas concentrations (SO$_2$, Ozone, NO, NO2, CO) for Sep 19 to Sep 23, 2017-----------------------------------------------188

Figure 4.S2. The camera pictures from the Addison New York State Mesonet station at morning time of Sep. 20-23---------------------------------------------------------------------------------189

Figure 4.S3. a): The PMF quality of fit parameter ($Q/Q_{\text{expected}}$) as a function of the number of factors; b) the time series of the mass concentrations of the four PMF factors; c): The time series
of the residual (measured-reconstructed) factors, including real residual, absolute residual, ratio of real to total, ratio of absolute to total, the Q/Q_{exp} for each point in time; d): The PMF quality of fit parameter (Q/Q_{expected}) as a function of f_{Peak}; (e) The mass spectra of the four PMF factors; (f) Mass concentration diurnal variation of each organic aerosol factor.

**Figure 4.S4.** The time series of (a) LO-OOA and solar irradiation; (b) MO-OOA and O_3.

**Figure 4.S5.** The time series of BSOA (BSOA-1+BSOA-2), NO_{3,org} and HNO_3 mass concentrations.

**Figure 4.S6.** The different periods for each day, as well as the variation for SO_{4}^{2-} mass concentration, RH, temperature and solar irradiation.

**Figure 4.S7.** The Addison Mesonet camera pictures for two stage of fog conditions on Sep. 20 and Sep.21 morning time (Left: light fog conditions before sunrise; Right: heavier fog conditions after sunrise).

**Figure 4.S8.** Averaged diurnal variations of planetary boundary layer heights (PBLH) at PSP from Sep. 19 to Sep. 23 2017.

**Figure 4.S9.** The correlation scatterplot of RH and the BSOA mass concentration for the nights 20-21, 21-22, and 22-23. All points are colored by temperature and sized by ALW.

**Figure 4.S10.** The correlation of ALW mass fraction and the Temperature for the four fog nights.

**Figure 4.S11.** The 1-hour time series of RH and temperature at the PSP site from 08/01/2017 to 10/09/2017 (red rectangle indicates the time period of this study).
Figure 5.1. The time series of (a) the aerosol component mass concentrations, (b) the aerosol components mass fractions and number concentration (half-filled diamonds) during the CPOC Pilot study period measured by HR-ToF-AMS-----------------------------------214

Figure 5.2. The classification of cloud layers, as well as the variation of aerosol compounds mass concentrations, number concentration (black half-filled diamonds), and NO+/NO2+ ratio (purple open circles and line) for each layer during the August 19 cloud event-----------------------------215

Figure 5.3. The total mass concentration (ug m⁻³) and the average mass concentration (ug m⁻³)/fraction of aerosols of each layer during urban influenced In-Cloud days, Aug 15, 18, 19-----218

Figure 5.4. The average aerosol number size distribution of each layer (a) for the urban influenced period (August 15 and August 18) and one clear day (August 22) and (b) on August 19, 2017--220

Figure 5.5. (a) The HR-ToF-AMS aerosol compounds mass size distribution for organic and SO₄ on 08/18/2017 and 08/22/2017; (b) The average SMPS aerosol number size distribution for the biogenic influenced periods-----------------------------------------------221

Figure 5.6. The comparison between f₄₄ and f₄₃ for LPT-measured aerosol in each cloud layer and clear days (the cloudy Aug. 20 was classified into BL)----------------------------------223

Figure 5.7. Summary of the measured d₅₀ versus instrument supersaturation for a) urban-influenced days and b) biogenic-influenced days------------------------------------------225

Figure 5.8. Average hygroscopicity parameter attributed to the organic fraction (κorg) versus a measure for the organic oxidation state for each day of ambient observations at WFM during the CPOC pilot study---------------------------------------------------------------226
Figure 5.S1. The experiment diagram for the mobile lab measurement at LPT-------------------242

Figure 5.S2. The time series of the cloud base height for In-cloud days------------------------243

Figure 5.S3. (a) The original schematic used for identifying the height of the cloud base at Whiteface Mountain and (b) the enlarged schematic----------------------------------244

Figure 5.S4. The classification of cloud layers, as well as the variation of aerosol compounds mass concentration, number concentration (black half-filled diamonds), and NO+/NO2+ ratio (purple open circles and line) for each layer of Aug. 15 (a), 18 (b) and 23 (c)---------------------245

Figure 5.S5. The webcam images of time points for separating TL layer and IL layer (TL/IL, left) and TL layer and BL layer (TL/BL, right) on the four cloud days---------------------------------246

Figure 5.S6. The time series of organic NO3 and inorganic NO3 during the LPT measurement period---------------------------------------------------------------------------------247

Figure 5.S7. Calculated ammonium (assuming full neutralization of nitrate and sulfate) vs. measured ammonium of aerosol in TL and IL layers on cloud days------------------------248

Figure 5.S8. The HYSPLIT back trajectories for (a)-(h) the LPT measurement days with ending heights of 1000 m, 1250 m, and 1500 m AMSL (above the mean sea-level); (i) 08/18/2017 with ending heights of 500m, 750m, and 1000m AMSL-------------------------------------249

Figure 5.S9. The LPT meteorological parameters, with relative humidity (%), temperature, wind direction, wind speed, and precipitation from 2017/08/17 to 2017/08/24--------------------------------250

Figure 5.S10. The Ozone Mapping Profiler Suite (OMPS) measured aerosol index on 08/21/2017
Positive AI (~2) was observed over northern NYS on Aug 21, which indicated the presence of absorbing aerosols, most likely due to wildfire smoke plumes.

**Figure 5.S11.** Measured CCN and CN concentrations on all days that the Sprinter Van was deployed for the CPOC pilot study. Biogenic-influenced days are highlighted in green. The measurements shown here do not include any corrections for inlet transmission efficiency or particle charging efficiency that would be necessary to infer the ambient particle size distribution, but rather show the observations used to infer the CCN active fraction as a function of dry particle diameter.

**Figure 6.1.** The aerosol mass concentration and mass fraction for different locations in NY state.
Lists of Tables

Table 2.1. The measurement locations (also in Fig. 2.1) and time period--------------------------23

Table 3.2.S1. The time duration for each period (BP: background period; EP: enhanced period; G: growth; M: Maturity; D: Decline. The gap between EPG and EPM was due to daytime on-road measurements) -------------------------------------------------------------------------------------------------97

Table 4.S1 The measurement uncertainty for the HR-ToF-AMS during PSP measurements (mass concentration units: µg m$^{-3}$) -------------------------------------------------------------------------------------------------------------------------------------------------199

Table 4.S2 The key features of the instruments used for these trace gas measurements (O$_3$, NO, NO$_y$, CO, SO$_2$, HNO$_3$), as well as meteorological sensors---------------------------------------------------------------200

Table 4.S3. The time intervals for each fog processing periods of four nights---------------------201

Table 4.S4 The value for each parameters and compounds concentration used in Eq. (1) and (2)------------------------------------------------------------------------------------------------------------------------------------------------- 202

Table 5.S1. Measured organic mass fraction (m$_{org}$), hygroscopicity parameter (κ) at 0.6% nominal supersaturation (~ 0.51% actual supersaturation), calculated κ$_{org}$ based on assumed organic density of 1.44 g/mL, and the measured O:C ratio following Aiken et al. (2008)$^3$ and Canagaratna et al. (2015)$^4$. Biogenic-influenced days are signified by green text---------------------------------------------------------------254

Table 5.S2. The time periods for each layer of the in-cloud days---------------------------------255

Table 5.S3. The mass concentration (µg m$^{-3}$) and mass fraction of the aerosol compounds of each layer of the cloud days (UI: urban influenced days; BI: biogenic influenced days; Cle.: clear day; Cdy: cloudy day) ------------------------------------------------------------------------------------------------- 256
Chapter 1: Introduction
1.1 Introduction and Motivation

The measured mass concentrations and chemical compositions of atmospheric aerosols are important for many reasons\textsuperscript{1-3}. A major motivation to study aerosols is that they can scatter and absorb solar and earth radiance, affect the formation of clouds, as well as play a role in atmospheric heterogeneous chemical reactions\textsuperscript{4-6}. At the same time, aerosols, also referred to as fine particulate matter are associated with adverse effects on human health, specifically increased morbidity and mortality rates\textsuperscript{7}. Exposure to large amounts of fine PM can be harmful to public health, with detrimental impacts on the respiratory and cardiopulmonary systems\textsuperscript{8-9}.

Atmospheric aerosols are empirically divided into primary aerosol and secondary aerosol, which are related but have different sources. Primary aerosols are directly emitted from a variety of sources, such as combustion, traffic, biomass burning, dust and sea salt, while secondary aerosols are formed through gas-to-particle conversion. Among secondary aerosols, there exist knowledge gaps in the understanding of the formation of secondary organic aerosol (SOA), which is produced from the oxidation of different volatile organic compounds (VOC)\textsuperscript{4}, followed by partitioning into a condensed phase. The SOA formation pathway variously involves new particle formation, condensation, and multiphase chemical reactions, particularly aqueous phase reactions\textsuperscript{10-11}. Aqueous phase reactions, which occur within cloud and fog droplets, have proven to be an important pathway for SOA formation\textsuperscript{11}. SOA formation may involve reactions of thousands of chemical species, many of which are products created during aqueous phase reactions. These species formed in aqueous reactions have garnered significant attention in recent studies.

From urban to mountain conditions, any newly formed aerosol goes through an evolution under different atmospheric conditions. Studies of the type described are relatively rare in the
northeastern U.S. New York State, with its urban, rural forest, and mountain areas provides ideal conditions to study the characterization of atmospheric aerosols and their evolution under a large variety atmospheric conditions in order to address the knowledge gaps identified above.

1.2 Literature Review

1.2.1 Urban aerosol properties

Aerosols in densely populated urban environments are particularly concerning due to their adverse effects on human health and air quality\textsuperscript{12}. A number of studies conducted in recent years have characterized aerosol properties in numerous urban locations of the world using aerosol mass spectrometry technologies\textsuperscript{13-18}. The results show that the organics and sulfate (SO\textsubscript{4}) are the main compounds of the urban aerosol, with SO\textsubscript{4} mostly regional in character and resulting from transport, and organics having contributions from both local and regional accumulation\textsuperscript{19-21}. Among the organic compounds, SOA, formed from the oxidation of gas-phase precursors, accounts for a greater mass fraction than the primary organic aerosol (POA), especially in summertime\textsuperscript{13}.

Besides the general primary urban emission sources for aerosol, aerosol concentrations can be influenced by regional metrological extreme conditions, such as a heatwave event. The occurrence of heatwave events is driven by the synoptic patterns, which produce conditions favorable for high pollution, such as high temperature, strong solar radiance, low precipitation and weak winds, resulting in O\textsubscript{3} and aerosol formation and accumulation\textsuperscript{22-24}. The high temperature during the heatwave events leads to an increase the anthropogenic pollution emissions, including NO\textsubscript{x} and different kinds of anthropogenic volatile organic compounds (AVOCs). These increased emission are due in part to the enhanced demand for energy generation caused by air conditioning, and also due the greater emission rate of biogenic VOCs, both of which are the precursors for O\textsubscript{3} and secondary aerosol formation. The enhanced pollution emissions combined with low wind
conditions induce higher pollutant concentrations due to accumulation, and these conditions last for a longer time, and set the stage to form even more O₃ and secondary aerosol through photochemical reactions under strong solar radiance.

For urban areas near large bodies of water there is interaction with the small-scale mesoscale phenomena such as sea, bay, or lake breeze. Sea breezes are formed due to a pressure difference between warm, continental air and cool, marine air²⁵-²⁷, and have been shown to sometimes contribute to poor air quality²⁸, especially dramatical O₃ concentration variation over short periods²⁸-³⁴.

Urban areas with their high population densities are especially susceptible to special case events such as Firework displays. Firework (FW) displays from national celebrations, such as Independence Day in the United States, Spring and Lantern Festivals in China, Diwali Festival in India, Guy Fawkes Night in the UK, and worldwide New Year’s Eve celebrations are known to cause short-term very high-intensity air quality degradation, especially atmospheric particulate matter (PM) pollution³⁵-⁴⁴. Besides substantial visibility reductions lasting for hours and heavy emissions of gaseous pollutants, such as nitrogen oxides and sulfur dioxide⁴⁵, FW events also produce large amounts of submicron particles (PM₁) that are rich in sulfate, organics, potassium, and heavy metals (e.g. Cu, Ba, Al)³⁵,⁴¹,⁴⁶-⁴⁷. The heavy metals come from the inorganic salts that are used in FW manufacturing to produce different colors, while the compounds used for oxidizing fireworks mixtures produce abundant potassium salts, such as potassium sulfate, nitrate, chlorate, and perchlorate. FW-produced aerosols with metal compounds were found to have greater toxicity than aerosols from traffic emissions³⁸, and to be harmful to public health, with detrimental impacts on the respiratory system⁹,⁴⁸.
1.2.2 Interaction between fog and aerosol under fog conditions in a rural forested location

In contrast to urban aerosol, biogenic volatile organic compounds (BVOCs) emitted from vegetation, particularly mature forests, undergo atmospheric oxidation to form biogenic secondary organic aerosol (BSOA), a major component of SOA in vegetated areas. The advanced aerosol mass spectrometry technologies have been widely used for identifying newly-formed BSOAs through their mass spectral fragments. For example, m/z 82 (C₅H₆O⁺) from the High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) spectrum has been used as a tracer for isoprene epoxydiol-derived SOA. Many of the more recent AMS studies were carried out in the Southern United States and Canada (hereafter “northern regions”). The northern regions have different BVOC species, temperatures, solar radiation (SR), relative humidity (RH), and oxidant gas concentrations, and so on. Previous AMS measurements taken in a rural location in British Columbia, Canada showed no significant ion signal at m/z 82, but a high ion signal at m/z 91 (C₇H₇⁺). To better understand the formation of BSOA in northern regions, more in-depth investigations are still needed.

Under conditions with high humidity, any hygroscopic aerosols absorb moisture to form aerosol liquid water (ALW), which is an abundant medium that facilitates partitioning of polar, water-soluble organic gases to the condensed phase, and can enhance SOA formation through oligomerization and functionalization of these organics via aqueous-phase oxidation. Under supersaturated conditions, such aerosols continue growing through water condensation, and can be activated to form fog or cloud drops. These fog drops also scavenge some fraction of the inactivated interstitial aerosols, and all the compounds in fog drops may undergo aqueous reaction or be removed through precipitation or direct droplet deposition. Many previous studies have examined fog processing in urban areas, where they are greatly affected by anthropogenic
emissions, while the influence of fog processing on the BSOA, especially its aqueous formation mechanisms, are still not well known.

1.2.3 Interaction between cloud and aerosol under cloud conditions

Many localized studies have investigated the physical and chemical characterization of ambient aerosols, cloud droplet residues, interstitial particles and clouds to better understand these types of cloud-aerosol interactions using aircraft and mountain field measurements. In these types of studies, the Aerodyne Aerosol Mass Spectrometer (AMS) is one of the most widely used instruments to evaluate: (1) accumulation of secondary compounds within wet aerosols and cloud droplets, and (2) changes to the oxidation state of organics via cloud processing, both of which can impact the aerosol hygroscopicity. The former includes enhancement of particle nitrate (NO₃), sulfate (SO₄) and ammonium (NH₄) via dissolution of soluble gases (HNO₃, SO₂ and NH₃) within cloud droplets and subsequent acid-based reactions. Likewise, enhanced concentrations of organic acids and other oxygenated organic compounds have been found in wet aerosols, fog and cloud droplets, as compared to aerosols at lower humidity (<70%), suggesting a similar formation pathway for secondary organic aerosol (SOA) via partitioning of volatile organic compounds to the aqueous phase and subsequent reactions.

Hill-tops and mountain-tops are desirable locations for studying aerosol-cloud interactions and for evaluation of chemical models, since: (1) the measurements can extend for long time periods, allowing for an abundant dataset that spans all times of day and can capture seasonal and episodic events like forest fire plumes; (2) high elevation sites can be frequently in-cloud, allowing for significant duration of in-cloud sampling; (3) high elevation sites are often representative of regional air quality, and back trajectory analysis can be used to identify the sources of air masses upwind of clouds. Several major field campaigns have been conducted within the past 25 years...
specifically to investigate cloud processing from high elevation sites, such as the Great Dun Fell experiments (1995 in northern England)\textsuperscript{76}, the FEBUKO project (2001-2002 in Germany)\textsuperscript{77}, and the HCCT experiment (2010 in Germany)\textsuperscript{78}. Coordinated high elevation studies like these that focus on multiphase (reactive trace gas, aerosol and cloud) chemical interactions have not been conducted in the northeastern United States in recent years, though the region is rich with historical precedent in the study of chemical processes occurring within clouds\textsuperscript{79-80}. Intense renewed interest in aqueous chemical reactions as a potential pathway to bridge the gap between observed and modeled SOA was an important science driver for three major field campaigns within the U.S. in the past decade: Deep Convective Clouds and Chemistry (DC3)\textsuperscript{81}, Southeast Atmosphere Studies (SAS)\textsuperscript{82} and Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS)\textsuperscript{83}.

1.3 Objective and Structure of this Dissertation

In contrast to what was observed in the above cited studies in other regions, the forested and humid environment of the northeastern U.S., which are frequently downwind of Midwestern urban and industrial centers, will have different aerosol properties. It is true that several studies have observed and studied the urban aerosol in New York metro area\textsuperscript{12,14}. At the same time, the interaction between the air quality and the extreme events, which including heatwave, extreme high O\textsubscript{3} caused by sea breeze, and Firework, are still relatively less studied in this area. For these reasons it is important to study the characterization of atmospheric aerosols at different locations of Northeastern U.S. (such as urban, forest, and Mountain areas) and their evolution under special atmospheric conditions (such as extreme weather, fog, and cloud, etc.). The remainder of this dissertation presents five distinct studies that investigate different aerosol properties under these kinds of special atmospheric conditions. The main tool used in these studies is University at Albany
Atmospheric Sciences Research Center (ASRC) mobile laboratory. More specifically, I expect to focus on the following questions in this dissertation:

1. For urban aerosol: (a). What is the interaction of the sea breeze and air quality on Long Island? (b) What is the aerosol evolution during the period of the co-occurrence of extremes in surface ozone, particulate matter, and temperature over New York metro area? (c) To what extent do firework displays produce harmful particle concentrations during the night of July 4th?

2. For rural forested area aerosol: What are properties of the aerosol in a rural forest in New York State, and its interaction with fog during late summer and fall?

3. For mountain area aerosol: Which kinds of aerosol dominate the mountain area aerosol, and what is the interaction between the cloud and aerosol?
1.4 References


6. IPCC: Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change. Cambridge University Press, 2014.


17. Aiken, A. C., de Foy, B., Wiedinmyer, C., et al.: Mexico city aerosol analysis during MILAGRO using high resolution aerosol mass spectrometry at the urban supersite (T0) – Part


Chapter 2: Experiment description
2.1 Instruments

A number of instruments and measurement systems were used in this work. The main instruments include:

(1) An Aerodyne High-Resolution time-of-flight Aerosol Mass Spectrometer (HR-ToF-AMS), which is used for measuring non-refractory (NR) submicron aerosol (NR-PM$_1$). This instrument measures chemical composition (including organics, nitrates, sulfate, ammonium, and chloride), as well as the size distribution of the aerosol components$^{1-3}$. The working principle of the HR-ToF-AMS has been reported in detail previously$^{1-3}$ and is shown in Fig. 2.1. In brief, the particle beam is first sampled though a critical orifice (100 μm) into an aerodynamic lens, which focuses particles of a vacuum aerodynamic diameter size range $\sim$50 nm to $\sim$1500 nm into a narrow beam$^{1-3}$. The particle beam will undergo a supersonic expansion at the exit of the aerodynamic lens (about 2 Torr) before into the sizing region ($10^{-5}$ Torr), which would accelerate the particles and resulting in size-dependent velocities of the particles. A rotating chopper is installed for separating the mass spectrum mode (MS: for aerosol compounds mass concentration) and the particle-of-flight mode (PTOF: for aerosol size distribution). When the rotating chopper is running, the aerosol size could be calculated based on the interval of the time of particle passing the chopper and the time of mass spectrometric detection. After passing the size region, the particle beam then impacts a tungsten vaporizer that is maintained at $\sim$660°C and the particles are fragmented and vaporized. After that, the vapoed fragments are ionized in the electron impact ionization field with a relative electrical potential of 70 eV, and the ions are focused and detected by a high-resolution time-of-flight mass analyzer. The organics mass concentration is defined as the sum of all fragment after subtracting all the identified signals originating from ambient gas molecules, inorganic compounds, and instrumental artifacts from surface ionization on the vaporizer$^4$. The aerosol mass concentration
for each species was obtained following\(^3\):

\[
\text{Massloading} = \frac{\text{Ionsignal} \times \text{MW}_{\text{NO}_3} \times 10^{12}}{\text{IE}_{\text{NO}_3} \times \text{RIE} \times \text{CE} \times \text{NA} \times \text{Flowrate}}
\]

Where \(\text{IE}_{\text{NO}_3}\) (number of ions detected per molecule vaporized) is the ionization efficiency for nitrate, \(\text{RIE}\) is the relative ionization efficiency of each species, \(\text{CE}\) is the collection efficiency of each species, \(\text{MW}_{\text{NO}_3}\) (62 g mol\(^{-1}\)) is the molecular weight of nitrate, \(10^{12}\) is used for unit conversion, \(\text{NA}\) is Avogadro’s number. The \(\text{IE}_{\text{NO}_3}\) was routinely calibrated through the comparison of the calculated \(\text{NO}_3\) mass concentration from a TSI Condensation Particle Counter and from the HR-ToF-AMS by supplying mono-disperse \(\text{NH}_4\text{NO}_3\) particles (generally diameter 300nm\(^3\)). For the ambient measured data, the experimental \(\text{RIE}\) (4 for ammonium, 1.1 for nitrate, 1.2 for sulfate, 1.3 for chloride, and 1.4 for organics) and \(\text{CE}\) (0.5 for each compounds) were used\(^1\)-\(^3\).

During the measurements, this HR-TOF-AMS is operated under the sensitive “V-mode” (mass resolution \(-\text{m/}\Delta\text{m of 2000}), and cycles through the MS mode and the POT mode (PTOF) every half minute for urban road measurements, and every five minutes for site measurements with a nominal detection limit of 0.003 \(\mu\text{g m}^{-3}\). The HR-TOF-AMS data was analyzed using standard HR-AMS data analysis software (SQUIRREL v1.59D and PIKA v1.19)\(^5\)-\(^6\) to obtain the mass concentrations for different aerosol compounds (organics, nitrates, sulfate, ammonium, chloride), as well as their size distribution. The high resolution AMS organic mass spectra was then divided into different organic aerosol compounds based on the PMF2 algorithm\(^7\), using PIKA to prepare an ion-speciated HRMS matrix and the corresponding error matrix\(^8\), with the PMF Evaluation Tool\(^9\) used to perform final analysis. The elemental analysis (oxygen-to-carbon (O/C) and hydrogen-to-carbon (H/C) ratios) was performed following the improved method proposed by Canagaratna et al\(^10\).
Figure 2.1. The Schematic of the Time-of-Flight Aerosol Mass Spectrometer (TOF-AMS)\textsuperscript{1}.

(2) A TSI Scanning Mobility particle Sizer (SMPS), which is used for measuring aerosol size distribution. This SMPS consists of an Electrostatic Classifier (EC, model 3080), a Differential Mobility Analyzer (DMA, model 3081), and a Condensation Particle Counter (CPC, model 3785). The SMPS is operated with a 10:1 sheath-to-sample flow ratio (sheath flow 3L min\textsuperscript{-1}, and sample flow 0.3L min\textsuperscript{-1}), which led to an effective measured aerosol size range of 14.9nm to 673.2nm.

(3) A PDR-1500 (Thermo Fisher Scientific Inc., 2014, hereafter PDR), which is a highly sensitive nephelometric monitor using an 880 nm wavelength LED source for particle scattering mass measurement. Its forward scattering angle covers 60 to 80\textdegree. The measurable mass range of PDR is 0.001 to 400 mg m\textsuperscript{-3}, and its size range is 0.1 to 10 µm. During the measurement, the flow rate of PDR is set to 1.5LPM. The PDR-1500 was factory calibrated against a gravimetric standard traceable to the National Institute of Standards and Testing (NIST) by the manufacturer using SAE Fine (ISO Fine) supplied by Powder Technology, Inc. For lab experiments in Albany it is used in tandem with a TSI DustTrak DRX (model 8543, hereafter DRX), a combined photometer and
optical counter that uses a 655 nm laser to illuminate a sample stream, and measures the intensity of scattered light perpendicular to the stream with a photodetector to infer the aerosol mass concentration\(^\text{11}\).

(4) A Droplet Measurement Technologies cloud condensation nuclei counter\(^\text{12}\) (CCNc). The CCN activation spectra were obtained by splitting the electrostatic classifier (EC) flow between the condensation particle counter (CPC, TSI 3785) and the CCNc, with a controlled and filtered dilution flow after the EC to maintain 0.6 LPM sample flow through the EC while providing sufficient flow to both the CPC and CCNc (1.0 and 0.5 LPM, respectively). The EC sheath flow was set to 4.5 LPM to obtain sufficient particle counting statistics and to obtain a consistent 7.5:1 sheath to aerosol ratio (SAR) as a SMPS operating concurrently at the WFM summit. Particle size scans 13-749 nm were acquired in 5-minute intervals. The CCNc was operated with 10:1 SAR and cycled through five supersaturations each hour (20 minutes at 0.2% followed by 10 minutes at 0.4%, 0.6%, 0.8% and 1.0% setpoints). Calibrations at the LPT with ammonium sulfate aerosol (assuming dynamic shape factor of 0.98 and van’t Hoff factor of 2.5) showed that the actual supersaturations were: 0.23%, 0.37%, 0.51%, 0.65% and 0.78%\(^\text{13}\).

(5) During the LISTOS stationary and on-road measurements, two O\(_3\) sensor (TAPI Model 430 and 2B Model 205), one NO\(_2\) sensor (Teledyne API Model T500U) and VOC canister samplers (Entech CS1200E passive flow regulation system) were used for measuring the O\(_3\) and NO\(_2\) concentration while driving, and for collection of VOC while parked for an hour or more. A commercial small GPS receiver (GlobalSat BU-353-S4) was used for providing the GPS information during on road measurement.

For the measurements taken in Albany, the HR-ToF-AMS, SMPS, PDR, and DRX were located in
a laboratory, and were together connected to a silica gel dryer (RH<37%). During the rural field campaigns (Pinnacle State Park and Whiteface Mountain, Table 2.1), the HR-ToF-AMS, SMPS, CCNs, and PDR were located in the mobile measurement Sprinter Van. A manifold vacuum pump was installed in the back of the mobile lab cabin providing a total flow 62 LPM. There were two sample systems inside the van and related sample inlets outside the van with one for gas measurements and one for particle measurements. Following the particle sample inlet, a URG PM cyclone installed in the cabin with a cutoff size of 1.8 μm (URG-2000-30EC, total flow 62 LPM leading to a cutoff size of about 1.8 μm). These instruments were together connected to the silica gel dryer before being connected to the aerosol sampling system after the PM$_{2.5}$ cyclone. For the measurements taken in Long Island (Table 2.1), only the HR-ToF-AMS and PDR were together connected to the silica gel dryer, while the CPC was directly connected to the aerosol sample system. The EC part of SMPS was restricted for using in NYC metro area due to containing radioactive material.

Except the van front air conditioning, the van has two extra cabin air conditioning for helping control the cabin temperature. During the field measurement, the van cabin air conditioning was generally used to provide suitable cabin temperature for the HR-ToF-AMS, especially during the summer measurement. For the stationary site measurements (Pinnacle State Park and Long Island-Flax Pond), the battery power system of the Sprinter Van was directly connected to the outside power supply. However, for the on-road measurement and the stop measurements without power supply, the battery power system of the Sprinter Van was turn on for supporting the active operation of all the instruments. The battery power system could provide up to 10 hours with the cabin air conditioning off, and for about 4 hours with the two cabin air conditioning on which was generally for the stop measurements without power supply. During the on road measurement, through setting
the van front air conditioning to be coolest and air recirculation, only one cabin air conditioning would be enough for the HR-ToF-AMS, and the battery power system could provide as long as 6-7 hours which would fulfil the general on-road measurement requirements. More detailed description of the instruments and the connection could be found in the method parts of each section and related papers\textsuperscript{12,13}.

### 2.2 Measurement locations and period

**Table 2.1.** The measurement locations (also in Fig. 2.1) and time period

<table>
<thead>
<tr>
<th></th>
<th>Time Period</th>
<th>Area description</th>
<th>Focus points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Long Island (mobile and stationary)</td>
<td>06/24/2018-08/16/2018</td>
<td>Downwind of NYC</td>
<td>Urban aerosol</td>
</tr>
<tr>
<td>Albany (laboratory)</td>
<td>06/27/2017-07/05/2017</td>
<td>Suburban</td>
<td>Firework burning influence;</td>
</tr>
<tr>
<td>Pinnacle State Park (PSP) (mobile lab)</td>
<td>09/19/2017-09/23/2017</td>
<td>Rural forest</td>
<td>Fog processing;</td>
</tr>
<tr>
<td>Whiteface Mountain (WFM) (mobile lab)</td>
<td>08/17/2017-08/23/2017</td>
<td>Mountain area</td>
<td>Cloud processing</td>
</tr>
</tbody>
</table>
Figure 2.2. The locations of the designed measurements in New York State
2.3 References


Chapter 3: Urban measured aerosol properties

3.1 The interaction of the sea breeze and air quality on Long Island
In this section, the LISTOS on-road measurement results are discussed, focusing on high O₃ conditions and dramatic O₃ spatial variations. These variations are caused by (1) the sea breeze circulation at the coast lines, or (2) photochemical NO₂-O₃-VOC reactions on the highways of the downwind direction of New York Metro area. The details of the interaction between these two influence factors and observed O₃/NO₂/aerosol based on case studies are presented, along with descriptions of the pollution processing using meteorological tools including scanning wind LiDAR and back trajectories. This study is useful to help understand the interaction between emitted pollution precursors, the metrological conditions, and photochemical production in New York metro area during summertime.

3.1.1. Introduction

Ground-level ozone (O₃) is a regional pollutant with an 8-hour standard mandated by the United States Environmental Protection Agency (US-EPA, 2017) of 70 parts per billion (ppb).¹ O₃ is mainly formed due to photochemical reactions involving nitrogen oxides (NOₓ), volatile organic compounds (VOCs) and heat/sunlight²⁻⁴. High ground-level O₃ concentrations lead to the formation of photochemical smog and negative human health and ecosystem impacts⁵⁻⁶. Generally, regional surface O₃ is related to (1) precursor emissions and mixing ratios, (2) photochemistry, and (3) large-scale meteorological conditions, including temperature, wind speed, and planetary boundary layer height (PBL)⁶⁻⁸. However, the factors influencing more local surface O₃ concentrations are more complex for coastal areas affected by local-scale phenomena such as sea, bay, or lake breezes (hereafter sea breeze)⁶⁻⁹⁻¹⁰.
Sea breezes are formed due to a pressure difference between warm, continental air and cool, marine air\textsuperscript{11-13}. Previous studies have indicated that sea breezes contribute to poor air quality\textsuperscript{14} and often lead to dramatic variations in O\textsubscript{3} levels over short time periods\textsuperscript{13-19}. The main characteristics that cause sea breeze circulation contributions to poor air quality are (1) sunny conditions, (2) relatively low synoptic wind speeds, (3) a capping inversion over the water, and (4) a period of pollutant transport occurring from the land to the sea, where O\textsubscript{3} is photochemically produced and undergoes less depositional loss\textsuperscript{6,20}, followed by transport back to the land by the developing or fully developed sea breeze\textsuperscript{13,19}. Previous studies assessing the impact of the sea breeze circulation on inland O\textsubscript{3} concentrations have been conducted at several coastal areas throughout the United States, including the Chesapeake Bay\textsuperscript{14,17,19}, the Great Lakes region\textsuperscript{13,15,16}, the Salt Lake Valley\textsuperscript{18}, and the Houston area\textsuperscript{9}. In addition, the sea and shore breeze circulations affecting the coast of Long Island Sound, the New York City Harbor area, and Brooklyn and Queens on Long Island, New York (NY) are well-characterized\textsuperscript{12,21,22}. However, to the best of our knowledge, the effect of these sea and shore breeze circulations on Long Island O\textsubscript{3} levels has not been examined by previous studies.

The New York City (NYC) metropolitan area has abundant NOx and VOC emissions\textsuperscript{23,24}. Consequently, summertime O\textsubscript{3} concentrations exceeding the 70 ppb National Ambient Air Quality Standard (NAAQS) can frequently occur in the NYC metropolitan area and locations downwind (Connecticut, Rhode Island, Massachusetts, eastern Long Island, etc.)\textsuperscript{25,26}. In these areas, the abundant NOx and VOC emissions interact with sea/shore breeze circulations to yield a complex ozone problem requiring further investigation. Therefore, the Long Island Sound Tropospheric Ozone Study (LISTOS) was organized by Northeast States for Coordinated Air Use Management (NESCAUM, http://www.nescaum.org/documents/listos) to examine ozone formation and transport in the NYC metropolitan area and locations downwind. Several institutions and agencies
participated in LISTOS, including NASA, EPA, NOAA, local state agencies, and numerous other research institutions and air quality management agencies (https://wwwair.larc.nasa.gov/missions/listos/index.html). As one of the LISTOS participants, the University at Albany Atmospheric Sciences Research Center (ASRC) deployed its mobile laboratory to (1) measure the surface NO$_2$, O$_3$, and aerosol number and mass concentration during high O$_3$ events, and (2) study the transport of pollutant plumes.

In this study, dramatic O$_3$ spatial distributions were captured by the ASRC mobile lab along the coast of Long Island (LI) and the northern suburbs of NYC, and the O$_3$ formation process and aerosol properties were assessed. Some of the dramatic ozone spatial distributions are explained below as being strongly influenced by sea and/or shore breeze circulations. Additionally, the influence of both in-situ traffic emissions and transported O$_3$ precursors on the O$_3$ concentration in downwind areas is also explored during O$_3$ exceedance days (over 70 ppb) not characterized by the sea/shore breeze circulation. The background NO$_2$, O$_3$, and aerosol properties on LI were also investigated.

3.1.2. Methodology

3.1.2.1 Study area

The measurements were made on Long Island and the northern suburbs of NYC from 06/24/2018 to 08/16/2018. LI is located east of the borough of Manhattan, and the two most-populated of the five boroughs of NYC (Brooklyn and Queens) are located on the western end of the island. On-road measurements were made on days when the Community Multiscale Air Quality (CMAQ) model predicted an O$_3$ exceedance somewhere on LI, and the mobile lab was driven to those locations. Several on-road measurements were also made on O$_3$ non-exceedance days to determine
typical summertime air pollutant concentrations on LI. For the remaining days, the mobile lab was parked at Flax Pond Marine Laboratory for continuous measurements. In this study, 7 on-road measurement days are analyzed in detail. Specifically, the days of interest were (1) 06/30, 07/01, and 08/06, which were characterized by significant \( \text{O}_3 \) spatial gradients influenced by the sea breeze circulation; (2) 07/10 and 07/16, which were characterized by significant \( \text{O}_3 \) spatial gradients attributable to variability in \( \text{NO}_2 \); and (3) 08/15 and 08/16, which were characterized by lower \( \text{O}_3 \) concentrations and elevated aerosol levels.

### 3.1.2.2 Mobile lab instruments and other data sources

The ASRC mobile lab was a modified 2007 Dodge Sprinter van containing (1) an Aerodyne high resolution time of flight aerosol mass spectrometer (HR-ToF-AMS), used for measuring the aerosol mass concentration\(^{27,28}\); (2) a TSI water CPC Model 3785, used for measuring the aerosol number concentration; (3) one Thermo Scientific MIE pDR-1500, used to provide an additional aerosol mass concentration measurement and draw a larger flow and reduce the sample line residence time for the HR-ToF-AMS; (4) two \( \text{O}_3 \) sensors (TAPI Model 430 and 2B Model 205); (5) one \( \text{NO}_2 \) sensor (TAPI Model 500U); (6) VOC canister samplers; (7) an 8-battery power supply system with 13.25 kWh of power and a lifetime of approximately 7 hours; and (8) a GPS. The mobile lab had one inlet for gases and one inlet for aerosols. A URG PM cyclone (URG-200-30EC) followed the aerosol sample inlet to remove large aerosol/cloud drops (>2 um) at a flow rate of 56 LPM. After the cyclone, a silica dryer was used to dry the aerosol (RH<40%) before going to the aerosol instruments’ inlets\(^{29}\). More details regarding the ASRC mobile lab can be found elsewhere\(^{30}\).

During the on-road measurements, the HR-ToF-AMS was only operated in “V” mode with a time
resolution of 30 s, which was the same time resolution as the CPC. The time resolution for the gas sensors were 1 min, and the VOC canister sample time resolution was about 1 h. The HR-ToF-AMS data was analyzed using SQUIRREL v1.59D and PIKA v1.19\textsuperscript{31,32}. In this software, the default relative ionization efficiency (RIE) values were used (4 for ammonium, 1.1 for nitrates, 1.2 for sulfate, 1.3 for chloride, and 1.4 for organics)\textsuperscript{33}, with a collection efficiency (CE) of 0.5 for all aerosol chemical compounds\textsuperscript{34}. The HR-ToF-AMS was calibrated before and after the field measurements, while the O\textsubscript{3} sensors and NO\textsubscript{2} sensor were calibrated based on the comparison with the New York State Department of Environmental Conservation (DEC) instruments at Flax Pond when the mobile lab was parked at Flax Pond Marine Laboratory.

To complete the analysis, this study also used (1) New York State Mesonet data for the lidar wind vertical profiles (Yang and Min, 2018, www.nysmesonet.org/data/), (2) New York State DEC air quality data for O\textsubscript{3} concentration and PM\textsubscript{2.5} mass concentration (http://www.nyaqinow.net/), and (3) TROPOMI satellite data for the tropospheric NO\textsubscript{2} column concentration\textsuperscript{35} (http://www.temis.nl/airpollution/no2.html).

3.1.2.3 Sea and shore breeze analysis

Part of the methodology presented by Sills et al. (2011) and Wentworth et al. (2015) for identifying lake-breeze circulations in the Great Lakes region was used to identify sea and shore breeze circulations off the LI coast\textsuperscript{11,13}. This was done to assess whether sea and shore breeze circulations may have contributed in part to the sharp spatial gradients in LI O\textsubscript{3} levels observed during the on-road measurement days. The approach taken to identify sea and shore breeze circulations consisted of three steps. First, consistent with Sills et al. (2011) and Wentworth et al. (2015)\textsuperscript{11,13}, the daily visible satellite imagery from the National Aeronautics and Space Administration Earth Observing
System Data and Information System (NASA EOSDIS) Worldview (https://worldview.earthdata.nasa.gov/) was used to help manually detect sea and shore breeze circulations. Second, an additional two tools were used for identifying a sea or shore breeze circulation that were not employed by Sills et al. (2011) and Wentworth et al. (2015)\textsuperscript{11,13}. These included (1) 24-hour back trajectories from the NOAA Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) model (https://ready.arl.noaa.gov/HYSPLIT.php), and (2) daily lidar vertical profiles with wind barbs included (www.nysmesonet.org/data). Since multiple sea and shore breeze circulations can develop off the coast of LI\textsuperscript{12,21,22}, back trajectories were constructed for six different locations on LI using 3 km resolution meteorological data from the High-Resolution Rapid Refresh (HRRR) model. The six locations were (1) southwestern LI (40.59° N, -73.97° W), (2) south-central LI (40.74° N, -73.10° W), (3) southeastern LI (40.89° N, -72.37° W), (4) northeastern LI (41.08° N, -72.44° W), (5) north-central LI (40.94° N, -73.13° W), and (6) northwestern LI (40.81° N, -73.68° W). The lidar vertical profiles were generated using data from the six profiler sites on or near LI that are maintained by the New York State Mesonet (NYSM). The six LI profiler sites are located in Staten Island, Bronx, Queens, Wantagh, Stony Brook, and East Hampton (Fig. 3.1.S1). Third, the images from the first two steps were visually inspected to identify clear evidence of a sea or shore breeze circulation, and only the images that support the formation of a sea and/or shore breeze circulation are presented and discussed here. Ultimately, it was concluded that a sea and/or shore breeze circulation formed if there was (1) an abrupt shift in the wind direction from offshore to onshore, and/or (2) a line of cumulus clouds virtually parallel to the LI shoreline that did not form due to a synoptic frontal passage or a gust front\textsuperscript{11,13}.

3.1.3. Result

The observed 8-hour average O\textsubscript{3} concentration on LI and the NYC metro area during the
measurement period (06/24/2018-08/16/2018) is shown in Fig. 3.1.1a. During this period, there were six days where the O₃ concentration exceeded the 70 ppb NAAQS – 06/30-07/02, 07/10, 07/16, and 08/06 (Fig. 3.1.1a). On-road measurements and sea/shore breeze circulation analyses were conducted for most of the O₃ exceedance days (06/30-07/01, 07/10, 07/16, and 08/06), the results of which are presented and discussed later.

Figure 3.1.1. (a) The observed 8-hour average O₃ concentration on Long Island and the NYC metro area during the on-road measurement period (red dashed line indicates the 70 ppb NAAQS). (b) The average diurnal variation of O₃ at Queens College on Long Island from 06/24-06/29 (black line) and 06/30-07/02 (red line).

Figure 3.1.1b shows the average diurnal variation of O₃ at Queens College on LI from 06/24-06/29 and 06/30-07/02. The average diurnal cycle of O₃ on the non-exceedance days (06/24-06/29) is representative of an urban/suburban site⁶. Specifically, O₃ concentrations increased during the morning due to photochemistry at a rate of 4.5 ppb h⁻¹ (Fig. 3.1.1b). In contrast, the average diurnal cycle of O₃ on the exceedance days (06/30-07/02) shows a higher growth rate of 8.5 ppb h⁻¹, with the peak growth rate occurring at approximately 15:00 Eastern Daylight Time (EDT; Fig. 3.1.1b). The enhanced O₃ growth rate observed from 06/30-07/02 is hypothesized to be partially due to the
sea breeze circulation, as discussed in the next section.

3.1.3.1 Dramatic O₃ spatial distribution caused by sea breeze

Sharp O₃ spatial gradients were observed through on-road measurements near LI coastlines on 06/30, 07/01, and 08/06, when maximum O₃ concentrations exceeded 100 ppb (Figs. 3.1.2a-3.1.2c). The O₃ gradient (∆O₃ ∆y⁻¹) was found to be (1) 18 ppb km⁻¹ at Robert Moses State Park (RMSP) on the south shore of LI on 06/30 (Fig. 3.1.2a), and (2) 15 and 20 ppb km⁻¹ near Port Washington on the north shore of LI on 07/01 and 08/06, respectively (Figs. 3.1.2b-3.1.2c). These large O₃ spatial gradients were missed in the hourly O₃ forecasts made by the Community Multiscale Air Quality (CMAQ) model (Fig. 3.1.S2). In addition, consistently low to moderate NO₂ concentrations were measured on 06/30, 07/01, and 08/06 at the times when there were large O₃ spatial gradients (Figs. 3.1.3-3.1.4). This suggests that the dramatic O₃ spatial variation on those days was influenced by factors other than simply NO-NO₂-O₃ cycling kinetics, which are discussed in Sect. 3.1.3.2. The most likely factor influencing the large O₃ spatial variability is the sea breeze circulation, a local-scale process. Due to the O₃ gradient being maximized at different locations on LI (south shore on 06/30, and north shore on 07/01 and 08/06), the influence of the sea and sea/shore breeze for the south and north shore, respectively, will be discussed using the 06/30, 07/01 and 08/06 on-road measurements as case studies.
Figure 3.1.2. The spatial distribution of the on-road $O_3$ concentration on (a) 06/30 (15:20-16:20), (b) 07/01 (15:10-19:00), and (c) 08/06 (11:40-18:20) (the arrows indicate the locations mentioned in the text. Sands P.: Sands Point, Port W.: Port Washington; RMSP: Robert Moses State Park).
3.1.3.1.1 Case study A-South coast (06/30)

Figure 3.1.3a shows the time series of O₃, NO₂, and the HR-ToF-AMS measured concentrations of organics, NO₃, SO₄, and NH₄ during the on-road measurement period on 06/30. As shown in Fig. 3.1.2a and 3.1.3a, the O₃ concentration dramatically increased from 76 to 112 ppb in about 2 km at RMSP on the LI south shore, yielding the aforementioned ΔO₃ Δy⁻¹ value of 18 ppb km⁻¹. Additionally, enhanced gradients for organics, SO₄, NO₃, and NH₄ of 0.6, 0.4, 0.1, and 0.2 ug m⁻³ km⁻¹, respectively, were simultaneously found at RMSP (Fig. 3.1.3a). The enhanced O₃ concentrations persisted during the 1-hour sampling time period at RMSP (about 110 ppb) and decreased to approximately 60 ppb when driving back to Flax Pond (Fig. 3.1.3a). Similar trends were observed for the aerosol compounds (Fig. 3.1.3a). Due to the combination of (1) the low NO₂ concentrations at the time of the dramatic increase in O₃, (2) the NYSM lidar signals, and (3) HYSPLIT back trajectories, the enhanced O₃ and aerosol concentrations at RMSP on 06/30 are likely attributable in part to the development of a sea breeze circulation.

Figure 3.1.3. (a) The time series of O₃ and aerosol compounds on 06/30; (b) Time series of sea salt aerosol signal on 06/30.

Figure 3.1.S3 shows the lidar vertical profiles for Staten Island (Fig. 3.1.S3a), Wantagh (Fig. 3.1.S3b), East Hampton (Fig. 3.1.S3c), Bronx (Fig. 3.1.S3d), Queens (Fig. 3.1.S3e), and Stony
Brook (Fig. 3.1.S3f), which demonstrate that a sea breeze circulation developed on LI at different times on the afternoon of 06/30. For example, at approximately 12:00 EDT on 06/30, the wind direction shifted from offshore to onshore and persisted for several hours at Wantagh (approximately 22 km northwest of RMSP), consistent with the formation of a sea breeze circulation (Fig. 3.1.S3b). The influence of the sea breeze circulation was also indicated by the enhanced sea salt aerosol signal (NaCl and I) detected by the AMS (Fig. 3.1.3b). Furthermore, the 24-hour HYSPLIT back trajectories for southwestern (Fig. 3.1.S4a), south-central (Fig. 3.1.S4b), southeastern (Fig. 3.1.S4c), northeastern (Fig. 3.1.S4d), north-central (Fig. 3.1.S4e), and northwestern (Fig. 3.1.S4f) LI ending at 20 UTC (16:00 EDT) on 06/30 provide additional evidence to suggest that a sea breeze circulation formed. For example, the back trajectory for south-central LI (Fig. 3.1.S4b) indicates that inland emissions were transported out over the Atlantic Ocean earlier in the day. Over water, pollutants were largely contained in the shallow marine boundary layer, where enhanced O$_3$ production likely occurred. Then, O$_3$ and its precursors were transported near the surface by the sea breeze circulation back inland (e.g., Fig. 3.1.S4b), thereby contributing to the enhanced O$_3$ and aerosol concentrations measured at RMSP. It is worth noting that the 1-hour sampling time period with O$_3$ concentrations over 110 ppb was from 16:30 to 17:30 (Fig. 3.1.3a), which was when the sea breeze front appeared to have passed Stony Brook on the north shore of LI (Fig. 3.1.S3). Therefore, three possible reasons for the high O$_3$ concentration at RMSP are (1) lower PBL height due to the site’s coastal location; (2) the more polluted plume developed and persisted after the passage of the sea breeze front; and/or (3) the transport of this more polluted plume was inhibited by the bay breeze wind from the Great South Bay, a local-scale phenomenon unique to south-central LI. Further measurements and work are needed to either confirm or refute these hypotheses.
In contrast to the O₃ trend during the sampling period (16:20-17:20 EDT), the aerosol compounds (organic, SO₄, NH₄, and I) increased again at approximately 17:00 EDT (Figs. 3.1.3a-3b). The second increase in aerosol concentrations was accompanied by enhanced aerosol number (Fig. 3.1.3a) and iodine concentrations (Fig. 3.1.3b), raising the possibility that the HR-ToF-AMS measured another plume containing higher concentrations of organic, SO₄, NH₄, and iodine. In addition, the aerosol mass spectra under high O₃ concentration at RMSP shows higher signals at m/z 28 (f₂₉, CO⁺) and m/z 44 (f₄₄, CO₂⁺), and lower signals at m/z 43 (f₄₃, C₂H₅O⁺) and hydrocarbon-like ions (CxHy family) compared to the aerosol mass spectra under low O₃ concentration at RMSP (Fig. 3.1.S5). This indicates that the aerosol had a higher oxidation state under high O₃ concentration at RMSP, implying that those aerosols were more oxidized.

3.1.3.1.2 Case study B- North coast (07/01 and 08/06)

The 07/01 and 08/06 on-road measurements both show large O₃ variation near Port Washington on the north shore of LI during late afternoon (Fig. 3.1.2b, 3.1.2c, and 3.1.4). Shortly before 16:30 on 07/01, the O₃ concentration rapidly increased from 60 ppb to 100 ppb when the van drove east, and it remained at 100 ppb for about 6 km (Fig. 3.1.4a). Then, the O₃ concentration rapidly decreased back to below 60 ppb by 16:40 with a ΔO₃ Δy⁻¹ of 15 ppb km⁻¹ (dashed blue box in Fig. 3.1.4a) when the van began to drive north (Fig. 3.1.4a). This dramatic O₃ variation was not observed again when driving the van back to Flax Pond, suggesting that the plume was not transported eastward. On 08/06, dramatic O₃ variation was observed when the van passed Port Washington at about 16:20, when the O₃ concentration decreased from 100 ppb to 60 ppb in 2 km, yielding a ΔO₃ Δy⁻¹ of 20 ppb km⁻¹ (dashed blue box in Fig. 3.1.4b).
Figure 3.1.4. The time series of O₃ and NO₂ during on-road measurements on (a) 07/01 and (b) 08/06 (dashed green line indicates 70 ppb of O₃, Sands P.: Sands Point, Port W.: Port Washington).

The 24-hour HYSPLIT back trajectory for northwestern LI on 07/01 indicates that the wind direction shifted from northwesterly in the morning to south-southwesterly in the late afternoon (Fig. 3.1.S6a). The late afternoon south-southwesterly winds were most likely due to the development of the sea breeze circulation that occurred throughout LI at different times on the afternoon of 07/01, as shown by the NYSM lidar vertical profiles (Figs. 3.1.S7a-3.1.S7f) and other back trajectories (Figs. 3.1.S6b-S6f). The delayed onset of the sea breeze at the northern sites indicates the movement of the sea breeze pattern from south to north across LI (Fig. 3.1.S7). For example, the wind direction measured by lidars deployed at the Queens and Stony Brook Mesonet sites in central and northern LI, respectively, illustrate the wind transport patterns on 07/01 (Figs. 3.1.S7e-S7f). Figure 3.1.S7e shows that the offshore wind noticeably weakened at Queens at approximately 11:00 EDT, and calm conditions persisted for the next three hours. Then, the wind direction abruptly shifted from offshore to onshore at approximately 14:00 EDT (Fig. 3.1.S7e), which further suggests that a sea breeze circulation developed on 07/01 and passed central LI at about 14:00 EDT. Meanwhile, weak northerly winds were present near the surface at the Stony Brook site at approximately 11:00 EDT (Fig. 3.1.S7f) and persisted for several hours until about
17:00 EDT, when the wind direction shifted to southwesterly, consistent with the presence of the sea breeze. Therefore, it is hypothesized that the convergence of the northward transport of O₃ and its precursors by the sea breeze circulation and the weak northerly winds at northern LI played a critical role in forming the observed O₃ gradient measured on 07/01 (Figs. 3.1.2b and 3.1.4a).

The sea breeze pattern on 08/06 was similar to 07/01, based on 24-hour HYSPLIT back trajectories (Figs. 3.1.S8a-S8f) and NYSM lidar vertical profiles (Figs. 3.1.S9a-3.1.S9f). However, the onset time of the sea breeze in southern LI was earlier on 08/06 compared to 07/01 (Figs. 3.1.S7 and 3.1.S9). Additionally, the 08/06 sea breeze likely contained a westerly wind component, as suggested by the southwesterly surface wind direction (Figs. 3.1.S8-S9). Furthermore, Fig. 3.1.S10 shows a distinct line of cumulus clouds over central LI, which strongly indicates that both a sea and a shore breeze formed on LI on 08/06.

**Figure 3.1.5.** The TROPOMI NO₂ column concentration spatial distribution on (a) 07/01, and (b) 08/06.

The difference between 07/01 and 08/06 is also reflected in the measured O₃ properties (Fig. 3.1.4). Figure 3.1.4 demonstrates that the 07/01 on-road measurements detected only one distinct O₃ peak (Fig. 3.1.4a), whereas the 08/06 on-road measurements detected several O₃ peaks (Fig. 3.1.4b, marked by the location name). It is also noteworthy that the measured O₃ concentrations on 08/06
were generally greater than those measured on 07/01, with most data points on 08/06 indicating that \( O_3 \) concentrations were 70 ppb or higher. In contrast to the 07/01 TROPOMI NO\(_2\) concentration (Fig. 3.1.5a), the TROPOMI NO\(_2\) concentration on 08/06 shows high NO\(_2\) levels over much of western LI (Fig. 3.1.5b). Consequently, NO\(_2\) photolysis was likely the dominant \( O_3 \) formation pathway on 08/06, and the high regional TROPOMI NO\(_2\) column concentrations likely imply high regional \( O_3 \) concentrations. This is qualitatively consistent with Figs. 3.1.2c and 3.1.4b, which illustrate that the on-road measured \( O_3 \) and NO\(_2\) concentrations at most areas north of Sands Point ranged from 85-90 and 6-10 ppb, respectively, from about 13:30-15:30 EDT. Meanwhile, Fig. 3.1.4b shows that another \( O_3 \) peak (> 90 ppb) was detected near Herricks at about 14:40 EDT, when the van was driven from south to north. This peak was not present when the van was driven from north to south near Herricks at around 13:50 EDT (Fig. 3.1.4b). Based on (1) the southerly wind over central LI after 14:00 EDT (Fig. 3.1.59e), and (2) the hourly averaged highest \( O_3 \) concentration (85 ppb) at Queens College occurring at 14:00-15:00 EDT (http://www.nyaqinow.net/), the \( O_3 \) peaks measured near Herricks (over 90 ppb) and Port Washington (over 100 ppb) at about 14:40 and 16:20 EDT, respectively, were likely due in part to northward \( O_3 \) transport by the sea breeze. The organic aerosol mass spectra from the \( O_3 \) peaks detected at Herricks and Port Washington show nearly identical signals (Fig. 3.1.6a), which supports the above hypothesis that the \( O_3 \) measured at the two locations originated from the same source. It is also important to note that the organic aerosol mass spectra during the Port Washington high \( O_3 \) period (16:10-16:30 EDT) had a lower oxidation state than the organic aerosol mass spectra during the Sands Point high \( O_3 \) period (15:30-16:00 EDT), with lower values at \( f_{44} \) and \( f_{28} \) (Fig. 3.1.6b). This suggests that the aerosols at Sands Point were oxidized for a longer time frame under high \( O_3 \) conditions (> 80 ppb), while the aerosols at Port Washington were transported and
less aged. Moreover, Fig. 3.1.S11 shows that the aerosol mass and number concentrations at Port Washington were higher than those at Sands Point, with mass concentrations of 21.1 (16.0) \( \text{ug m}^{-3} \) and number concentrations of 18000 (9000) \( \text{# cm}^{-3} \) at Port Washington (Sands Point). These results imply that the plume at Port Washington was more polluted.

**Figure 3.1.6.** (a) Relative aerosol mass spectra at Sands Point (red diamonds), Herricks (black asterisks), and Port Washington (blue bars) on 08/06. (b) Differential fraction of mass spectra signal – defined as Port Washington mass spectra signal minus Sands Point mass spectra signal – on 08/06.

The 08/06 on-road measurements also suggest that there were several significant \( \text{O}_3 \) variations related to the variability in \( \text{NO}_2 \). For example, from 13:00-13:30 EDT, \( \text{O}_3 \) and \( \text{NO}_2 \) concentrations at Port Washington (Sands Point) were 75 (85) ppb and 35 (10) ppb, respectively (Fig. 3.1.4b). In addition, \( \text{O}_3 \) concentrations as low as 30 ppb were observed on 08/06 at times corresponding to \( \text{NO}_2 \) concentrations up to 100 ppb (Fig. 3.1.4b), consistent with the high volume of traffic on the roadway. In contrast, any low \( \text{O}_3 \) concentrations measured on 07/01 was likely not due to high \( \text{NO}_2 \) levels, since \( \text{NO}_2 \) concentrations on 07/01 were typically less than 20 ppb (Fig. 3.1.4a). In sum, as previously discussed, the measured \( \text{O}_3 \) concentration gradient on 07/01 and 08/06 were largely influenced by the interaction of the southerly sea breeze and the northerly wind. Meanwhile, the
high measured O₃ concentrations on 08/06 were also influenced by regionally high O₃ levels related to high NO₂ concentrations.

3.1.3.2 Dramatic O₃ spatial distribution caused by NO₂ reaction

Figure 3.1.7. The time series of on-road measured O₃ and NO₂ on 07/10 and 07/16

In contrast to 06/30, 07/01, and 08/06, two other on-road measurement days – 07/10 and 07/16 – were simultaneously characterized by sharp O₃ concentration gradients and high NO₂ concentrations on the highway (Fig. 3.1.7). Specifically, the highest measured O₃ concentrations were approximately 100 ppb on LI on 07/10 and at White Plains on 07/16 (Fig. 3.1.S12). Such high O₃ concentrations were consistent with (1) the high NO₂ column concentration measured by TROPOMI (Figs. 3.1.8a-3.1.8b), and (2) the 24-hour HYSPLIT back trajectories for central LI on 07/10 (Fig. 3.1.8c) and White Plains on 07/16 (Fig. 3.1.8d). The back trajectories for the locations where high O₃ was measured suggest that a west-northwesterly and southwesterly wind was prevalent on 07/10 and 07/16, respectively (Figs. 3.1.8c-3.1.8d). Nonetheless, it is thought that the NO2 in the above areas was transported downwind (Figs. 3.1.8a-3.1.8b), where it photolyzed and produced the high O₃ concentrations measured on the afternoons of 07/10 and 07/16. Under the high O₃ conditions, the NO emitted by the highway traffic reacted with O₃ to form NO₂. This likely contributed to the strong anti-correlation between O₃ and NO₂ on 07/10 and 07/16 (Fig. 3.1.9a;
$r^2 = 0.84, p<0.05$). If the only formation pathway for NO$_2$ was NO+O$_3$, the amount of NO$_2$ formed would be equal to the amount of O$_3$ reacted$^{36}$. Therefore, the slope of a graph of O$_3$ versus NO$_2$ would be -1. However, Fig. 3.1.9 indicates the slope of O$_3$ versus NO$_2$ was -0.44. This suggests that about 44% of the measured NO$_2$ was likely due to NO titration, and the other 56% may have been due to the reactions of NO and VOCs from fresh traffic emissions$^{36}$.

**Figure 3.1.8.** (a) The TROPOMI NO$_2$ column concentration for 07/10. (b) The TROPOMI NO$_2$ column concentration for 07/16. (c) 07/10 back trajectory for central Long Island (40.74° N, 73.61° W). The back trajectory ended at 19 UTC (15:00 EDT), and the source heights of 100, 300, and 500 m correspond to the red, blue, and green lines, respectively. (d) 07/16 back trajectory for White Plains (40.99° N, 73.78° W). The ending time and the source heights are the same as in (c).
3.1.3.3 Background measurements

The measurements made on 08/15 and 08/16 were considered “background days” due to the relatively low observed O$_3$ concentrations. The maximum O$_3$ value on 08/15 was approximately 55 ppb, and most O$_3$ values on 08/16 were below 70 ppb (Fig. 3.1.S13). Nevertheless, the on-road measured aerosol on 08/15 and 08/16 showed contrasting spatial patterns (Fig. 3.1.10), even though the on-road measured aerosol on both days was likely influenced by the long-range transport of wildfire smoke originating from the western US and Canada$^{37}$ (Fig. 3.1.S14). As shown in Fig. 10a, relatively low aerosol mass concentrations were observed in eastern LI compared to central and western LI (7 ug m$^{-3}$ vs. 15 ug m$^{-3}$). In contrast, enhanced aerosol mass concentrations were found throughout LI on 08/16, with reduced spatial variability (east vs west: 17 ug m$^{-3}$ vs 21 ug m$^{-3}$; Fig. 3.1.10b). The difference in the measured aerosol spatial variability on 08/15 versus 08/16 was likely attributable in part to increasing subsidence of the biomass burning plume from 08/15 to 08/16 (Fig. 3.1.S15). By 08/16, the biomass burning plume was affecting much of LI, as shown by the lidar vertical profiles in Fig. 3.1.S15. Ultimately, the lidar measurements (Fig. 3.1.S15) and the PM$_{2.5}$ mass concentrations for several of the LI DEC sites (Queens College, Maspeth, and Eisenhower Park; Fig. 3.1.S16) show that the plume impacted LI.
from approximately 08/15 to 08/18, and it appeared to have the greatest effect on LI aerosol mass concentrations from 08/16-08/17.

Figure 3.1.10. The spatial distribution of the on-road measured aerosol mass concentration on (a) 08/15 (12:00-19:00), and (b) 08/16 (14:40-19:00).

3.1.4. Conclusions

The LISTOS on-road measurements were made from 06/24/2018 to 08/16/2018. Seven of the on-road measurement days – 06/30-07/01, 07/10, 07/16, 08/06, and 08/15-08/16 – were analyzed and discussed. The 06/30, 07/01, and 08/06 on-road measurement days were characterized by (1) sharp O₃ concentration gradients (ΔO₃ Δy⁻¹) of over 15 ppb km⁻¹ (Fig. 2), and (2) maximum O₃ concentrations of 100 ppb or greater (Figs. 3.1.3-3.1.4). The large O₃ gradients were measured on the south shore of LI on 06/30 and on the north shore of LI on 07/01 and 08/06. It was found that
the O₃ spatial variability observed on 06/30, 07/01, and 08/06 was likely attributable in part to the sea and/or shore breeze circulation, photochemically dominant conditions, or a combination of the two. Aerosol measurements supported the above hypotheses (e.g., Figs. 3.1.3 and 3.1.6).

Although the 07/10 and 07/16 on-road measurements also yielded maximum O₃ levels well above the 70 ppb NAAQS (approximately 100 ppb; Fig. 3.1.7), the processes driving the high O₃ concentrations differed from 06/30-07/01 and 08/06. Ultimately, it was hypothesized that the abundant NO₂ that formed in the New York City metropolitan area on both days (Figs. 3.1.8a-3.1.8b) was transported downwind, where it photolyzed and produced the high O₃ measured on the highway. Then, widespread NO titration due to the highway traffic likely contributed to the strong anti-correlation between O₃ and NO₂ on 07/10 and 07/16 (Fig. 3.1.9a; \( r^2 = 0.84, p<0.05 \)).

In contrast, O₃ concentrations on 08/15 and 08/16 were mainly below the 70 ppb NAAQS (Fig. 3.1.S13). However, elevated aerosol mass concentrations of 15 µg m⁻³ or larger were detected throughout LI on both days (Fig. 3.1.10), which was approximately three times greater than the aerosol mass concentration measured on the previous day (4.8 µg m⁻³). Such elevated aerosol levels were likely influenced by the long-range transport of wildfire smoke originating from the western US and Canada (Fig. 3.1.S14). Furthermore, aerosol mass concentrations on 08/16 exhibited less spatial variability compared to 08/15 (Fig. 3.1.10). This was likely due in part to increasing subsidence of the biomass burning plume from 08/15 to 08/16 (Fig. 3.1.S15).

Overall, the on-road measurements presented in this study demonstrate that both meteorological and photochemical processes contribute to O₃ exceedances and enhanced aerosol levels on LI. Even though this study’s findings begin to elucidate the interaction between the emitted pollution and the meteorological conditions on LI, additional on-road measurements over multiple summers are needed to potentially have a greater influence on future air quality policy.
Acknowledgements. This work has been supported by the Northeast States for Coordinated Air Use Management (NESCAUM) contract number 2411 and the New York State Energy Research and Development Authority (NYSERDA) contract number 48971. We acknowledge the free use of the tropospheric NO₂ column data from the TROPOMI sensor from www.temis.nl, the New York State Mesonet lidar profile data from www.nysmesonet.org, the New York State Department of Environmental Conservation (NYS DEC) air quality data from http://www.nyaqinow.net/, and the NOAA back trajectories from https://ready.arl.noaa.gov/HYSPLIT.php. Special thanks go to Paul Miller, George Allen, and other LISTOS participants for supporting the on-road measurements. We acknowledge the support and assistance of NYS DEC personnel, Stony Brook University, and in particular, the curator of the Flax Pond Marine laboratory, Mr. Stephen Abrams.
3.1.5. References


3.1.6. Supplement

Figure 3.1.S1. The names and locations of the six New York State Mesonet (NYSM) profiler sites on Long Island.

SI = Staten Island
BX = Bronx
QN = Queens
WANT = Wantagh
SB = Stony Brook
EH = East Hampton
Figure 3.1.S2: The BSI forecasted $O_3$ concentration distribution for 06/30/2018, 07/01/2018 and 08/16/2018
Figure 3.1.S3. Lidar wind vertical profile for (a) Staten Island; (b) Wantagh; (c) East Hampton; (d) Bronx; (e) Queens; (f) Stony Brook on 06/30. The red arrows indicate the approximate sea breeze onset time.

The onset of the sea breeze on 06/30 was approximately (1) 12:00 EDT at Staten Island, (2) 13:00 EDT at Wantagh, (3) 14:00 EDT at East Hampton, (4) 16:00 EDT at Bronx, (5) 14:00 EDT at Queens, and (6) 16:00 EDT at Stony Brook. (EDT: Eastern Daylight Time, which is equal to local time in this study)
Figure 3.1.S4. The 24-hour HYSPLIT back trajectory for (a) southwestern Long Island (40.59° N, -73.97° W), (b) south-central Long Island (40.74° N, -73.10° W), (c) southeastern Long Island (40.89° N, -72.37° W), (d) northeastern Long Island (41.08° N, -72.44° W), (e) north-central Long Island (40.94° N, -73.13° W), (f) northwestern Long Island (40.81° N, -73.68° W) on 06/30. The back trajectory ended at 20 UTC (16:00 EDT), and the source heights of 100, 300, and 500 m correspond to the green, blue, and red lines, respectively.
Figure 3.1.S5. The mass spectra of the aerosol under high/low O$_3$ concentration.
Figure 3.1.S6. The 24-hour HYSPLIT back trajectory for (a) northwestern Long Island (40.81° N, -73.68° W), (b) north-central Long Island (40.94° N, -73.13° W), (c) northeastern Long Island (41.08° N, -72.44° W), (d) southwestern Long Island (40.59° N, -73.97° W), (e) south-central Long Island (40.74° N, -73.10° W), (f) southeastern Long Island (40.89° N, -72.37° W) on 07/01. The back trajectory ended at 21 UTC (17:00 EDT), and the source heights of 100, 300, and 500 m correspond to the red, blue, and green lines, respectively.
The onset of the sea breeze on 07/01 was approximately (1) 15:00 EDT at Staten Island, (2) 15:00 EDT at Wantagh, (3) 16:00 EDT at East Hampton, (4) 17:00 EDT at Bronx, (5) 16:00 EDT at Queens, and (6) 17:00 EDT at Stony Brook.
Figure 3.1.S8. The 24-hour HYSPLIT back trajectory for (a) northwestern Long Island (40.81° N, -73.68° W), (b) north-central Long Island (40.94° N, -73.13° W), (c) northeastern Long Island (41.08° N, -72.44° W), (d) southwestern Long Island (40.59° N, -73.97° W), (e) south-central Long Island (40.74° N, -73.10° W), (f) southeastern Long Island (40.89° N, -72.37° W) on 08/06. The back trajectory ended at 21 UTC (17:00 EDT), and the source heights of 100, 300, and 500 m correspond to the red, blue, and green lines, respectively.
Figure 3.1.59. Lidar wind vertical profile for (a) Staten Island; (b) Wantagh; (c) East Hampton; (d) Bronx; (e) Queens; (f) Stony Brook on 08/06. The red arrows indicate the approximate sea breeze onset time. (The blanket area for Staten Island, Wantagh, East Hampton, and Bronx after 20:00 EDT was due to the missing data)

The onset of the sea breeze on 08/06 was approximately (1) 11:00 EDT at Staten Island, (2) 11:00 EDT at Wantagh, (3) 12:00 EDT at East Hampton, (4) 18:00 EDT at Bronx, (5) 14:00 EDT at Queens, and (6) 16:00 EDT at Stony Brook.
Figure 3.1.S10. NASA EOSDIS Worldview visible satellite image for Long Island on 08/06. The line of cumulus clouds virtually parallel to the shoreline suggests that both a sea and a shore breeze circulation developed.
Figure 3.1.S11. The mass concentration/fraction of the aerosol during (a) the Sands Point high $O_3$ period, and (b) the Port Washington high $O_3$ period on 08/06 (unit: $\mu g \text{ m}^{-3}$).
Figure 3.1.S12. The spatial distribution of the on-road O₃ concentration on (a) 07/10 (13:00-16:50), and (b) 07/16 (11:40-17:50).
Figure 3.1.S13. The spatial distribution of the on-road $O_3$ concentration on (a) 08/15 (12:00-19:00), and (b) 08/16 (14:40-19:00).
Figure 3.1.S14. NASA EOSDIS Worldview visible satellite image for North American on 08/16.

The star indicates the location of Long Island.
Figure 3.1.S15. Lidar CNR vertical profile for (a) Queens, (b) Wantagh, (c) Stony Brook, and (d) East Hampton. The sites are ordered going from western to eastern Long Island. The red arrow indicates the start time of the subsiding plume.
Figure 3.1.S16. The time series of PM$_{2.5}$ mass concentration for three DEC sites (Queens College, Maspeth, and Eisenhower Park) on Long Island from 08/15 to 08/19.
Chapter 3: Urban measured aerosol properties

3.2. The aerosol evolution during the period of the co-occurrence of extremes in surface ozone, particulate matter, and temperature over New York metro area
In this section, the enhanced aerosol event (06/29-07/04) in 2018 is highlighted due to its long duration and relationship with heat wave weather and enhanced daytime $O_3$ concentrations. In addition to the overall enhanced aerosol period, three sub-periods with different aerosol characteristics were also studied, focusing on the comparisons of aerosol chemical components, mass fraction, size distributions, and organic oxidation state. The aerosol evolution during the enhanced aerosol period is considered in detail. After examination of the above aerosol properties and their evolution, we identified two pollution processing conditions: (1) the formation of less-oxidized oxygenated organic aerosol (LO-OOA) formed by the photo-chemical reactions of the anthropogenic VOCs emitted during the heatwave period; and (2) production of more-oxidized oxygenated organic aerosol (MO-OOA) from the further oxidation reactions hypothesized to occur in the sea surface boundary layer and followed by transport of the pollution back over land by the sea breeze circulation. This study identifies conditions affecting the New York metro area during the summertime heat wave periods, and will likely suitable for other urban areas adjacent to large bodies of water.

3.2.1. Introduction

Persistently high temperatures (i.e., heatwaves), high ozone ($O_3$) concentrations, and high fine particulate matter ($PM_{2.5}$) concentrations adversely affect human health$^{1-3}$. Heatwaves lead to health issues such as heat stroke, dehydration, respiratory illness, and even death$^{4-6}$, and high $O_3$ and $PM_{2.5}$ concentrations also negatively impact human morbidity and mortality$^{2,7}$. Such negative human health effects are exacerbated when heatwaves, high $O_3$ concentrations, and high $PM_{2.5}$
concentrations occur simultaneously\(^2,8,9\).

High temperatures, strong insolation, low precipitation, and weak winds typically characterize heatwaves. These meteorological conditions are also conducive to the formation and accumulation of O\(_3\) and PM\(_{2.5}\)\(^2,3,10\). In sum, high temperatures, strong insolation, low precipitation, and weak winds lead to (1) an increased photochemical reaction rate between volatile organic compounds (VOCs) and oxides of nitrogen (NO\(_x\)), (2) the accumulation of anthropogenic NO\(_x\), anthropogenic VOC, and biogenic VOC emissions, and (3) increased production of O\(_3\) and secondary organic aerosol (SOA)\(^2\). However, to the best of our knowledge, few studies have examined the chemical properties and the evolution of SOA during heatwaves in urban areas\(^11-13\), where the combined effect of heatwaves, high O\(_3\) concentrations, and high PM\(_{2.5}\) concentrations on human health and welfare is likely greatest.

The New York City (NYC) combined statistical area is densely populated, with more than 23.8 million people living in an area of nearly 35,000 km\(^2\)\(^14\). The NYC metropolitan area is a major source of O\(_3\) precursors (i.e., NO\(_x\) and VOCs), which often leads to summertime O\(_3\) exceedance events and SOA formation in the NYC metropolitan area and locations downwind\(^3,15-17\). In addition, the NYC metropolitan area is more susceptible to heatwaves than the surrounding area due to the urban heat island effect, a phenomenon that has been well-studied in NYC\(^18\). Furthermore, the NYC metropolitan area and locations downwind are frequently affected by the sea breeze circulation\(^19,20\). The sea breeze circulation can transport marine secondary organic aerosol (MSOA) inland\(^21\). A tracer for MSOA is methanesulfonic acid (MSA), which is formed exclusively by the oxidation of dimethylsulfide (DMS) released by phytoplankton\(^21-24\). Overall, the NYC metropolitan area and surrounding locations are characterized by complex chemical and meteorological processes, many of which would benefit from further study.
Therefore, the 2018 Long Island Sound Tropospheric Ozone Study (LISTOS) was organized by the Northeast States for Coordinated Air Use Management (NESCAUM; http://www.nescaum.org/documents/listos) to investigate the evolving nature of summertime O\textsubscript{3} formation and transport in the NYC region and locations downwind. In this study, the University at Albany Atmospheric Sciences Research Center (ASRC) mobile laboratory observed a heatwave in the NYC metropolitan area during LISTOS that was also characterized by high O\textsubscript{3} and aerosol concentrations. This section describes the evolution and chemical properties of aerosols on central Long Island during, shortly before, and shortly after the heatwave.

3.2.2. Method

3.2.2.1 Measurement period and location

The ASRC mobile laboratory measured the surface NO\textsubscript{2}, O\textsubscript{3}, and aerosol mass concentration during LISTOS using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and collocated instruments from 24 June-16 August 2018 in Long Island, NY. The mobile laboratory made a combination of on-road measurements and measurements at the Flax Pond Marine Laboratory on Long Island. Long Island (LI) is located east of the NYC metropolitan area, and it is often affected by pollutants transported eastward from NYC\textsuperscript{13}.

3.2.2.2 Measurement instruments and data sources

The ASRC mobile laboratory contained one HR-ToF-AMS, which measured the submicron aerosol size and mass concentration\textsuperscript{25,26}; one PDR to measure the aerosol mass concentration and serve as an extra pump for the HR-ToF-AMS; two O\textsubscript{3} sensors (TAPI Model 430 and 2B Model 205) for measuring the O\textsubscript{3} concentration at a 1-minute time resolution; and one NO\textsubscript{2} sensor (TAPI Model 500U) for measuring the NO\textsubscript{2} concentration at a 1-minute time resolution. More details
regarding the ASRC mobile laboratory can be found elsewhere. The HR-ToF-AMS was operated in “V” mode and cycled through the mass spectrum (MS) mode and the particle time-of-flight (PToF) mode every five minutes.

Volatile organic compounds (VOCs) were measured at the Flax Pond Marine Laboratory by a high-resolution proton transfer time-of-flight mass spectrometer (PTR-ToF-MS). The basic operating principles of the PTR-ToF-MS are described elsewhere. Meteorological and lidar data were collected at the Stony Brook Mesonet site, located about 4 km from the Flax Pond Marine Laboratory. The meteorological parameters included temperature, relative humidity (RH), solar radiation, wind speed, and wind direction, while the lidar measured the vertical wind and backscatter profiles. In addition, aerosol and gas species were measured at Queens College the New York State Department of Environmental Conservation (DEC) air quality monitoring site using a Fast Mobility Particle Sizer (FMPS) for measuring the aerosol size distribution and different commercial gas sensors to measure trace gases. Finally, the hour-averaged PM$_{2.5}$ data from the DEC sites in the NYC metropolitan area were utilized (http://www.nyaqinow.net/).

3.2.2.3 Data analysis

The HR-ToF-AMS data were processed using the standard data analysis software (SQUIRREL v1.59D and PIKA v1.19) to obtain the aerosol mass concentration and size distribution for organics (Org), sulfate (SO$_4$), nitrate (NO$_3$), ammonium (NH$_4$), and chloride (Cl). The default collection efficiency (CE = 0.5) was used for each compound. Meanwhile, the PIKA software reported the oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratio based on the method developed by Canagaratna et al.

The PMF Evaluation Tool (PET) version 2.06 was used to separate the organics into several
organic aerosol factors based on the PMF2 algorithm\textsuperscript{32}. In this study, three organic factors were identified by PMF, including a hydrocarbon-like OA (HOA), a less oxidized oxygenated OA (LO-OOA), and a more oxidized oxygenated OA (MO-OOA). The mass spectrum of HOA (Fig. 3.2.S1a) is characterized by the C\textsubscript{x}H\textsubscript{2x-1}\textsuperscript{+} and C\textsubscript{x}H\textsubscript{2x+1}\textsuperscript{+} ion series with a high H:C ratio, a low O:C ratio, and elevated concentrations in mid-morning and early evening (Fig. 3.2.S1b). Therefore, HOA is hypothesized to be directly emitted from gasoline and diesel combustion sources, as suggested by previous studies\textsuperscript{17}. The LO-OOA and MO-OOA were classified to be secondary organic factors based on their diurnal variation and the high O:C ratio and f\textsubscript{44} signal (Fig. 3.2.S1). Figure 3.2.S1a shows that MO-OOA was characterized by a higher f\textsubscript{44} signal than LO-OOA, with values of 0.20 and 0.08, respectively. Furthermore, the diurnal peak in MO-OOA was about 2-3 hours later than LO-OOA, with diurnal peaks occurring at approximately 2 p.m. and noon local time, respectively (Fig. 3.2.S1b). This is consistent with the MO-OOA being more aged. These differences between LO-OOA and MO-OOA are further discussed in section 3.2.3.2.

The methanesulfonic acid (MSA) measurements were calibrated following the method developed by Huang et al. (2017) and other previous studies\textsuperscript{21,33-34}. First, an MSA dilution in water was atomized by a TSI atomizer. Second, a differential mobility analyzer (DMA) was used for selecting the MSA particles with a diameter of 250 nm. Third, the selected particles were detected by the AMS and a condensation particle counter (CPC). A comparison between the HR-ToF-AMS and CPC yielded (1) a relative ionization efficiency (RIE) of 1.16 assuming an MSA CE of 1 and (2) a f\textsubscript{79} (CH\textsubscript{3}SO\textsubscript{2}\textsuperscript{+}) of 6.4\% (Fig. 3.2.S2)\textsuperscript{21}. This value of f\textsubscript{79} was used to estimate the total MSA mass concentration (m\textsubscript{MSA}=m\textsubscript{79}/6.4\%).
3.2.3. Result

3.2.3.1 Overview

Figure 3.2.3 shows the daily-averaged PM$_{2.5}$ mass concentration for the DEC sites in the NYC metropolitan area from January 2016 to December 2018. The blue boxes in Fig. 3.2.3c indicate the three time periods in 2018 – 29 June-4 July, 15-17 August, and 27-29 August – that corresponded to elevated aerosol concentrations in the NYC metropolitan area. Specifically, the highest daily PM$_{2.5}$ mass concentration during those three periods (32 µg m$^{-3}$) approached the 35 µg m$^{-3}$ 24-hour National Ambient Air Quality Standard (NAAQS) for PM$_{2.5}$ mandated by the EPA. The 29 June-4 July time period (hereafter defined as the enhanced aerosol period or EP) will be discussed in more detail later due to its duration and co-occurrence with high temperatures and O$_3$ concentrations. In contrast, the 15-17 August and 27-29 August time periods were likely influenced by the transport of biomass burning plumes$^{35}$, and analyses of these periods is beyond the scope of this work.

The hour-averaged PM$_{2.5}$ mass concentration at the DEC sites and the PM1 mass concentration measured by the HR-ToF-AMS located at the Flax Pond Marine Laboratory are shown in Fig. 3.2.1 for the 27 June-7 July 2018 time period. With the exception of the 4 July fireworks that occurred on the night of 4 July, similar PM$_{2.5}$ mass concentrations were found for the DEC sites in the NYC metropolitan area from 27 June-7 July (Fig. 3.2.1). This indicates that the elevated PM$_{2.5}$ mass concentrations from 29 June-4 July had a regional impact. Additionally, the PM$_1$ mass concentration exhibited a trend similar to the PM$_{2.5}$ mass concentration (Fig. 3.2.1), and the average PM$_1$/PM$_{2.5}$ ratio was 0.8. This reveals that PM1 was the major component of PM$_{2.5}$ for the NYC metropolitan area. Due to the improper heat bias setting for the HR-ToF-AMS$^{36}$, which made the quantification of potassium (K) difficult, this fireworks period (4 July 21:30-5 July 06:00) will not
be discussed further.

![Figure 3.2.1](image)

**Figure 3.2.1.** The hour-averaged PM$_{2.5}$ mass concentration at the DEC sites in the NYC metropolitan area from 27 June-7 July, and the PM$_1$ mass concentration (light blue line) measured by the HR-ToF-AMS at the Flax Pond Marine Laboratory.

As seen in Figure 3.2.S4, the temperature, wind direction, wind speed, solar radiation, and O$_3$ concentration over the NYC metropolitan area from 27 June-7 July exhibited similar behavior. This implies that atmospheric conditions were largely homogeneous over the greater NYC metro area. Given this, it is likely that the extent of photochemical activity and aerosol evolution from 27 June-7 July was similar across the NYC metropolitan area. Figure 3.2.S4 illustrates that this enhance period (EP) was characterized by (1) daily maximum temperatures exceeding 30 °C, (2) weak southerly winds, (3) high solar radiation, and (4) ground-level O$_3$ concentrations that sometimes exceeded 100 ppb, well above the 70 ppb O$_3$ NAAQS. Thus, it is reasonable to classify this period as a heatwave event with extreme O$_3$. In addition, Figs. 3.2.1, 3.2.S4a, and 3.2.S4e
show that enhanced temperatures, aerosol mass concentrations, and O₃ concentrations often co-occurred from 27 June-7 July. As a result, it is meaningful to study the evolution of aerosols during this period, which is done in the next section.

3.2.3.2 Sources and atmospheric evolution of PM₁

Figure 3.2.2a shows the total aerosol mass concentration, temperature, wind speed, wind direction, and relative humidity from 27 June-7 July. In addition to the EP, there were two background aerosol periods (BPs). First, 27-28 June (BP1) was characterized by southerly winds, low total aerosol mass concentration, and enhanced SO₄ mass fraction (Figs. 3.2.2a and 3.2.S5a). Therefore, BP1 was likely influenced by a clean marine air mass. Second, the morning of 5 July to the evening of 6 July (BP2) had a similar wind pattern to EP, but the total aerosol mass concentration was low (Fig. 3.2.2a). The EP was divided further sub-into three sub-periods. The first sub-period was an aerosol growth period (EPG) when the total aerosol mass concentration consistently increased and the prevailing wind direction was northerly. The second sub-period was a mature aerosol period (EPM) when the total aerosol mass concentration changed little. The third sub-period was an aerosol brief decline period (EPD) when the total aerosol mass concentration consistently decreased. The BP1, BP2, EPG, EPM, and EPD periods are also shown in Table 3.2.S1 and Fig. 3.2.2.
Figure 3.2.2. The time series of (a) total aerosol mass concentration, temperature, wind speed, wind direction, and relative humidity; (b) speciated aerosol mass concentration with the time scale for different periods included; (c) aerosol size distribution; (d) PMF organic factors and MSA mass concentrations for the 27 June-7 July study period. (BP: background period; EP: enhanced period; G: growth; M: Maturity; D: Decline).
### 3.2.3.2.1 Comparison of the aerosol periods

The average aerosol mass concentration and mass fraction for each period are shown in Fig. 3.2.3, and the aerosol number and mass distributions as a function of aerosol size are shown in Fig. 3.2.S6. The aerosol during BP1 had the lowest aerosol mass concentration (about 2.6 µg m\(^{-3}\)) and a relatively high mass fraction of SO\(_4\) (about 27%), consistent with previous studies\(^{13,17}\) (Fig. 3.2.3). Progressing from BP1 to EPM, the total aerosol mass, organic mass, and SO\(_4\) mass concentrations increased (Fig. 3.2.3). Additionally, Figs. 3.2.2c and 3.2.S6a demonstrate that there was an increase in the number concentration of accumulation-mode aerosols (100-200 nm) from BP1 to EPM that may have been due in part to the increasing size of organics and SO\(_4\) (Figs. 3.2.S6b-3.2.S6c). Moreover, Figs. 3.2.2, 3.2.3, and 3.2.S6 suggest that BP2 may have been characterized by a mixture of marine and urban aerosols due to (1) relatively low aerosol mass concentrations, (2) a high mass fraction of LO-OOA and SO\(_4\), and (3) an organic mass distribution similar to the aerosols present during EPG.

![Figure 3.2.3](image.png)

**Figure 3.2.3.** The average aerosol mass concentration and mass fraction for each period.

During the EP period (29 June-4 July), the aerosol mass fraction largely consisted of organics
(74%), followed by SO$_4$ (17%), NH$_4$ (6%), and NO$_3$ (3%) (Figs. 3.2.2b and 3.2.S5a). The predominance of organics and sulfate in PM$_1$ is consistent with previous studies conducted in NYC during the summers of 2001, 2009, and 2011$^{13,16,17}$. However, it is noteworthy that the organic and SO$_4$ mass fractions found during the EP period are approximately 10-49% higher and 7-20% lower, respectively, than those found by Drewnick et al. (2004a)$^{16}$, Sun et al. (2011)$^{17}$, and Zhou et al. (2016)$^{13}$. These differences are likely attributable in part to ongoing reductions in SO$_2$ concentrations$^{37}$, which likely contributed to the reduced SO$_4$ mass fraction during the EP period.

The EPG, EPM, and EPD sub-periods show the variability in the aerosol mass concentrations and mass fractions in more detail. During the EPG sub-period, LO-OOA was the main aerosol organics factor during EPG, with an average mass fraction of 44% (Fig. 3.2.3). This is noticeably higher than during the EPM and EPD, which had LO-OOA mass fractions of 28 and 20%, respectively. Meanwhile, the time series of the LO-OOA mass concentration during EPG indicates that LO-OOA increased on average at a rate of 1.4 µg m$^{-3}$ day$^{-1}$ (Fig. 3.2.S7). This suggests that the formation and accumulation of LO-OOA over Long Island and the NYC metropolitan area occurred during EPG. During the next sub-period, peak LO-OOA concentrations of about 8.5 µg m$^{-3}$ occurred on the morning of 1 July during the EPM period, then subsequently decreased (Fig. 3.2.2e). A proposed reason for the decreasing LO-OOA concentrations is that the weaker wind speeds of less than approximately 2 m s$^{-1}$ persisted for several hours after the morning of 1 July (Fig. 3.2.2a). Such stagnant conditions likely slowed the formation and accumulation of LO-OOA because precursor AVOCs were not advected in the region sufficiently. The EPM period also had the highest aerosol mass concentration and fractional contribution of MO-OOA to the aerosol mass concentration, with values of 17.5 µg m$^{-3}$ and 40%, respectively (Fig. 3.2.3). Furthermore, the EPM period had higher O:C (0.71 vs. 0.60 and 0.51) and lower H:C (1.43 vs. 1.49 and 1.59) ratios.
than the EPG and EPD periods. Thus, the greater aerosol oxidation state observed during EPM under stagnant meteorological conditions also corresponds to the enhanced aerosol number concentration in the accumulation mode (100-200 nm; Figs. 3.2.2c and 3.2.S6a). Finally, the average total aerosol mass concentration rapidly decreased from 20 µg m\(^{-3}\) to a background value (about 5 µg m\(^{-3}\)) in about 6 hours during the decline period (EPD; Fig. 3.2.2a). Fig. 3.2.2a also indicates that the surface wind speed and wind direction varied little during EPD. However, the aerosol vertical profile measured by lidar showed the lifting of the near-ground aerosol layer (Fig. 3.2.S8a) and enhanced vertical wind speed (Fig. 3.2.S8b). This suggests that vertical mixing may have contributed to the rapid decrease in total aerosol mass concentrations during EPD.

### 3.2.3.2.2 Conceptual Aerosol Evolution during the enhanced aerosol period

Figure 3.2.S5b,c shows the concentration of VOCs measured by the PTR-MS during the study period. The most abundant anthropogenic VOCs (AVOC) chosen for analysis were acetaldehyde, methanol, toluene, acetone and benzene (Fig. 3.2.S5b), and the measured biogenic VOCs (BVOC) were isoprene, 2-methyl-3-buten-2-ol (MBO), and alpha-pinene (α-pinene) (Fig. 3.2.S5b). Methanol and acetone were the most abundant AVOCs during the measurement period (Fig. 3.2.S5b). Fig. 3.2.4 shows that the temporal variability of LO-OOA was similar to that of the measured AVOCs, with a high correlation coefficient (\(r^2=0.72\)). This suggests that (1) LO-OOA and the AVOCs have similar sources, and/or (2) the measured AVOCs are LO-OOA precursors. It is noteworthy that LO-OOA exhibited three nighttime peaks that corresponded to instances when AVOC concentrations and RH were generally low and high, respectively (Fig. 3.2.4a, red arrows). This indicates that enhanced LO-OOA formation may have occurred with contribution from aqueous-phase chemical processing at higher RH\(^{38}\). Moreover, O\(_3\) and AVOC concentration peaks generally co-occurred during the heat wave period (Fig. 3.2.S9), which suggests that peak O\(_3\) levels...
were largely associated with VOCs from urban and local emissions\(^3\).
NO$^{41}$. Overall, further study with longer-term measurements is needed to either confirm or refute the above hypotheses.

Meanwhile, the MO-OOA was well-correlated with SO$_4$ and MSA, with r$^2$ values of 0.68 and 0.71, respectively (Fig. 3.2.S10). SO$_4$ and MSA both showed enhanced mass concentrations during EPM (Figs. 3.2.2b and 3.2.2d). Previous studies have indicated that MSA can also enhance the formation of molecular clusters of sulfuric acid and amines, which then enhances the SO$_4$ concentration and contributes significantly to particle growth$^{42,43}$. During EPM, maximum MSA mass concentrations were approximately 0.2 ug m$^{-3}$ (Fig. 3.2.2e). Such concentrations are consistent with the MSA levels found by Huang et al. (2017) in South Atlantic Ocean$^{21}$. Additionally, the relatively high chlorophyll-α (Chl-α) mass distribution detected from MODIS (Fig. 3.2.S11) suggests that the MSA mass concentrations may have been influenced by phytoplankton activity$^{21}$. Furthermore, the detected Na$^+$ signal is negligible during the EP period (not shown). As a result, it is reasonable to assume that the measured SO$_4$ was mainly non-sea-salt SO$_4$ (nssSO$_4$). The ratio of MSA to nssSO$_4$ has previously been used to determine the DMS contribution to the measured SO$_4$$^{21}$. The MSA:nssSO$_4$ ratio ranged from 0.02 to 0.08 during EPM, with an average value of 0.04, which is about 2-3 times lower the reference values with only a biogenic origin measured at the remote ocean areas (0.08-0.14)$^{44-47}$. Therefore, it is hypothesized that the measured SO$_4$ mass concentration during EPM was influenced by the combination of the oxidation of DMS that was transported northward from the Atlantic Ocean to LI (Fig. 3.2.S12a) and transported reginal anthropogenic sulfate$^{21}$. Using the averaged value of 0.11 for the MSA:nssSO$_4$ ratio considering only a biogenic value, the DMS related SO$_4$ could be estimated based on the calculated MSA and the contribution from the DMS related SO$_4$ to the total SO$_4$ was estimated obtained to be about 37%, which was near the value measured at Paris$^{48}$. Moreover, Fig. 3.2.S13 shows the average
SO₄, MO-OOA, and MSA size distributions during EPM and is consistent with these aerosols being largely internally mixed. This suggests that (1) SO₄, MO-OOA, and MSA shared similar formation pathways, and/or (2) SO₄ and MSA accumulated along with MO-OOA.

Based on the above discussion, it is thought that the aerosol evolution during EP was influenced by two different mechanisms. First, during EPG, the AVOCs formed LO-OOA and O₃ via photochemical reactions, and the variation of LO-OOA closely followed the variation of VOCs (Fig. 3.2.4a). Second, some of the AVOCs and the newly-formed LO-OOA were transported seaward when the wind direction was northerly, and biological activity then yielded high DMS concentrations (Fig. 3.2.S12a). In the shallow sea-surface layer, the AVOCs and LO-OOA may experience further photochemical oxidation to form MO-OOA. Then, the newly-formed MO-OOA may have provided the necessary surface area for DMS oxidation to occur, leading to MSA and nssSO₄ formation. Ultimately, the MSA, nssSO₄, and DMS were transported inland by the southerly flow present during the beginning of EPM (Fig. 3.2.2a). Once over land, these species likely accumulated and underwent photochemical oxidation during most of EPM due to the stagnant meteorological conditions (Fig. 3.3.2a). This hypothesis is supported by the daytime peak MO-OOA mass concentrations that were frequently found at times when temperature and solar radiation were both high (Fig. 3.2.S14, red arrows). In sum, the second mechanism appears to mainly affect the NYC metropolitan area. Specifically, the PM₂.₅ data for the DEC sites in upstate NY was also influenced by the second mechanism as indicated by a temporal variability matched that of LO-OOA (Fig. 3.2.S12b), which indicates that only the first mechanism likely dominated the aerosol evolution in upstate NY during EP. In contrast, the PM₂.₅ data for the NYC metropolitan area had a temporal variability that sometimes similar variation to MO-OOA, particularly during the middle of the EP period (2-4 July; Fig. 3.2.S12b). Overall, it is possible that the second
mechanism described above may affect other coastal, urban areas.

### 3.2.4. Conclusion

The Metro NYC and LI area suffered enhanced aerosol events in 2018, with highest daily value (32 ppb) near to EPA standard (35 ppb), and the one between 06/29-07/04 was studied in detail due to its long duration and co-occurrence with heat wave weather and enhanced daytime O3 concentrations. The enhanced aerosol period was characterized by homogeneous atmospheric conditions for the whole New York metro area, indicating that analysis at Long Island could be representative of wider regional conditions. In this section, the time period of 06/25-07/09 was studied, which includes the enhanced aerosol event (06/29-07/04) and other background cases, such as plumes from mainland, marine, and nearby biomass burning. Five sub-periods were divided from the whole period, containing three for the enhanced aerosol event, namely Growth, Maturity, and Decline periods. The aerosol properties during each sub-period were analyzed, including the aerosol chemical composition, mass fractions, size distributions, and organic oxidation state.

The PMF analysis identified three organic factors for the aerosol organic compounds - MO-OOA, LO-OOA and HOA. LO-OOA shows a strong correlation the sum of the anthropogenic VOC (methanol, acetone, acetaldehyde, toluene, acetone, and benzene) with an $r^2$ of 0.74, implying they have same source or that these AVOCs were the precursors of LO-OOA. At the same time, no trace for the biogenic secondary organic aerosol formation was observed in spite of the high concentration of isoprene, indicating the anthropogenic emissions were still the main source of the secondary organic aerosol in New York metro area during these polluted conditions. Unlike LO-OOA, MO-OOA shows high correlation with $SO_4$ ($r^2$=0.68) and MSA ($r^2$=0.71), and all of them showed enhanced mass concentration during the EPM (Maturity) period, which implied these three
species shared similar oxidation pathways. This formation pathways were hypothesized to occur at the same time as DMS oxidation in the ocean surface boundary layer, and was distinct from the above pathway for LO-OOA, which was taken to be the direct photo-oxidation of anthropogenic VOC. These pathways represent two different pollution patterns. The pathway forming LO-OOA dominated the aerosol evolution in the whole upstate area during the heatwave period, while the pathway forming MO-OOA was unique to New York metro area. These details of aerosol evolution and processing during this NYC metro area heat wave influenced period may also provide clues for other urban cities with similar conditions, especially other areas influenced by the sea breeze and similar emissions.

ACKNOWLEDGMENTS

This work has been supported through the Northeast States for Coordinated Air Use Management (NESCAUM) with funds from the New York State Energy Research and Development Authority (NYSERDA) contract number 48971. We acknowledge the free use of the New York State Mesonet lidar profile data from www.nysmesonet.org, the New York State Department of Environmental Conservation (NYS DEC) air quality data from http://www.nyaqinow.net/, and the NOAA back trajectories from https://ready.arl.noaa.gov/HYSPLIT.php. We acknowledge the support and assistance of NYS DEC personnel, Stony Brook University, and in particular, the curator of the Flax Pond Marine laboratory, Mr. Stephen Abrams.
3.2.5. References


### 3.2.6. Supplement

Table 3.2.S1. The time duration for each period (BP: background period; EP: enhanced period; G: growth; M: Maturity; D: Decline. The gap between EPG and EPM was due to daytime on-road measurements).

<table>
<thead>
<tr>
<th>Period name</th>
<th>Period time</th>
<th>Wind direction/Wind speed</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP1</td>
<td>06/27 00:00-06/28 21:00</td>
<td>South</td>
</tr>
<tr>
<td>EPG</td>
<td>06/28 21:00-06/30 10:00</td>
<td>North</td>
</tr>
<tr>
<td>EPM</td>
<td>06/30 10:00-07/04 15:40</td>
<td>Alternately South/North</td>
</tr>
<tr>
<td>EPD</td>
<td>07/04 15:40-07/04 21:30</td>
<td>South</td>
</tr>
<tr>
<td>BP2</td>
<td>07/05 05:00-07/07 00:00</td>
<td>Alternately South/North</td>
</tr>
</tbody>
</table>
Figure 3.2.S1. (a) The mass spectra of three PMF factors, and (b) the diurnal variability in their mass concentration.
Figure 3.2.S2. The mass spectra of MSA from the lab calibration using a pure MSA dilution in water
Figure 3.2.S3. (a-c) The daily-averaged PM$_{2.5}$ mass concentration for the DEC sites in the NYC metropolitan area from January 2016-December 2018. The blue dashed line indicates the 35 µg m$^{-3}$ 24-hour NAAQS for PM$_{2.5}$.
Figure 3.2.S4. (a-d) The hour-averaged meteorological parameters observed by Mesonet sites, and (e) O$_3$ measured by the DEC sites.
Figure 3.2.S5. The time series of (a) aerosol mass fraction; (b) PTR-MS anthropogenic VOCs (A-VOC); (c) PTR-MS biogenic VOCs for the 27 June-7 July study period.
Figure 3.2.S6. (a) The average aerosol number distribution of each period as a function of aerosol diameter; (b) the average organic and SO$_4$ mode size of each period.
Figure 3.2.S7. The time series of total aerosol mass concentration and LO-OOA mass concentration during EPG and the linear fitting result when comparing the two variables.
Figure 3.2.S8. (a) The vertical profile of CNR and (b) the vertical wind speed from the Stony Brook New York State Mesonet site.
Figure 3.2.S9. The time series of anthropogenic VOCs and O₃. O₃ is color-coded by temperature.
Figure 3.2.S10. The relationship between (a) MO-OOA and SO$_4$ mass concentration, and (b) MO-OOA and MSA mass concentration.
Figure 3.2.S11. (a) The 24-hour back trajectories during the EP period, and (b)-(e) the MODIS detected Chl-a mass distribution (https://modis.gsfc.nasa.gov/data/dataprod/chlor_a.php). The black box in each figure denotes the study area.
Figure 3.2.S12. The time series of (a) DMS concentration (colored by wind direction), and (b) PM$_{2.5}$ concentrations from the DEC sites in upstate NY and in the NYC metropolitan area, in addition to LO-OOA and MO-OOA.
Figure 3.2.S13. The HR-ToF-AMS measured average SO$_4$, m/z 44 (representing MO-OOA), and MSA mass size distribution during the EPM period.
Figure 3.2.S14. The time series of MO-OOA mass concentration and solar radiation values. Solar radiation was colored by temperature, and the red arrows indicate the daytime peaks for MO-OOA.
Chapter 3: Urban measured aerosol properties

3.3. Urban Firework event
"Detailed measurements of submicron particles from an Independence Day fireworks event in Albany, NY using HR-ToF-AMS"

In this section, aerosol particles from FW displays were measured using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and collocated instruments during the Independence Day (July 4, 2017) holiday period at Albany, NY, USA. These measurements and analysis address the question about the influence of FW burning on fine aerosol mass concentration and chemical characteristics while large numbers of people were clustered together and breathing the outdoor air.

3.3.1 Introduction

Firework (FW) displays from national celebrations, such as Independence Day in the United States, Spring and Lantern Festivals in China, Diwali Festival in India, Guy Fawkes Night in the UK, and worldwide New Year’s Eve celebrations are known to cause short-term very high-intensity air quality degradation, especially atmospheric particulate matter (PM) pollution$^{1-10}$. Besides substantial visibility reductions lasting for hours and heavy emissions of gaseous pollutants, such as nitrogen oxides and sulfur dioxide$^{11}$, FW events also produce large amounts of submicron particles (PM$_1$) that are rich in sulfate, organics, potassium, and heavy metals (e.g. Cu, Ba, Al)$^{1,7,12-13}$. The heavy metals come from the inorganic salts that are used in FW manufacturing to produce different colors, while the compounds used for oxidizing fireworks mixtures produce abundant potassium salts, such as potassium sulfate, nitrate, chlorate, and perchlorate. FW-produced aerosols with metal compounds were found to have greater toxicity than aerosols from traffic emissions$^4$, and to be harmful to public health, with detrimental impacts on the respiratory system$^{14,15}$. 
The Independence Day holiday in the United States (July 4) has been celebrated for more than two hundred years and is associated with grand FW displays around the whole country, from small towns to megacities. According to the American Pyrotechnics Association (APA) fireworks consumption figures, about 120 million kg of fireworks were detonated by U.S. consumers in 2017 and about 12 million kg were used for public displays, about 44% of 2017 fireworks displays were held on the July 4 holiday itself. Nationwide on Independence Day, there has been an average increase in 24-hr PM$_{2.5}$ mass concentration by 42% ($17 \mu$g m$^{-3}$ vs. $12 \mu$g m$^{-3}$) across the U.S. in comparison to the adjacent days based on data of 315 sites over US from 1999 to 2013$^9$. This indicates the importance of studying the fine PM emission from the FW displays that are a feature of Independence Day celebrations.

Previous studies of FW fine PM include filter-based methods to analyze the particle composition mass concentration$^6,8$, as well as bulk particle size distribution characteristics$^{16}$. The long integration time for collection of filter samples (12 hours or 24 hours) loses the real-time information (temporal evolution as well as composition and size distribution) of FW aerosol, and creates uncertainties in accurately quantifying these parameters$^7$. The chemical composition and size distribution of particles, as measured by more advanced aerosol mass spectrometry technology$^{17-21}$, provide new perspectives on FW PM characteristics$^1,7$. Firework particle emissions have been shown to have high potassium and organic mass concentrations$^7$. Potassium comes from the black powder used as a propellant, and the organics are likely influenced by oxidized materials originally present as binding agents or from the shell linings.

The high mass concentration and complex emission sources of background aerosols in megacities, such as Beijing$^7$, will to some extent mask information about the contribution of FW to ambient aerosol, and in particular any distinct features of the organic aerosol species directly emitted from
FW burning. Albany, the capital of New York State (a city with a population of approximately 100,000, about 240 km north of New York City), features relatively clean air (PM mass concentration generally below 15 μg m⁻³). Albany hosted a large FW display for the Independence Day holiday, which lasted for approximately half hour from 21:00 to 21:30 local time (EDT: Eastern Daylight Time) on July 4, 2017. This FW display detonated about 10,000 shells, or about 2,000-10,000 kg for the fireworks compounds (www.skylighter.com). This event, accompanied by the favorable meteorological conditions described below, provided an opportunity for a detailed investigation of the contribution of FW displays to the ambient aerosol mass concentration and chemical content from this intense, but episodic source of aerosols.

3.3.2 Experimental Section

3.3.2.1 Measurement site and sampling instruments

The primary (“uptown”) measurement site is located at the Atmospheric Sciences Research Center (latitude: 42.7 °N, longitude: 73.8 °W, elevation: 81 m above sea level, hereafter ASRC site, as shown in Fig. 3.3.S1), near the main campus of the University at Albany, which is located in uptown (Northwest) Albany, and near the intersection of interstate highways I-90 and I-87. The uptown site is about 8 km away from the Albany FW launch site (at the Empire State Plaza, Fig. 3.3.S1). The measurements of aerosol concentrations were conducted from June 27 00:00 local time (EDT) to July 7 12:00, except the period from July 1 00:00 to July 2 20:00. During this period, the aerosol dryer failed, and this failure to dry the aerosol caused the HR-ToF-AMS to work abnormally. The measurement period covered the Independence Day holiday, during which the Albany FW event occurred. A second (“downtown”) measurement site is located at the Albany County Health Department (latitude: 42.63 °N, longitude: 73.75 °W, elevation: 8 m above sea level,
hereafter ACHD site, also shown in Fig. 3.3.S1), only about 1 km southeast of the Empire State Plaza where fireworks were launched.

The key instrument at ASRC site is an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS), which was used to measure non-refractory (NR) submicron aerosol (NR-PM$_1$) chemical composition (including organics, nitrate, sulfate, ammonium, and chloride), and the mass size distributions of selected aerosol chemical species$^{18,23}$. This HR-ToF-AMS was operated in the sensitive “V-mode” and cycled through the mass spectrum (MS) mode and the particle-of-flight mode (PToF) every minute. A TSI Scanning Mobility Particle Sizer (SMPS) was used to measure particle number size distributions. Total PM$_{2.5}$ mass concentration was also obtained from an optical scattering based aerosol mass measurement instrument (PDR-1500, Thermo Fisher Scientific Inc.), which measures the scattered light flux and uses this signal to estimate the aerosol mass concentrations. Detailed information about the instrument setup and sampling is shown in Supplement (S1). Also, at the ASRC site, a Leosphere Windcube 100S scanning LiDAR (hereafter LiDAR) was operated from the roof. The LiDAR provided high resolution (25 m range gates) vertical wind and backscatter profiles starting at 50 m above the instrument. At the ACHD site roof (about 6m above ground level), a Teledyne API Model T640 PM mass monitor (hereafter ACHD T640) was used to provide the mass concentration of PM$_{2.5}$, and black carbon (BC) was measured by a Teledyne API Aethalometer (Model 633).

3.3.2.2 Meteorological parameters

Surface meteorological data was obtained from the Voorheesville New York State Mesonet station (NYSM, latitude: 42.65 °N, longitude: 73.92 °N, elevation: 100 m), located approximately 8 km southwest of the ASRC site. The Mesonet site provides meteorological data in 5-minute intervals
and includes temperature (at 2 m and 9 m), relative humidity, complementary measurements of wind direction and wind speed, and irradiance.

### 3.3.2.3 Data analysis methods

The HR-ToF-AMS data was analyzed using the SQUIRREL v1.59D and PIKA v1.19\textsuperscript{24,25} data analysis software to obtain the mass concentrations of different aerosol components: organics, nitrate (NO\textsubscript{3}\textsuperscript{-}, hereafter NO\textsubscript{3}), sulfate (SO\textsubscript{4}\textsuperscript{2-}, hereafter SO\textsubscript{4}), ammonium (NH\textsubscript{4}\textsuperscript{+}, hereafter NH\textsubscript{4}), chloride (Cl\textsuperscript{-}, hereafter Cl), and their size distributions. The default relative ionization efficiency (RIE) values were used in the analysis\textsuperscript{26,27} (4 for NH\textsubscript{4}, 1.1 for NO\textsubscript{3}, 1.2 for SO\textsubscript{4}, 1.3 for Cl, and 1.4 for organics). A collection efficiency (CE) of 0.5 was used as suggested in previous studies\textsuperscript{26}, except for potassium (K\textsuperscript{+}, hereafter K), SO\textsubscript{4}, NO\textsubscript{3} and Cl during the period affected by the FW events, as described below and supported by the comparison with a Scanning Mobility Particle Spectrometer (SMPS) as shown in the Supplement (S2 and S3). The elemental analysis (oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratio) was performed following the improved method proposed by Canagaratna et al.\textsuperscript{28}

The slow vaporization of potassium salts (Fig. 3.3.S2), especially K\textsubscript{2}SO\textsubscript{4}, and the surface ionization of K make the quantification of K mass concentrations challenging and prone to large uncertainties, and potassium signals are often ignored when reporting ambient measurements with most AMS instruments\textsuperscript{1,7,29,30}. However, during FW events, K signals generally increase dramatically\textsuperscript{1,7} due to the K-rich salts used in FW materials, providing a good opportunity to quantify K concentrations. To quantify the mass spectral signals and obtain the mass concentration of K, a laboratory determined RIE for K (RIE\textsubscript{K}: 58) was obtained based on pure K\textsubscript{2}SO\textsubscript{4} calibrations (as shown in S3). This significantly higher ionization efficiency, as compared to former studies
(10 for Slowik et al.\textsuperscript{29}, 2.9 for Drewnick et al.\textsuperscript{1}), confirms the need to calibrate RIE\textsubscript{k} for individual instruments under controlled measurement conditions. Because the aerosol was almost entirely freshly emitted, and the FW inorganic aerosol was mainly present as K\textsubscript{2}SO\textsubscript{4}, a CE of 0.15 was used for K and SO\textsubscript{4} during the FW influence period based on the laboratory calibration described in S3. As shown below, the inorganic K salts were internally mixed in the aerosol, so a CE of 0.15 was also used for the other anion compounds produced by the FW events, namely NO\textsubscript{3} and Cl. The CE for organics was set to be the default value of 0.5, rather than 0.15, based on the externally mixed properties of the FW aerosol, as shown in Section 3.1. The resulting maximum for K hourly-averaged mass concentration was 17.5 μg m\textsuperscript{–3}, with a K mass fraction of about 30%, which was roughly equal to the result of Drewnick et al.\textsuperscript{1} At the same time, a strong correlation (r\textsuperscript{2}=0.98) with a slope of 1.14 (Fig. 3.3.S5a) between the HR-ToF-AMS+BC mass concentration and SMPS measured mass concentration verified that the calibrated values of RIE\textsubscript{k} and CE for K and SO\textsubscript{4} during fireworks events were appropriate for our HR-ToF-AMS instrument and measurement conditions. It should be noted that the difference of 14% would be increased to be about 19% after considering the aerosol shape factor (Supplement 3.3.S3), and the 19% provides a lower limit to the estimate of uncertainty for these measurements, including the study specific RIE and CEs as well as the usual sources of uncertainty for the AMS.

Given that the aerosol is charge-balanced, and that the ionic species can be identified from the mass spectra\textsuperscript{31}, the mass concentrations of the predominant inorganic salts can be estimated using ion-balance considerations. NH\textsubscript{4} is apportioned first into (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} and then into NH\textsubscript{4}NO\textsubscript{3}, based on the ratio of SO\textsubscript{4} to NO\textsubscript{3} during the non-FW influenced periods. Cl is not apportioned in this way due to its very low concentration before the FW event. The residual SO\textsubscript{4} (calculated by subtracting SO\textsubscript{4}-in-(NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4} from total SO\textsubscript{4}), residual NO\textsubscript{3}, and all Cl are used to balance the measured K
to form K$_2$SO$_4$, KNO$_3$, and KCl. The strong correlation ($r^2 = 0.97$), with a slope of 0.88, between the concentration of K required to attain charge balance and the concentration of K measured by the HR-ToF-AMS supports the hypothesis that K$_2$SO$_4$, KNO$_3$, and KCl are the main K-rich salts measured by HR-ToF-AMS (shown in Fig. 3.3.S5b).

The HR-ToF-AMS organics mass spectra were analysed using positive matrix factorization (PMF) to resolve different organic aerosol factors, and the solutions were evaluated using the PMF Evaluation Tool (PET, v2.08D)$^{32}$. In this study, the PMF analysis was only applied to the period without the FW significantly influence (07/04 23:00-07/05 03:00, defined in Section 3.1) to avoid the rotational ambiguity (or mixing of factors) in the PMF solution when including the episodic firework event. The PMF analysis which excluded the FW significantly influenced period identified four factors based on the evaluation of spectral profiles, diurnal variation, and correlations with external tracers$^{33}$ (Supplement 3.3.S4 and Fig. 3.3.S6, 3.3.S7). Then a linear variation for the four factors during the FW influenced period is assumed, and difference between the HR-ToF-AMS measured organics and the sum of the four factors during the FW significantly influenced period was used to be the contribution of FW (Fig. 3.3.S8). At the same time, the difference spectra between the average organic mass spectrum during the FW significantly influenced period and the immediately preceding period (averaged for 2 hours) was calculated to be the mass spectra of the organic aerosol from FW.

3.3.3 Results and discussion

The time series of aerosol hourly-averaged mass concentrations measured by instruments at both sites exhibited very similar behavior during the measurement period (Fig. 3.3.S9a). During the night of July 4 and extending into the early morning of July 5, the wind speed was low (generally
< 2.0 m s\(^{-1}\)) and wind direction variable (Fig. 3.3.9b), conditions that resulted in slow advection and diffusion of the FW aerosol plume. The maximum recorded hourly-averaged concentrations were 55 µg m\(^{-3}\) for the ACHD plume (T640 PM\(_{2.5}\) data) and 61.8 µg m\(^{-3}\) for the ASRC plume (HR-ToF-AMS NR-PM\(_{1}\)), rapidly increasing by more than a factor of 8 over the baseline aerosol mass loading prior to the FW significantly influenced period. A time difference of about two hours between the peak hours of the ACHD T640 data (at about 07/04 22:00) and ASRC instruments (at about 07/05 00:00) was observed (Fig. 3.3.9a). Taken as the transport time of aerosol from the launch site downtown to the ASRC measurement site, this indicates an advection velocity of about 1 m s\(^{-1}\). Excluding the peaks during the night of July 4 (the FW influenced period), the high coefficient of determination (\(r^2=0.72\)) between ACHD T640 PM\(_{2.5}\) and ASRC (HR-ToF-AMS NR-PM\(_{1}\)) suggests generally similar conditions, typical of regional aerosol pollution during normal non-FW influenced periods.

### 3.3.3.1 Identification of firework events and aerosol composition

The PM event on the night of July 4 was identified as a significant FW influenced event based on the prominent potassium signal peak in Fig. 3.3.1, as well as enhanced signal for Rb\(^8\) (shown in Fig. 3.3.S10). Enhanced signals for most other common metals used in fireworks, such as Na, Se, and Cu, were not observed. As shown in Fig. 3.3.1a and Fig. 3.3.S10b, the highest K and Rb concentrations occurred on the night of July 4. The observed concentrations of K were as high as 17.4 µg m\(^{-3}\) (July 5 00:00 EDT), which is about 350 times the background value (0.05 µg m\(^{-3}\), averaged July 4 09:00 to 17:00 EDT). Elevated K signals were present until about 09:00 EDT the following morning. Based on the time variation of K, we define the Independence Day FW significantly influenced period at the ASRC site as July 4 23:00 to July 5 03:00 EDT (hereafter FW significantly influenced period). Apart from the prominent peak on the 4\(^{th}\), there were also
some peaks of K during the nights of July 2 and July 3, evenings during which nearby smaller towns also had fireworks displays.

Figure 3.3.1. The time series of 1 h (a) mass concentrations of aerosol components (Organic, NO$_3$, NH$_4$, Cl, K, and SO$_4$) from AMS; and (b) mass fraction of each component from 06/27/2017 to 07/07/2017.

During the FW significantly influenced period, the averaged mass concentrations of total aerosol, organics, K, SO$_4$, NO$_3$, and Cl were all clearly elevated compared to earlier that day (July 4 9:00 to 17:00 EDT), increasing by factors of 6.5 (total), 2.7 (organics), 248 (K), 21 (SO$_4$), 20 (NO$_3$), and 280 (Cl) respectively, as shown in Fig. 3.3.2. These enhancements, as well as the mass fractions of each component of the FW aerosol, were similar to the measurements of FW aerosols in Germany$^1$, implying that similar kinds of FW aerosols were observed in these two studies. The observed FW influenced event had only minor effects on NH$_4$ (as shown in Fig. 3.3.1 and 3.3.2), due to either a lack of NH$_4$-containing material in the fireworks or their oxidation during the fireworks burning process. The insignificant increase in ammonium is also consistent with the hypothesis that the increased SO$_4$ and NO$_3$ originated from K-rich salts instead of (NH$_4$)$_2$SO$_4$ and
NH₄NO₃.

**Figure 3.3.2.** Components of the NR-PM₁ measured by HR-ToF-AMS during FW event (a), during July 4 daytime (b), before July 1 (c) and after July 5 (d) (The compounds with mass fractions lower than 1% were ignored) (unit: ug m⁻³).

For the time periods less affected by FW (before July 1 00:00 and after July 5 12:00 EDT), the mass fractions of the HR-ToF-AMS chemical components were fairly stable, with organic compounds constituting the major fraction of NR-PM₁ (at 79%) before July 1 and 87% after July 5 on average, followed by SO₄ (13% and 7% before July 1 and after July 5, respectively, Fig. 3.3.1b and Fig. 3.3.2). During the FW influenced periods, and especially during the Independence Day FW significantly influenced period, the mass of individual aerosol components clearly increased (including organics), but the average organic mass fraction decreased to 36% and SO₄ mass fraction increased to 27% during the four-hour FW significantly influenced period (Fig. 3.3.2).
3.3.2), highlighting the influence of FW burning on the aerosol chemical composition. The most prominent indicator of FW aerosol, K, displayed large increases during the FW significantly influenced period, contributing roughly 26% to the ambient aerosol during the same time period.

![Graph showing mass size distribution](image)

**Figure 3.3.3.** HR-ToF-AMS measured mass size distribution (vacuum aerodynamic diameter: $D_{va}$) for SO$_4$, NO$_3$, organics and K compounds during the FW significantly influenced period (July 4 23:00 to July 5 03:00) and during July 4 daytime (09:00 to 17:00). (note: the mass concentrations have been normalized to their respective highest value, and the NO$_3$ distribution for July 4 daytime is not shown due to very low signal-to-noise in the size distribution at such low mass concentration).

Examining particle number size distributions, most of Independence Day FW PM$_1$ aerosols measured at ASRC were in the size range of 50 to 250 nm ($D_m$: electrical mobility diameter, Fig. 3.3.S11a), with FW PM$_1$ mass size distribution from the SMPS showing the largest mass contribution from particles in the range of 200 to 500 nm (Fig. 3.3.S11b). The FW-averaged mass size distributions of NR-PM$_1$ aerosol chemical components (Fig. 3.3.3) show externally mixed characteristics, with NO$_3$ and SO$_4$ masses peaking at 550-600 nm ($D_{va}$: vacuum aerodynamic diameter), and organics peaking at ~370 nm ($D_{va}$). The size distribution of K is not presented here.
due to its artificially broadened size distribution caused by the surface ionization of K, or the attachment of K to the ionizer walls followed by its slow removal\textsuperscript{30}. Different mode diameters for the different chemical components indicate a non-uniform mixing state for organics and inorganics, suggesting different sources of freshly emitted aerosols associated with FW displays. As discussed above, the majority of the \(\text{SO}_4\) and \(\text{NO}_3\) were from K-rich inorganic salts, such as \(\text{K}_2\text{SO}_4\) or \(\text{KNO}_3\), and the organics are from burning of carbonaceous materials or reactions with the FW oxidizer, which will be discussed in the next section. In addition to the peaks in the mass distributions on about 07/05 00:00, there were several peaks in the number distribution at smaller sizes (mode diameter of 30-40nm, Fig. 3.3.S11a), likely associated with freshly emitted traffic aerosol emissions from nearby roads or highways.

### 3.3.3.2 Source apportionment

#### 3.3.3.2.1 PMF results

Based on the evaluation of mass spectral profiles, diurnal variation, and correlations with external tracers, four organic aerosol (OA) components are identified, including hydrocarbon-like OA (HOA), a cooking OA (COA), a less oxidized oxygenated OA (LO-OOA), and one more oxidized oxygenated OA (MO-OOAs) (Fig. 3.3.S6 and Fig. 3.3.S7). HOA and COA are the two smallest contributors to OA in this dataset. The HOA is characterized by hydrocarbon-like ions (\(\text{C}_x\text{H}_y^+\) family), with evident morning and evening rush hour peaks (Fig. 3.3.S6d). The COA is characterized by prominent signal at m/z 41 (\(\text{C}_3\text{H}_5^+\)) and m/z 55 (\(\text{C}_4\text{H}_7^+\))\textsuperscript{34,35}, with increasing concentrations during evening hours (Fig. 3.3.S6d). The HOA and COA shows similar mass spectra in unit mass resolution data, matching the previous studies, and implies a mixing between these two\textsuperscript{35,36}. Based on this, the two components (HOA and COA) was considered together (namely HOA+COA). The sum of HOA and COA measured at ASRC site had similar time
variation as the BC data from ACHD (Fig. 3.3.S7a), with a moderate $r^2$ (0.38) between ASRC HOA+COA and the ACHD BC (excluding the FW significantly influenced period). The LO-OOA spectral profile is characterized by an O:C ratio of roughly 0.6, and a high $f_{43}/f_{44}$ ratio of ~1. LO-OOA also exhibited local maxima during early morning and mid-afternoon, and it was moderately correlated with concurrent NO$_3$ before July 1 00:00 EDT, with an $R^2 = 0.48$ (Fig. S7b), giving some indication of the local source characteristics of LO-OOA$^{21,37-39}$. The MO-OOA shows a more traditional spectral character comparable to those seen in earlier studies$^{21,40}$. It has a high O:C ratio (0.84), a low $f_{43}/f_{44}$ ratio (0.25), and a high coefficient of determination ($r^2=0.86$) with concurrent SO$_4$ before July 1 00:00 EDT (Fig. 3.3.S7c). This is thought to be related to highly oxidized secondary organic aerosol$^{21}$. In this study, LO-OOA showed a high coefficient of determination ($r^2=0.94$) with MO-OOA before 07/01 00:00 (Fig. 3.3.S7d), indicating that the bulk of the MO-OOA was likely produced regionally through oxidation of LO-OOA during the measurement period, instead of being carried in via long-distance transport. In calculating the correlation coefficients here, we only considered the time period before 07/01 00:00, to exclude the impact of FW on the individual organic, SO$_4$ and NO$_3$ trends.

The mass spectra of the MO-OOA and FW-OOA factors were very similar in this study, as shown in Fig. 3.3.4a and Fig. 3.3.S6b. In comparison to MO-OOA, FW-OOA contains higher relative signals at m/z 29 (CHO$^+$: 0.05 vs. 0.03), m/z 41 (C$_2$HO$^+$: 0.05 vs. 0.01), m/z 60 (C$_2$H$_4$O$_2^+$: 0.007 vs. 0.002) and m/z 73 (C$_3$H$_5$O$_2^+$: 0.004 vs. 0.002), and lower signals at m/z 28 (CO$^+$: 0.16 vs. 0.19), m/z 43 (C$_2$H$_3$O$^+$: 0.03 vs. 0.05) and m/z 44 (CO$_2^+$: 0.16 vs. 0.19), as shown in Fig. 3.3.4b. These enhancements are used to identify a unique organic aerosol factor that we have termed FW-OOA, which appears to be directly associated with FW burning. The FW-OOA contribution was ~40% (6.7 μg m$^{-3}$) of the organic aerosol (16.9 μg m$^{-3}$) during the Independence Day FW significantly
influenced period. Similar mass spectra of the FW-OOA to MO-OOA factors indicates that FW-OOA was highly oxidized or secondary in nature\textsuperscript{1,7}, having been rapidly oxidized in the high temperatures of FW burning. At the same time, the higher m/z 60 and 73 signals imply that FW-OOA was also likely mixed with the aerosol produced by the burning of binding agents, such as dextrin, or the shell paper.

**Figure 3.3.4.** (a) The mass spectra of FW-OOA based on the differences between the average organic mass spectrum during the FW significantly influenced period and the immediately preceding period (averaged for 2 hours); (b) Differences in the mass spectra of the FW-OOA and MO-OOA factors.

### 3.3.3.2.2 Mass closure and source apportionment for the FW significantly influenced period

Figure 3.3.5 shows the time series of each inorganic salt from HR-ToF-AMS measurements further speciated by the ion balance calculation, and the different OA components from PMF analysis. Here, OOA is the sum of MO-OOA and LO-OOA. Little variability in concentration is observed for OOA, (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}, and NH\textsubscript{4}NO\textsubscript{3} from July 4 12:00 to the end of the study period, indicating that these species comprised the local background concentration, which contributed about 13\% of total PM during the FW significantly influenced period (July 4 23:00 - July 5 03:00). COA+HOA exhibited elevated concentrations from the night of July 4 to early morning of July 5, likely related
to traffic emissions, and cooking, a result that is supported by the large numbers of smaller particles emitted before and after the FW displays (Fig. 3.3.11a), and contributed a relatively small amount, about 10% of the total PM. The biggest contribution came from FW burning, as inorganic K-containing compounds and FW-OOA comprised 77% of the total (36.3 μg m⁻³ of 47.0 μg m⁻³), and among them, inorganic K-containing species contributed 63% and FW-OOA another 14%.

![Graph](image)

**Figure 3.3.5.** The time series of 1 h mass concentration of inorganic salt and organic compounds estimated based on the PMF and ion-balance calculations from 06/27/2017 to 07/07/2017.

Assuming a point source dispersion for FW aerosol, and combining the estimated advection/dispersion speed of 1 m s⁻¹, the emission strength of the FW aerosol can be roughly estimated as about 70 kg h⁻¹ (see Supplement S5). According to the EPA air emission inventories (www.epa.gov/air-emissions-inventories), the annual PM₂.₅ emissions from highway traffic was about 4×10⁶ kg for all of New York State in 2017, with about 5×10⁴ kg for the Albany area (a simple estimation using the ratio of Albany area highway length to the state total: 35km vs. 2692km), which in turn results in an estimate of the daily PM₂.₅ emission from Albany area highways of about 140 kg (or 6 kg emitted in a typical hour). Based on these values, the FW aerosol
emission from this Albany Independence Day FW display is more than ten times greater than the
typical hourly rate of vehicular emissions in the Albany area, signifying the importance of intense
episodic emissions from FW displays. Health impacts are likely amplified given that the FW plume
occurs at a time when many more people than usual are exposed to the outdoor air, and FW take
place at night when the boundary layer tends to be much more stable (resulting in higher particulate
concentrations at the surface and longer dissipation times).

3.3.3.3 Pollution processing and meteorological conditions

**Figure 3.3.6.** The time series of 10-mins averaged LiDAR data on Independence Day from July 4
20:00 to July 5 12:00 EDT

The wind LiDAR on the roof of the ASRC uptown site measures the backscatter strength as the
carrier-to-noise ratio (CNR), and also estimates the components of the wind (hence wind speed
and wind direction), and these data are used to describe the aerosol transport and mixing process\(^1\).
The LiDAR CNR is taken to be linearly proportional to aerosol backscatter\(^1\), with larger CNR
corresponding to higher aerosol backscatter, indicating a larger aerosol mass concentration. The
LiDAR data for the Independence Day FW event is shown in Fig. 3.3.6. During the late evening on Independence Day (July 4 21:00 - 23:00 EDT), the wind in the lower levels of the atmosphere (below 500m) was weak and variable, mainly due to the dominant high pressure over New York State, as shown in Fig. 3.3.S12. At July 4 23:00, there was a relatively short maximum of CNR at about 400 meters above ground level, accompanied by weak easterly winds at levels between 200-500m. However, the winds at even lower levels (below 200m) were still variable with lower CNR. One reasonable explanation for this phenomenon is that weak easterly winds slowly advected the higher level FW aerosol plume (at levels corresponding to high altitude bursting fireworks), while the FW aerosol plume in lower levels (below 200m and caused by low bursting shells) mainly diffused to the west at even slower speeds. High CNR values at the lowest measurement levels occurred above the ASRC sampling site on July 4 23:20, coincident with the increases in aerosol mass concentrations measured by the ASRC instruments. This aerosol plume had a thickness of about 200m and enveloped the ASRC site for hours. After about an hour, the winds above 100m became stronger, which appears to have divided the plume into two layers. The higher layer became elevated with time, finally diverging from the lower layer aerosol after July 5 01:30. The CNR of the lower layer aerosol decayed after July 5 03:00, and began to rise in altitude as well, which coincided with the reduced aerosol mass concentration measured at the ASRC site. At about July 5 06:30, the elevated aerosol layer mixed down to create another increase in CNR and aerosol concentration (July 5 07:00 to 10:00, as shown in Fig. 3.3.5), which is consistent with the increase in convective mixing before sunrise. The organic aerosol mass spectrum of the second peak time period (July 5 07:00-08:00) showed higher signals at m/z 28 (CO⁺) and m/z 44 (CO₂⁺) than the previous hour (July 5 05:00-06:00) as shown in Fig. S13, implying more oxidized organics in the higher layer plume. The aerosol size distribution from this later detected “higher layer plume”
shows a greater spread (larger FWHM) than the FW displays aerosol, with a mode diameter (~270nm) between that of the FW event aerosol (~300nm) and the 07/04 daytime average (~250nm) (Fig. 3.3.S14). After July 5 09:00, the aerosol layer was again elevated, due to the increasing planetary boundary layer height, and instruments at ASRC site recorded reductions in aerosol mass concentration. The firework emissions, which occurred in an environment with a nearly stable nocturnal boundary layer, resulted in high aerosol mass concentrations over the Albany area for several hours, lasting through the night.

### 3.3.4 Conclusion

This study provides a comprehensive study of the influence of aerosol particles from fireworks (FW) displays on the air quality of Albany, NY region using a High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and collocated instruments during the 2017 Independence Day holiday. The strongly elevated potassium (K) signal in the HR-ToF-AMS mass spectra during the FW periods indicated K-rich materials in the FW aerosol plumes mostly associated with K$_2$SO$_4$. Quantifying the K mass concentration was challenging due to the surface ionization and the slow vaporization of the potassium salt, and required careful lab calibration, especially the AMS heater bias voltage setting (as detailed in the supplemental materials). The lab calibration process and ambient aerosol K mass spectra signal in this study provide useful information for further K measurements using similar instruments. In addition, An FW-related oxidized organic aerosol factor (FW-OOA) was identified during the most intense FW event of the measurement period. The sum of the potassium salts and FW-OOA revealed that 77% of the aerosol mass within the FW plume was associated with FW emissions. Estimated FW aerosol emission strength during this event were at least 70 kg h$^{-1}$, more than 10 times higher than the expected hourly vehicular emissions rate in the Albany area, highlighting the importance of this
intense episodic source of aerosols. Pollution from FW events may be more severe and harmful to nearby area residents in communities with larger FW displays under comparatively calm atmospheric conditions, which are usually when these FW events occur, as rain or high winds will typically result in a postponement of the FW displays. Additional studies including field measurements in other regions with more comprehensive measurements, air quality simulations and human health studies, are warranted, to provide clear guidance on FW aerosol pollution for other U.S. and foreign cities.

ACKNOWLEDGMENTS

This work has been supported by the New York State Energy Research and Development Authority (NYSERDA) contract number 48971. Special thanks go to New York State Department of Health for providing data from the ACHD site.
3.3.5 References


3.3.6 Supplement

Figure 3.3.S1. Locations of measurement sites (from Google maps)

ASRC: Atmospheric Sciences Research Center, University at Albany – the uptown site; ACHD: Albany County Health Department – downtown measurement site; Empire State Plaza: the fireworks burning location.
3.3.S1 Instrument setup and sampling information (ASRC site)

These aerosol measurement instruments were located in a second floor lab and sampled from a common silica gel diffusion dryer (output RH < 37%), which was downstream from a PM2.5 cyclone and a ~9 m long sample duct with 10 cm inner diameter. The sample inlet is about 2 meters above the roof of Center for Environmental Sciences and Technology Management building (about 15 m above ground level). A supplemental airflow was continually drawn through the sample inlet, and aerosols were drawn from the centerline of this sample duct. After the sample duct, roughly 0.5 m of black conductive tubing (4.5mm ID) was used to connect the duct with the dryer. After the dryer the flow was split three ways, connecting the SMPS, the HR-TOF-AMS and the PDR each with 0.3 m long, 4.5 mm ID sampling lines, which resulted in an estimated particle loss of less than 2% (www.mpch-mainz.mpg.de/~drewnick/PLC/).
3.3.S2 High background values of K and SO$_4$ for HR-ToF-AMS chopper closed periods during the FW influenced period

Figure 3.3.S2. High-resolution mass spectra from the HR-ToF-AMS (Top: the mass spectra during chopper open mode; Middle: the mass spectra during chopper closed mode; Bottom: the difference between open and closed periods). (a) The m/z 39 ($^{39}$K$^+$) ion peak at July 5 00:30; (b) the m/z 48 (SO$^+$) ion peak at July 5 00:30. (Black markers indicate the measured data, orange lines are Gaussian fitting lines for each ion, blue lines are the Gaussian fitting lines for the whole signal, gray vertical lines indicate the location of each ion, and different color vertical lines indicate the fitting height for each ion)

During the FW event period, the background value (chopper closed) of SO (the dominant ion fragment from SO$_4$) increased to about 10% of the value with the chopper open, which is caused by the slow vaporization of K$_2$SO$_4$, which is common for refractory species.$^2$ However, the background value of $^{39}$K$^+$ was almost equal to the chopper open value, which is caused by the surface ionization of K, or the attachment of K to the ionizer walls followed by its slow removal.$^3$ As a result of this process there were not valid size distribution measurements for K. Since SO$_4$ does not suffer from interaction with the ionizer, its signal can be used to derive valid size distributions, as shown in Section 3.1 of the manuscript.
3.3.S3 Estimation of K and SO$_4$ mass concentrations during the FW influenced period

The CE for both K and SO$_4$ was determined using pure K$_2$SO$_4$ aerosols, produced from an aqueous solution by a TSI atomizer (Model 3076) and dried within a diffusion dryer to an average of 37% relative humidity, by comparing the AMS sulfate signal with the sulfate mass concentration determined by the SMPS. Designating the sulfate mass concentration derived from the SMPS measurements as C$_{SO4}$(SMPS) and the sulfate mass concentration derived from the AMS measurements (assuming a CE of 1) as C$_{SO4}$(AMS, CE=1), the actual CE for SO$_4$ (and also for K) is obtained from the ratio of C$_{SO4}$(AMS, CE=1) to C$_{SO4}$(SMPS), which yielded a CE of 0.15 for the pure K$_2$SO$_4$ used in this calibration. This CE was only used during the FW affected periods (07/02 21:00-07/03 04:00, 07/03 21:00-07/04 01:00, 07/04 21:00 to 07/05 08:00), periods during which the HR-ToF-AMS K raw signal was significantly elevated, to determine K, SO$_4$, NO$_3$ and Cl mass concentrations. Otherwise, the nominal CE of 0.5 was used. We then derived RIE$_K$ in a similar manner based on the K$_2$SO$_4$ calibrations. K mass concentrations were derived from the SMPS measurements (C$_K$(SMPS)), and calculations for C$_K$(AMS, RIE=1) were derived from the AMS measurements using the calibrated CE of 0.15. The ratio of C$_K$(AMS, RIE=1) to C$_K$(SMPS) yielded a value of 58, which corresponds to an RIE of K for pure K$_2$SO$_4$ aerosol, as shown in the following equations based on the fundamental AMS mass concentration equation$^4$.

$$\begin{align*}
C_K(\text{AMS}) &= \frac{1}{C_{E_K}} \times \frac{1}{\text{RIE}_K} \times \frac{\text{MW}_{\text{NO}_3}}{\text{IE}_{\text{NO}_3}} \times \frac{10^{12}}{Q \times N_A} \times I_K \quad (1) \\
C_K(\text{AMS}) &= C_K(\text{SMPS}) \quad (2)
\end{align*}$$

$$\text{RIE}_K = \left( \frac{1}{C_{E_K}} \times \frac{\text{MW}_{\text{NO}_3}}{\text{IE}_{\text{NO}_3}} \times \frac{10^{12}}{Q \times N_A} \times I_K \right) \div C_K(\text{SMPS}) \quad (3)$$

Where RIE$_K$ is the RIE of K, CE$_K$ is the CE for K (0.15), MW$_{\text{NO}_3}$ (62 g mol$^{-1}$) is the molecular weight of nitrate, IE$_{\text{NO}_3}$ (number of ions detected per molecule vaporized) is the ionization
efficiency for nitrate, $10^{12}$ is used for unit conversion, $Q$ is the flow rate, $N_A$ is Avogadro’s number, and $I_K$ is the ion count rate for K. Here K is sum of $^{39}\text{K}^+$ and $^{41}\text{K}^+$. In this equation, $I_{\text{NO}_3}$, $Q$, and $I_K$ were obtained from the HR-ToF-AMS software, $C_{E_K}$ was set to 0.15, and we assumed that $C_K$ (AMS) was equal to the K mass concentration determined from SMPS measurements of the $\text{K}_2\text{SO}_4$ aerosol.

The $R_{E_K}$ determined using this method was 58, an unusually high value. A value this high can only occur if the surface ionization of potassium adds significantly to the electron impact ionization efficiency. This does seem to be the case, as the potassium and sulfate mass concentrations determined with the laboratory determined values for CE (0.15) and $R_{E_K}$ (58) give consistent results with other instruments, as shown below. Based on the $R_{E_K}$ (58) and CE (0.15), the maximum mass concentrations of K and SO$_4$ during the FW significantly period on 7/4-5 were 17.5 µg m$^{-3}$ and 18.5 µg m$^{-3}$, respectively, which yields a K/S mass ratio of 2.8, within 2% of the expected K/S value of 2.75 for fireworks. Identical settings for all HR-ToF-AMS adjustable voltages were used for the laboratory calibration and the FW period measurements, especially the heater bias voltage (30V was used in calibration as well as the ambient measurements). This voltage is particularly important because the heater bias voltage is directly related to the K surface ionization process and improper settings will cause distortion of the $^{39}\text{K}^+$ peak in the mass spectra (Fig.S3). Taking this into account, when using an HR-ToF-AMS for future FW aerosol measurements, the heater bias voltage should be carefully set based on a pure $\text{K}_2\text{SO}_4$ calibration and checked during FW aerosol measurement periods to make sure the $^{39}\text{K}^+$ peak (chopper open) shows a “normal” shape like shown in Fig.S3b and Fig. S2a rather than the distorted shape illustrated in Fig. S3a.
Figure 3.3.S3. High-resolution mass spectra of the measurements of HR-ToF-AMS for K under different heater bias voltage settings during lab calibrations with K₂SO₄ (Top: the mass spectra from chopper open periods; Middle: the mass spectra from chopper closed periods; Bottom: the difference mass spectra between the above two). (a) heater bias voltage set to 31 V; (b) heater bias voltage set to 30 V. (Black markers indicate the measured data and blue lines are the Gaussian fitting lines)

Figures S4a and S4b show the “Diff³⁹K⁺ signal” (open-closed) signals of July 4 2017 at noon and July 4 23:00. From the noon period to the FW period the signal increased by a factor of 80 (Fig. S4a vs. Fig. S4b), implying a significant influence from this FW display. However, the signal of “Diff³⁹K⁺⁺” on the high-resolution mass spectra grew in magnitude and lost its Gaussian peak shape after July 5 00:30, and showed a “collapse” at the peak location as shown in Fig. S4c, which was clearly related to the very high levels of potassium in the AMS heater and ionizer regions, also illustrated in Fig. S4c, and S4d. Due to the accumulation of K on the vaporizer and the complicated dynamics which included surface ionization, the apparent mass concentration observed for K for chopper open and closed periods increased rapidly after 07/05 00:00 and kept a constant high value
from 07/05 00:30 to about 02:30, and the highest open-close values occurred between 07/05 00:00 to 00:30. Under these conditions, directly fitting the “Diff $^{39}K^+$ signal” with a Gaussian function was unsuccessful. In addition, the method of fitting the closed and open high resolution spectra separately and subtracting the closed value from the open value was also problematic, as shown in Fig. S4e. Fig. S4e shows the isotope ratio of $^{41}K^+$ to $^{39}K^+$ for chopper open and closed was quite reasonable for non-FW influenced period (about 0.072), but rapidly increased after 07/05 00:00 until about 02:30. This failure to properly track the well-determined isotope ratio makes it clear that the values determined for $^{39}K^+$ from open and closed mass spectra fitting were not correct during this period. We hypothesize that the problem with mass concentrations determined using m/z of 39 for potassium during this period was caused by mass spectra saturation of $^{39}K^+$ signal due to sudden large quantities of K salts input into HR-ToF-AMS. For this case, the fragment table of the SQUIRREL software was modified to fit $^{41}K$ by itself instead of including $^{39}K$ as it normally would. Under these conditions, the peak for the “Diff $^{41}K^+$ isotope” was checked, and did show a reasonable Gaussian distribution (Fig. S4f), and could be fitted by the default Gaussian function. Based on this, the mass concentration of isotopic $^{41}K^+$, calculated based on the RIE = 58, CE=0.15 and the isotopic ratio of 0.0722, was used to estimate the mass concentration of $^{39}K^+$. The summed concentrations of $^{41}K^+$ and $^{39}K^+$ were taken to be the K mass concentration in this study.
Figure 3.3.S4. High-resolution mass spectra of the measurements of AMS (mass spectra from chopper open minus chopper closed). (a) the m/z 39 (^39K^+) ion peak at 07/04 12:01 EDT; (b) the m/z 39 (^39K^+) ion peak at July 4 23:00; (c) the m/z 39 (^39K^+) ion peak at July 5 00:30; (d) the 1-
min averaged time series of chopper open, closed and open-closed $^{39}$K$^{+}$ mass concentration for the night of July 4-5. (e) the 1-min averaged time series of the isotope ratio of $^{41}$K$^{+}$ to $^{39}$K$^{+}$ for chopper open and close signals; (f) the m/z 41 ($^{41}$K$^{+}$) ion peak at July 5 00:30. (Black markers indicate the measured data and red lines are the Gaussian fitting lines)

As described in the literature$^{5-7}$, the RIE$_{K}$ can vary depend on the tuning of the spectrometer, especially the temperature of the vaporizer and the setting of the heater bias voltage (which strongly affects the surface ionization of K). From previous work, Slowik et al. (2010) used KNO$_{3}$ to determine RIE$_{K}$ of 10. This paper did not include information about the heater bias voltage setting$^{6}$, which means it would be inappropriate to adopt this value for our measurements. Drewnick et al. (2015) estimated the RIE$_{K}$ to be 2.9 based on the ratio of K/S (2.75) from measured black powder$^{5}$, and this value (2.9) was also used in Jiang et al. (2015)$^{7}$. Using our calibrated RIE$_{K}$ and CE for K and SO$_{4}$, we calculated the K and SO$_{4}$ respectively from the HR-ToF-AMS mass spectrum, and resulted in a ratio of K/S equal to 2.8, which was near to 2.75$^{5}$ and confirms that our RIE$_{K}$ of 58 was suitable for this study. Considering these three quite different determinations for RIE$_{K}$, significant variation between instruments is expected and calibrations are needed.

Building on our laboratory calibrations to determine CE and RIE$_{K}$, the AMS mass concentrations determined using these values are quite consistent with other measurements of mass concentration, as shown in Figure S9. This provides an extra measure of confidence in the unexpectedly high value determined for RIE$_{K}$.

Ambient aerosol density varies with composition, and an accurate determination of ambient aerosol mass concentration for the SMPS depends directly on density. At the same time, once density is determined, the SMPS data can be used to provide an independent measure of submicron aerosol mass for comparison with concentrations determined by the AMS. Assuming the ambient
background SO$_4$, NO$_3$, and Cl would not change during the FW event, the aerosol during this event could be broken down into predominantly (NH$_4$)$_2$SO$_4$, NH$_4$NO$_3$, K salts (such as K$_2$SO$_4$, KNO$_3$, KCl), and organics. We also assume the BC contribution to total concentration was constant for the ACHD and ASRC sites. Using the densities of organics as 1.4 g cm$^{-3}$, (NH$_4$)$_2$SO$_4$ as 1.79 g cm$^{-3}$, NH$_4$NO$_3$ as 1.72 g m$^{-3}$, K$_2$SO$_4$ as 2.66 g m$^{-3}$, KNO$_3$ as 2.11 g m$^{-3}$, KCl as 1.99 g m$^{-3}$, and BC 1.8 g m$^{-3}$, the averaged FW aerosol density was then calculated from

$$\rho_{ambient} = \frac{m_{total}}{\rho_{organic} m_{organic} + \rho_{(NH_4)_2SO_4} m_{(NH_4)_2SO_4} + \rho_{NH_4NO_3} m_{NH_4NO_3} + \rho_{K_2SO_4} m_{K_2SO_4} + \rho_{KNO_3} m_{KNO_3} + \rho_{KCl} m_{KCl} + \rho_{BC} m_{BC}}$$  \hspace{1cm} (4)

Where $\rho$ is density and $m$'s are the mass concentrations (determined by the AMS except for BC). During the Independence Day FW event period, the density reached values as high as 2.0 g m$^{-3}$, highlighting the influence of the inorganic compounds from FW displays. Using the ambient aerosol densities determined above with the SMPS volume distributions, Figure S5a shows the correlation between SMPS measurements of mass concentrations and the HR-ToF-AMS measurements for the whole period (from June 27 to July 7 2017). A high correlation ($r^2=0.98$) with a slope of 1.14 increases the confidence in use of the above RIE$_K$ (58) and CE (0.15) for K, and CE (0.15) for K-salt related compounds (SO$_4$, NO$_3$, and Cl) influenced by FW events. When calculating the SMPS mass concentration, the aerosols were assumed to be spherical and with a dynamic shape factor of 1, which may cause some uncertainty. To estimate this potential error, the “Jayne shape factor” was calculated based on the AMS measured mass size distribution and SMPS measured mass size distribution as follows,$^{10}$

$$S = \frac{d_{va}}{d_m} \times \frac{\rho_e}{\rho_m} \hspace{1cm} (5)$$

Where S is the Jayne shape factor, which is proportional to the aerosol dynamic shape factor$^{10}$, $d_{va}$
is the aerosol vacuum aerodynamic diameter measured by HR-ToF-AMS, $d_m$ is the aerosol electrical mobility diameter measured by SMPS, $\rho_0$ is the standard density of 1.0 g cm$^{-3}$, and $\rho_m$ is the density of the material in the particle.\textsuperscript{10} Due to the observed externally mixed character of this aerosol (different mode diameters for inorganic and organic compounds as shown in Figures 3.3.3 and 3.3.S13), the shape factors for inorganic and organic were estimated separately. For inorganics, the peak mode for the averaged SMPS measured mass size distribution during the FW influenced period (about 290 nm, Fig. 3.3.S13) was used as $d_{m,\text{inorg}}$, and the peak mode for the averaged HR-ToF-AMS measured SO$_4$ size distribution during the FW influenced period (about 600 nm, Fig. 3.3.3) was used as $d_{va,\text{inorg}}$. $\rho_{m,\text{inorg}}$ was equal to the averaged FW aerosol inorganic density calculated from Eq. (4) (2.20 g cm$^{-3}$). With these values, Equation 5 gave a $S_{\text{inorg}}$ of about 0.94.

For organics, the secondary peak from SMPS measured mass size distribution during the FW influenced period was less clear, so the 07/04 daytime measured SMPS mass mode diameter was used based on the consideration that organics was the main component of this aerosol (about 87%, in Fig. 3.3.2). Then $d_{m,\text{org}}$ was equal to the peak mode for averaged SMPS measured mass size distribution during the 07/04 daytime (about 250 nm, Fig. 3.3.S13), and $d_{va,\text{org}}$ was equal to the peak mode for the averaged HR-ToF-AMS measured organic size distribution during 07/04 daytime (about 350 nm, Fig. 3.3.S13). With these input values, and a density of 1.40 g cm$^{-3}$ for organics, $S_{\text{org}}$ was calculated to be indistinguishable from 1.0. Applying these shape factors into SMPS measured mass concentration causes an increase in the slope of Fig. 3.3.S5a from 1.14 to 1.19. This roughly 19% difference between AMS and SMPS mass concentrations is a decent estimate of the uncertainty for these measurements, which, in addition to the usual error sources (flows, instrument parameters, etc.), also include the unique to this study CE of pure K$_2$SO$_4$ from our lab calibration and the use of this CE for K-salt related compounds for the FW events.
Figure 3.3.S5. The correlation between (a) the reported mass concentration by HR-ToF-AMS and by SMPS from June 27 2017 to July 7 2017 (including the FW periods); (b) the K needed to balance charge for inorganic compounds (SO$_4$, Cl, and NO$_3$) and the HR-ToF-AMS measured K.
3.3.S4 The results of PMF analysis excluding the FW significantly influenced period

Figure 3.3.S6. a): The PMF quality of fit parameter ($Q/Q_{\text{expected}}$) as a function of the number of factors; b): mass spectra of four identified OA component factors; c): the time series of mass concentration of each organic aerosol factor; d): mass concentration diurnal variation of each organic aerosol factor.
Figure 3.3.S7. The time series of mass concentrations of (a) BBOA+HOA (measured at ASRC site) and BC (measured at ACHD site); (b): LO-OOA and NO$_3^*$; (c) MO-OOA and SO$_4^-$; (d) MO-OOA and LO-OOA.
Figure 3.3.S8. The time series of 1 h mass concentration of the four organic aerosol factors determined by the PMF analysis, their sum and the total organic from 06/27/2017 to 07/07/2017.
Figure 3.3.S9. Time series of (a) aerosol hourly-averaged mass concentration measured by ASRC AMS (PM$_1$), PDR (PM$_{2.5}$), and ACHD T640 (PM$_{2.5}$) ($\mu$g m$^{-3}$); (b) NYSM meteorological parameters, with relative humidity (%), wind direction, and wind speed (m s$^{-1}$).
Figure 3.3.S10. (a) The m/z 85 ($^{85}\text{Rb}^+$) ion peak at 07/05 00:30 pm; (b) the time series of Rb ion signal during the measurement period.
Figure 3.3.S11. (a): Aerosol number size distribution (mobility diameter) measured by SMPS from July 4 12:00 to July 5 12:00; (b) aerosol mass size distribution measured by SMPS for the same time period.
3.3.S5 Estimation of FW aerosol from Albany Empire State Plaza FW display

The Gaussian dispersion equation for single point source was used (http://courses.washington.edu/cee490/PlumeD4.pdf), as shown:

\[ C(x,y,z) = \frac{Q}{2\pi u \sigma_y \sigma_z} \times \exp\left(\frac{-(y - y_0)^2}{2\sigma_y^2}\right) \times \exp\left(\frac{-(z - z_0)^2}{2\sigma_z^2}\right) \]

Here, \( y_0 \) represents the initial location of FW plume, \( z_0 \) represents the initial height of FW plume, \( Q \) is emission strength of source (g s\(^{-1}\)), \( u \) is average wind speed thru the plume (m s\(^{-1}\)), \( C \) is the measured concentration (g m\(^{-3}\)), and \( \sigma_y \) and \( \sigma_z \) represent the horizontal and vertical standard deviations in meters.

In this study, for the location at ASRC, we simply assume the emission height of the FW to be equal to the relative vertical location of ASRC (in comparison to the Empire State Plaza, taking into account the relative altitudes and height of sample inlets above ground), and \( y \) and \( y_0 \) were assumed to be zero. At the same time, \( u \) is the estimated advection speed of 1 m s\(^{-1}\), \( \sigma_z \) was taken as the vertical mixed height (about 200 m, as shown in Fig. 3.3.6), \( \sigma_y \) was estimated to be about 300 m based on the result of Turner\(^{11}\), \( C \) is then the maximum hourly value of FW mass concentration at the ASRC site (about 50 \( \mu \)g m\(^{-3}\) after deducting background aerosol concentration), so \( Q \) could be estimated using \( Q = 2\pi \sigma_y \sigma_z C \), and would be about 19 g s\(^{-1}\) (or about 70 kg emitted in a typical hour). Assuming the length of the FW event to be one half hour, the total aerosol emission from FW the display at Albany would be about 35 kg. Here we only estimated the plume near the ground and assume that we sampled from the center of plume rather from the edge, and ignored plumes at higher altitudes (like the one near 400 m, as shown in Fig. 3.3.6). These assumptions and omissions increase the uncertainty. Based on the estimate of total firework mass (2000 - 10,000 kg), an estimated emission factor of 0.07 for PM\(_{10}\) from Camilleri et al.\(^{12}\), the estimated aerosol
mass emission should be about 140-700 kg for all FW in the event. Our Gaussian plume estimate is lower than this by about 75-95%. Due to the uncertainties for both estimation methods, total fireworks mass and the emission factor, 35 kg was still considered to be reasonable.
**Figure 3.3.S12.** The surface weather map for the Northeastern United States for July 4\textsuperscript{th} 23:00 (red circle indicates the location of Albany, [https://www.wpc.ncep.noaa.gov/html/sfc-zoom.php](https://www.wpc.ncep.noaa.gov/html/sfc-zoom.php))
Figure 3.3.S13. (a) AMS organic mass spectra of July 5 05:00-06:00 and July 5 07:00-08:00; (b) the spectra difference between these two periods.
Figure 3.3.S14. SMPS-measured total mass size distribution (mobility diameter) during the FW event (July 4 23:00 to July 5 03:00), during July 4 daytime (09:00 to 17:00), and the second peak hour (July 5 07:00-08:00).

References:


(10). DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., Jimenez, J. L. Particle


Chapter 4: The interaction between Aerosol and fog
“Fog processing of aerosols in a rural forest environment: insights from high resolution aerosol mass spectrometry”

In this section, SOA formed at Pinnacle State Park, NY, thought to be the result of nighttime NO$_3$+BVOC reaction is observed and analyzed, and the effect of foggy conditions and fog processing on the characteristics of secondary aerosol was examined using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and collocated instruments at the ASRC PSP site. This work helps to provide general information about the interaction of fog and biogenic secondary organic aerosol in a rural forest at northeastern U.S.

4.1 Introduction

The measured mass concentrations and compositions of atmospheric aerosols are important due to their influences on the radiation budget and climate, the formation of clouds, air quality and human health.$^{1-8}$ Among ambient aerosols, secondary organic aerosols (SOA) are major constituents, and are generally formed through gas-to-particle conversion.$^6$ Despite recent advances, there still exists great uncertainty in the understanding of the detailed formation of SOA, which may involve reactions of thousands of chemical species via different formation pathways including new particle formation, condensation, and multiphase chemical reactions, particularly aqueous phase reactions.$^{9-10}$

Biogenic volatile organic compounds (BVOCs) emitted from vegetation, particularly mature forests, undergo atmospheric oxidation to form biogenic secondary organic aerosol (BSOA),$^{11-14}$ a major component of SOA. Advanced aerosol mass spectrometry technologies$^{15-16}$ have been widely used for identifying newly-formed BSOAs through their mass spectral fragments. For example, m/z 82 ($C_5H_6O^+$) from the High-Resolution Time-of-Flight Aerosol Mass Spectrometer
(HR-ToF-AMS) spectrum has been used as a tracer for isoprene epoxydiol-derived SOA. Many of the more recent AMS studies were carried out in the Southern United States, and there are fewer observations in the Northern United States and Canada regions (hereafter “northern regions”), which have different BVOC species, temperatures, solar radiation (SR) conditions, relative humidity (RH), and oxidant gas concentration, and so on. Previous AMS measurements taken during a summer period in British Columbia, Canada showed no significant ion signal at m/z 82, but a high ion signal at m/z 91 (C7H7+). To better understand the formation of BSOA in northern regions, more in-depth investigations are still needed.

Under conditions with high humidity, any hygroscopic aerosols absorb water vapor to form aerosol liquid water (ALW), which is an abundant medium that facilitates partitioning of polar, water-soluble organic gases to the condensed phase, and can enhance SOA formation through oligomerization and functionalization of these organics via aqueous-phase oxidation. Under supersaturated conditions, such aerosols continue growing through additional water vapor condensation, and can be activated to form fog or cloud drops. In the case of fog, fog drops also scavenge some fraction of the inactivated interstitial aerosols, and all the compounds in fog drops may undergo aqueous reaction or be removed through direct droplet deposition (i.e., impaction or sedimentation).

Many previous studies have examined fog processing in urban areas, where they are greatly affected by anthropogenic emissions, and the influence of fog processing on the BSOA, especially its formation mechanisms, are still not well known. Here we provide direct observations from a rural forested area of the influence of fog processing on BSOA formation using an Aerodyne HR-ToF-AMS and additional instruments. This study presents a detailed investigation of the fog processing focusing on (1) the SOA source apportionment; (2) the influence of different fog
periods on the aerosol composition, including oxidative properties; and (3) the relationship between ALW and BSOA formation.

4.2 Methods

4.2.1 Sampling location and periods

The aerosols were sampled at Pinnacle State Park (henceforth PSP, latitude: 42.09° N, longitude: 77.21° W, elevation: 504 m) in Addison, New York, which is surrounded by mixed deciduous and coniferous forests. The village of Addison (population 1,800) is about 4 km to the northwest, and the city of Corning (population 12,000) is 15 km to the northeast. In this study, we focus on the measurements from Sep. 19 to Sep. 23, 2017, during which several fog processing periods occurred.

4.2.2 Aerosol measurements

Submicron aerosols were measured at PSP using a HR-ToF-AMS complemented by additional instruments, including a TSI Scanning Mobility Particle Sizer Spectrometer (SMPS), and a Cloud Condensation Nuclei Counter (CCNc, Droplet Measurement Technologies), deployed in a mobile measurement vehicle (a 2007 Dodge Sprinter van, the ASRC mobile measurement platform). The HR-ToF-AMS was used for measuring the chemical composition of the non-refractory (NR) submicron aerosol (NR-PM$_1$), including organics, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, and Cl$^-$. The measurement uncertainty of the HR-ToF-AMS for component mass concentrations ranged from 3 ng m$^{-3}$ for NH$_4^+$ and Cl$^-$ to 24 ng m$^{-3}$ for organics in this study (Table 4.S1).

In addition to the above instruments, several trace gas analyzers (Table 4.S2) were on site to measure gases including O$_3$, NO, NO$_y$, CO, SO$_2$, HNO$_3$, and meteorological sensors provided temperature, relative humidity, solar radiation, wind speed, wind direction at the PSP measurement
During the field campaign, the HR-ToF-AMS, SMPS, and CCNc were connected to the output of a silica gel diffusion dryer (RH<40%) downstream of a sampling inlet through a URG PM cyclone (URG-2000-30EC, total flow 56 LPM leading to a cutoff size of about 2 μm). The cutoff of the PM cyclone and of the instruments themselves did not allow direct measurement of most fog drops, but some fine fog drops could still pass through the PM cyclone and evaporate at the silica gel dryer to form residual aerosols. During foggy periods, the instruments would measure the interstitial aerosols, which were not activated into fog drops, and the residual aerosols from the fine fog drops that evaporated in the silica dryer. For simplicity, these forms of aerosols are collectively defined as interstitial aerosols in this study.

4.2.3 Data analysis

The HR-ToF-AMS data was analyzed using standard HR-AMS data analysis software,31-32 SQUIRREL v1.59D and PIKA v1.19. During the analysis, the default relative ionization efficiency (RIE) values were used. The applied collection efficiency (CE) of 0.5 followed a suggested value used in previous studies.33-34 The PMF Evaluation Tool (PET, v2.08D) was used to divide the organic matter into different organic factors based on the PMF2 algorithm,35-36 and the final result was verified based on the criterion method demonstrated in previous studies.37 The elemental analysis (oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratio) is calculated based on the improved method proposed by Canagaratna et al. (2015).38

The ALW was estimated based on the sum of calculated ALW from inorganic compounds and that of organic compounds. In this study, (1) the ALW of inorganic aerosol compounds was calculated using the thermodynamic model ISORROPIA-II,39 which uses the AMS particle mass concentration of the inorganic species (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Cl$^-$), the ambient RH and ambient air
temperature as the inputs. (2) For the ALW of the organic aerosol compounds, an empirical equation (Eq. (1)) was used:\(^{40}\):

\[
\text{ALW} = \frac{M_{\text{org}}}{\rho_{\text{org}}} \times \kappa_{\text{org}} \times \frac{a_w}{1-a_w}
\]  

Here, \(M_{\text{org}}\) is the mass concentration of organic compounds, \(\rho_{\text{org}}\) is the density of organic compounds (1.4 g cm\(^{-3}\) is used\(^{39}\)), \(\kappa_{\text{org}}\) is related to the organic hygroscopicity (0.1 is used following previous studies\(^{40,41}\)), and \(a_w\) is the water activity (\(a_w\) is assumed to be equal to RH)\(^{40}\).

### 4.3 Results and discussion

Figure 4.S1 shows the time series of various measurements from Sep. 19 to Sep. 23 2017, including the aerosol chemical compound mass concentrations, weather conditions, and some gaseous species. During the measurement period, the dry aerosol PM\(_1\) mass concentration at PSP was 1.26-8.52 μg m\(^{-3}\) with an average value of 5.55 μg m\(^{-3}\). Organics were the main component of PM\(_1\), and on average comprised about 76% of the aerosol mass concentration, with proportions as high as 84%. The averaged mass fractions for other species were 14% for SO\(_4^2-\), 2% for NO\(_3^-\), 7% for NH\(_4^+\), and 1% for Cl\(^-\). During this period, there were four nights with RH> 96%, and the first three nights were verified as having fog conditions from images captured by the camera from the Addison New York State Mesonet station (Text 4.S1 and Figure 4.S2). At the same time, during the four overnight periods, the temperature was generally below 15 °C, and the wind speed was generally below 1 m s\(^{-1}\) from west, indicating a stagnant boundary layer with low atmospheric temperature and moist conditions (Figure 4.S1).

#### 4.3.1 OA source apportionment

Four OA factors, including two biogenic secondary OAs (BSOAs: BSOA-1 and BSOA-2), one less-oxidized oxygenated OA (LO-OOA), and one more-oxidized oxygenated OA (MO-OOA),
were identified by the PMF analysis, as shown in Figure 4.S3. The MO-OOA represented the more aged organic aerosol with a higher $f_{44}$ (0.20) and O:C ratio (0.86), which indicated a high degree of oxygenation (Figure 4.S3e). In contrast, the LO-OOA had a lower $f_{44}$ (0.14) and O:C ratio (0.78), with a daily maximum at around noon, which was followed by the daily peak of MO-OOA during late afternoon or early evening (around 18:00 local time; Figure 4.S3f). LO-OOA showed similar variation to $\text{SO}_4^{2-}$ ($r=0.63$) more so than $\text{NO}_3^-$, which indicated similar oxidative processing in aged air masses. The matching peaks between LO-OOA and solar radiation shown in Figure 4.S4a suggest that such oxidative processing may have been due in part to OH oxidation. Moreover, the time series of MO-OOA closely matched that of $\text{O}_3$, especially for the first three days (Figure 4.S4b). This is consistent with the higher oxidation state of MO-OOA.

![Figure 4.1. The scatter plot between BSOA-1 with $\text{NO}_3^-$,org](image)

Among the four OA factors, the two BSOAs (BSOA-1 and BSOA-2) were less oxidized and less aged, and BSOA-1 had the least oxidized state based on its mass spectra properties (Figure 4.S3e). Both BSOA-1 and BSOA-2 exhibited high concentrations during the night (Figure 4.S3f), and decreased quickly with increasing solar radiation during the daytime. The sum of BSOA-1 and BSOA-2 showed high correlation ($R^2 = 0.64$; Figure 4.1) with organic nitrate ($\text{NO}_3^-$,org, Text 4.S1)
and trended with HNO$_3$ (Figure 4.S5). This suggests that BSOA and NO$_3^{-}$org likely formed through nighttime NO$_3$+BVOC reactions$^{42-44}$. The BVOCs were most likely to be monoterpenes ($\beta$-pinene) due to the relatively high signals at m/z 91 (C$_7$H$_7^+$, average $f_{91}$ of 0.01, Figure 4.S3e$^{14}$). BSOA-1 shows a similar O:C ratio and a lower H:C ratio than BSOA-2 (Figure 4.S3e), and is consistent with fragmentation (or C-C bond cleavage$^{45}$). Meanwhile, BSOA-2 has a similar mass spectrum to LO-OOA ($R^2 = 0.96$, not shown), with lower O:C (0.59 vs. 0.78) and OM:OC (1.92 vs. 2.14) ratios (Figure 4.S3e). However, BSOA-2 and LO-OOA had a similar H:C ratio (1.39 vs. 1.42) and similar $f_{44}$ (0.138 vs. 0.144; Figure 4.S3e). This is likely due to the addition of OH/OOH functional groups on the carbon skeleton through OH oxidation$^{46}$. One plausible mechanism to explain this is that BSOA-1 was the initial product of the NO$_3$+BVOC reaction during nighttime. Then, BSOA-1 was fragmented and/or oxidized further to form BSOA-2, which converts to LO-OOA via reaction with OH before oxidizing to form MO-OOA$^{18}$. Since BSOA-1 and BSOA-2 were closely related based on their similar diurnal variability and mass spectral characteristics (Figures 4.S3e and 4.S3f), they were considered together (BSOA=BSOA-1+BSOA-2) in the following sections.

4.3.2 Fog periods

Three fog episodes were observed (the nights of Sep. 19-20, 20-21, 21-22) during the study period while the fourth night (Sep. 22-23) was characterized by moist condition with high relative humidity (RH > 96%). Based on the transition points of the aerosol compounds, as well as RH and solar irradiation variations, the entire fog life cycle was divided into five fog processing periods in a manner similar to a previous study$^{47}$, namely fog_before_forming (F-B), fog_forming (F-F), fog_scavenging (F-S), fog_dissipating (F-D) and fog_post_dissipating (F-P). The detailed properties for each period can be found in the supporting information (Text 4.S2 and Table 4.S3). There were not significant F-S and F-D periods during night of 22-23, mostly due to the lower
peak RH values (Figure 4.S6). The F-S periods of Sep. 19-20 and 20-21 were further divided into another two sub-periods labeled F-S-L for light fog conditions and F-S-H for heavier fog conditions based on the visibility variation, as shown in Figure 4.S6-4.S7. During the fog scavenging periods for each day, as shown in Figure 4.2 and Figure 4.S6, the aerosol compound mass concentrations experienced significant reductions. We define the scavenging efficiency that occurred during these periods as\(^{20,27}\):

\[
SE = \frac{C_{F-B} - C_{F-S}}{C_{F-B}}
\]

where SE is the scavenging efficiency, C is the mass concentration for MO-OOA, LO-OOA, or \(\text{SO}_4^{2-}\). For BSOA, \(C_{F-F}\) was used to replace \(C_{F-B}\) due to enhancement of BSOA during the F-F period.

**Figure 4.2.** The mass concentrations of aerosol compounds for each of the fog processing periods averaged over the four nights. The exact time periods are shown in Figure 4.S6 and listed in Table 4.S3. Black closed squares are RH values, and purple half-open diamonds are O:C ratio values.
The observed scavenging was most dramatic in these conditions for MO-OOA, and occurred during F-S-H periods, indicating its highest solubility and scavenging efficiency (SE_{MO-OOA} ranged from 78\%-91\% with an average value of 90\%). LO-OOA and SO_4^{2-} were the other two species that were readily scavenged, with fairly high and similar average scavenging efficiencies (SE_{LO-OOA}: 30\%-88\% with an average value of 45\%, SE_{SO_4}: 39\%-72\% with an average value of 50\%). This is consistent with the aforementioned similar formation pathway for LO-OOA and SO_4^{2-}.

BSOA increased during the F-F period compared to the F-B period, before decreasing during the F-S period. For this factor, the scavenging efficiency is calculated with respect to the concentration in the F-F period. With this caveat, BSOA showed lower scavenging efficiencies (17\%-36\% with an average value of 24\%) compared to LO-OOA and SO_4^{2-}, possibly due to the increased BSOA production or lower solubility. Here, the effect of changes in the planetary boundary layer height (PBLH) over the foggy period on the aerosol mass concentration was neglected, and PBLH was assumed to be constant for the whole duration of the fog based on the MERRA-2 dataset (Figure 4.S8) during the fog life cycle. However, it is noteworthy that fog evolution may lead to variability in PBLH, and further studies based on model simulations or accurate PBLH measurements are warranted.

The high scavenging efficiency of LO-OOA and MO-OOA resulted in a decreasing O:C ratio during the fog forming and scavenging periods, and with the dissipation of fog, the mass concentration of the residual aerosol from the evaporation of the fog drops increased for the interstitial aerosol, accompanied by an increase in the O:C ratio (Figure 4.2). The aerosol at the F-P period represents the final residual aerosols from fog drops and the interstitial aerosols during the F-S period. Comparing to the initial period (F-B), the total mass concentrations of the F-P aerosols slightly increased about 7\% to 15\% for the first three nights with an average value of
11%, and the O:C ratios decreased while the H:C ratios increased, which was likely related to the deceased amount of MO-OOA and enhancement of LO-OOA and BSOA. For the organic factors, MO-OOA showed an average reduction of 0.71 µg m$^{-3}$ (73% reduction), which was possibly due in part to fog droplet removal by sedimentation. However, this reduction was in contrast to the behavior of LO-OOA and BSOA, which showed average enhancements of 0.52 µg m$^{-3}$ (33% enhancement) for LO-OOA and 0.58 µg m$^{-3}$ (41% enhancement) for BSOA during these moist conditions. When combining LO-OOA and BSOA, the enhancement for each fog event was relatively consistent, with 1.27, 1.07, and 0.95 µg m$^{-3}$ enhancements for the nights of Sep. 19-20, 20-21, and 21-22, respectively (Figure 4.2). Different from the previous three nights, the night of Sep. 22-23 lacked significant F-S and F-D periods. Instead, LO-OOA and MO-OOA continued decreasing during the high RH period (RH > 96%), while the BSOA kept increasing until 04:30 am (local time) at a near-constant rate of 0.32 µg m$^{-3}$ hr$^{-1}$ (Figure 4.S5). This is consistent with the calculated BSOA formation from β-pinene and NO$_3$ based on the two-product model$^{48-51}$ (Text 4.S4).

4.3.3 Relationship between BSOA and ALW

During the four nights with high RH, the temperature was generally below 15 °C, and the wind speed was generally below 1 m s$^{-1}$ from the west (Figure 4.S1). A stagnant boundary layer, lower temperatures, and high RH provided an ideal opportunity to study the effect of RH (or ALW) on the BSOA (BSOA-1+BSOA-2). Figure 4.3a and Figure 4.S9 show the scatterplot of RH and the BSOA mass concentration for each night (only F-B and F-F periods are considered). Markers are colored by temperature and sized by calculated ALW values. Generally speaking, when RH was below 96%, but with increasing RH, BSOA mass concentrations increased in combination with the enhanced RH. Additionally, the air temperature decreased during the periods of increasing RH
(Figure 4.3a). This tended to keep the BSOA stable in the aerosol phase or enhance organic compound formation\textsuperscript{52}. The increased RH or ALW likely has two important effects. First, a higher RH or ALW implies that soluble species have a greater opportunity to dissolve onto liquid droplets to increase the aerosol bulk reaction rate to produce more BSOA. Second, a higher RH or ALW reduces the viscosity and increases the diffusivity of smaller BSOA or related organic matter, thereby these species mix with existed inorganic/organic components and enhance particle mass growth\textsuperscript{53-55}.

Figure 4.3. (a) The correlation scatterplot of RH and the BSOA mass concentration for the night of 19-20 September. All points are colored by temperature and sized by ALW. (b) The correlation of ALW mass fraction and the BSOA mass concentration for each night from Sep 19 to Sep 23.

To better understand the effect of aerosol water on the BSOA mass concentration, the ALW mass fraction (ALW\textsubscript{R}, which is calculated the ALW divided by the sum of the AMS total mass and the ALW) is used and its relationship with BSOA mass concentration is shown in Figure 4.3b. In Figure 4.3b, BSOA is only regressed against ALW\textsubscript{R} when the ALW\textsubscript{R} is larger than 0.3 (corresponding to RH larger than 75%) and smaller than 0.8 (RH less than 96%), due to the clear disconnects at these two points. The first disconnect appears to be consistent with a moisture-
induced phase transition, transforming the amorphous aerosol from a solid/glassy state to a semisolid state and the second one due to the change from semisolid state to a less-viscous liquid\textsuperscript{53}. When $ALW_R < 0.3$ and $> 0.8$, the points are much more scattered (as shown in red rectangles in Figure 4.3b), and there is no obvious relationship, which supports the assertion that low RH has little effect on SOA formation\textsuperscript{56}. For $ALW_R$ values between 0.3 and 0.8, the linear regression analysis between the BSOA mass concentration and $ALW_R$ for each night showed moderate to high correlation coefficients ($r^2=0.49-0.90$, $p<0.01$) with positive slopes (Figure 4.3b), which is consistent with the hypothesized influence of ALW on the detected BSOA\textsuperscript{55}. The slopes of these four nights are 0.9-2.6 with an averaged value of 1.9, which means during this study that an increase of 0.1 in the ALW ratio, accompanied by a -1.1 °C decrease in temperature (Figure 4.S10), would on average lead to an increase of about 0.2 μg m\textsuperscript{-3} BSOA.

However, based on the current field measurements results, we cannot entirely separate out the linked variations (mainly diurnal variations) of temperature and ALW on BSOA formation. Further lab chamber experiments in high RH conditions (from 75% to 95%) and variable temperature, in addition to model simulations, are warranted. Nonetheless, our fitting results between BSOA and ALW may give an estimation of BSOA formation in this rural forested area of northeastern USA under similar RH/ALW and temperature conditions, which are common during late summer and early fall (as shown in Figure 4.S11). These observations and results should help improve the estimation of the organic aerosol mass formation and character in atmospheric modelling, and encourage additional work in the area of aqueous processing of aerosols.

**4.4 Conclusion**
Organic aerosol formation from September 19-23, 2017 at Pinnacle State Park, NY, including the BSOA hypothesized to have formed through nighttime NO$_3$+BVOC reactions, was measured using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and collocated instruments. The effect of foggy conditions and fog processing on the characteristics of secondary organic aerosol was studied during different fog periods – fog_before_forming (F-B), fog_forming (F-F), fog_scavenging (F-S), fog_dissipating (F-D), and fog_post_dissipating (F-P). Results indicated that BSOA was found to be highly correlated with RH or ALW. This relationship can possibly be used to improve the estimation of the organic aerosol mass formation during nighttime in the northeastern United States during the study period.

ACKNOWLEDGEMENTS
This work has been supported by the New York State Energy Research and Development Authority (NYSERDA) contract number 48971.
4.5 References


8. IPCC. Climate change 2013: the physical science basis: Working Group I contribution to the Fifth assessment report of the Intergovernmental Panel on Climate Change. Cambridge University Press, 2014.


4.6 Supplement

**Text 4.S1 The description of Addison New York State Mesonet station and organic nitrate calculation**

The Addison New York State Mesonet station (http://www.nysmesonet.org/) is about 6 km south-west of the PSP site with a similar elevation (508m vs. 504m at PSP), so the weather conditions are the same for the Addison New York State Mesonet station and the PSP site. Using the background tree in the distance (marked in red circle) as a reference (Fig. 4.S2), the visibilities for the early morning of Sep.20, 21, and 22 were around 300m, which indicates the formation of fog. Following the organic nitrate (hereafter NO$_3$-org) estimation method proposed by Farmer et al. (2010)$^1$, and combining the NO$^+/NO_2^+$ ratios for ammonium nitrate (2.05 based on IE calibration) and for organic nitrate (taken to be 8)$^1$, values for the estimated organic nitrate were obtained, as shown in Fig. 4.1 and Fig. 4.S4, and averaged 67% of total nitrates, indicating an enhanced presence of organic nitrate in the aerosol.

**Text 4.S2 Fog processing periods**

Generally, as shown in Fig. 4.S5, the F-B period was used to describe the period when the RH was increasing after sunset until fog began forming, and included the time period from when solar irradiation drops to zero, to the point when RH reaches 96%. The F-F period began at the end of the F-B period and continued until the point in time when the SO$_4^{2-}$ concentration dramatic drops; the F-S period was after F-F period until the SO$_4^{2-}$ concentration began increasing again; the F-D period was after the F-S period until RH decreased to below 96% again; and the F-P period was defined as a half-hour period following F-D to describe the time after the fog has dissipated. The points in time for these periods for the four nights are listed in Table 4.S3.
**Text 4.S3 PBLH calculation**

In this study, the MERRA-2 data (https://disc.gsfc.nasa.gov/) was used for estimating the averaged PBLH of PSP during Sep. 19 to Sep. 23. From the MERRA-2 estimation, the PBLH drops quickly after sunset (general about 18:00 local time, Fig. 4.S7), and remains stable after about 20:00, which supports the exclusion of the influence of PBLH variation on the BSOA mass concentration during time periods of high RH.

Comparing to Sep. 21-22, the F-S period lasted longer for Sep. 19-20 and Sep. 20-21, and included two stages of fog with one for light fog conditions and one for heavier fog conditions, as shown in Fig. 4.S6 as examples. Significant visibility reduction occurred during the heavier fog, and the appearance time of heavier fog was just before sunrise and lasted for about 1-2 hours (about 06:30-08:20 on Sep.20 and 06:40-08:10 on Sep.21), which is likely related to the increase in convective mixing just after sunrise (solar irradiation increased from 0, as shown in Fig. 4.S5). Base on this, the F-S periods on Sep.20 and Sep.21 were divided into another two sub-periods as F-S-L for light fog conditions and F-S-H for heavier fog conditions. The F-S period on Sep.21 also occurred around the same time (06:30-07:30 on Sep.22), and was likely influenced by the convective mixing.

**Text 4.S4 BSOA formation rate estimation**

The BSOA formation rate was estimated following the two-product model proposed in previous studies:2-5:

\[
\frac{dS_{SOA}}{dt} = M_0 \left( \frac{\alpha_1 K_1}{1 + K_1 M_0} + \frac{\alpha_2 K_2}{1 + K_2 M_0} \right) \frac{d(HC)}{dt}
\]  

(1),

where \(M_0\) is the total absorbing organic aerosol mass (\(\mu g\ \text{m}^{-3}\)); \(\alpha\) is the stoichiometric coefficient of the reaction product; \(K\) is the partitioning coefficient of the product to the organic phase; and
HC is the parent hydrocarbon, thought to be β-pinene in this study\(^5\). The value for each parameter is shown in Table 4.S4.

In this study, \((d(HC))/dt\) was estimated based on the reaction rate of β-pinene:

\[
\frac{d(HC)}{dt} = \kappa_{(NO_3+\beta\text{-pin})} \times C_{NO_3} \times C_{(\beta\text{-pin})}
\]

where \(\kappa\) is the rate constant and \(C\) is the concentration for NO\(_3\) or β-pinene.

Based on the reported values for \(\kappa\) and \(C\) (Table 4.S4), \((d(HC))/dt\) was estimated to be 3.62 ug m\(^{-3}\) hr\(^{-1}\). The BSOA formation rate was estimated to be about 0.04-0.60 ug m\(^{-3}\) hr\(^{-1}\) based on the \(\alpha\) and \(K\) values from previous chamber studies\(^4\,6\).
Figure 4.S1. Time series of (a) aerosol chemical compound five minute-averaged mass concentrations; (b) PSP meteorological parameters, with relative humidity (%), wind direction, wind speed (m s$^{-1}$), and temperature (°C); and (c) PSP trace gas concentrations (SO$_2$, Ozone, NO, NO$_2$, CO) for Sep 19 to Sep 23, 2017.
Figure 4.S2. The camera pictures from the Addison New York State Mesonet station during early morning on Sep. 20-23 (The trees in red circle were used as a reference).
Figure 4.S3. a): The PMF quality of fit parameter ($Q/Q_{\text{expected}}$) as a function of the number of factors; b) the time series of the mass concentrations of the four PMF factors; c): The time series of the residual (measured-reconstructed) factors, including real residual, absolute residual, ratio of real to total, ratio of absolute to total, the $Q/Q_{\text{exp}}$ for each point in time; d): The PMF quality of fit parameter ($Q/Q_{\text{expected}}$) as a function of $f_{\text{peak}}$; (e) The mass spectra of the four PMF factors; (f) Mass concentration diurnal variation of each organic aerosol factor.
Figure 4.S4. The time series of (a) LO-OOA and solar irradiation; (b) MO-OOA and O₃
Figure 4.55. The time series of BSOA (BSOA-1+BSOA-2), NO$_{3\text{,org}}$ and HNO$_3$ mass concentrations.
Figure 4.6. The different periods for each day, as well as the variation of $\text{SO}_4^{2-}$ mass concentration, RH, temperature and solar irradiation.
Figure 4.87. The Addison Mesonet camera pictures for two stages of fog conditions on Sep. 20 and Sep. 21. (Left: light fog conditions before sunrise; Right: heavier fog conditions after sunrise).
Figure 4.88. Averaged diurnal variations of planetary boundary layer heights (PBLH) at PSP from Sep. 19 to Sep. 23 2017 from MERRA-2 data.
Figure 4.S9. The correlation scatterplot of RH and the BSOA mass concentration for the nights 20-21, 21-22, and 22-23. All points are colored by temperature and sized by ALW.
Figure 4.S10. The correlation of ALW mass fraction and the Temperature for the four fog nights
Figure 4.S11. The 1-hour time series of RH and temperature at the PSP site from 08/01/2017 to 10/09/2017 (red rectangle indicates the time period of this study).
**Table 4.S1** The measurement uncertainty for the HR-ToF-AMS during PSP measurements (mass concentration units: µg m\(^{-3}\))

<table>
<thead>
<tr>
<th></th>
<th>Mass concentration range</th>
<th>Uncertainty range</th>
<th>Averaged uncertainty</th>
<th>Uncertainty range (%)</th>
<th>Averaged uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>1.00-6.29</td>
<td>0.022-0.034</td>
<td>0.024</td>
<td>0.4%-2.3%</td>
<td>0.7%</td>
</tr>
<tr>
<td>NO(_3^-)</td>
<td>0.02-0.54</td>
<td>0.004-0.005</td>
<td>0.004</td>
<td>0.9%-17.0%</td>
<td>4.3%</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>0.15-1.96</td>
<td>0.003-0.008</td>
<td>0.005</td>
<td>0.3%-2.0%</td>
<td>0.7%</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>0.06-0.62</td>
<td>0.002-0.003</td>
<td>0.003</td>
<td>0.4%-4.0%</td>
<td>1.0%</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>0.001-0.17</td>
<td>0.002-0.004</td>
<td>0.003</td>
<td>2.0%-300%</td>
<td>28.0%</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>1.26-8.52</strong></td>
<td><strong>0.035-0.054</strong></td>
<td><strong>0.038</strong></td>
<td><strong>0.5%-2.8%</strong></td>
<td><strong>0.8%</strong></td>
</tr>
</tbody>
</table>
Table 4.52 The key features of the instruments used for these trace gas measurements (O$_3$, NO, NO$_y$, CO, SO$_2$, HNO$_3$), as well as meteorological sensors, and more detailed information about these instruments can be found elsewhere$^7$.

<table>
<thead>
<tr>
<th>Measured Parameters</th>
<th>Instrument models</th>
<th>Detection limit</th>
<th>Measurement Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>O$_3$</td>
<td>Thermo 49i</td>
<td>&lt;0.4 ppb</td>
<td>UV photometry</td>
</tr>
<tr>
<td>NO</td>
<td>Thermo 42C-TL</td>
<td>0.05 ppb</td>
<td>Chemiluminescence</td>
</tr>
<tr>
<td>NO$_y$</td>
<td>Thermo 42i-Y</td>
<td>0.05 ppb</td>
<td>Chemiluminescence</td>
</tr>
<tr>
<td>CO</td>
<td>Teledyne API Model 300EU</td>
<td>10 ppb</td>
<td>NDIR gas filter correlation with native zeroing</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>Thermo Model 43i-TLE</td>
<td>0.06 ppb</td>
<td>Pulsed fluorescence</td>
</tr>
<tr>
<td>HNO$_3$</td>
<td>Thermo 42i-Y</td>
<td>N/A</td>
<td>Denuder difference</td>
</tr>
<tr>
<td>Temperature</td>
<td>MetOne 060</td>
<td>0.10°C</td>
<td>Thermistor Device</td>
</tr>
<tr>
<td>Relative Humidity</td>
<td>MetOne 083</td>
<td>3%</td>
<td>Thin Film Capacitor</td>
</tr>
<tr>
<td>Wind Speed</td>
<td>MetOne 010</td>
<td>0.22 m s$^{-1}$</td>
<td>Cup Anemometer</td>
</tr>
<tr>
<td>Wind Direction</td>
<td>MetOne 020</td>
<td>3%</td>
<td>Wind Vane</td>
</tr>
<tr>
<td>Barametric Pressure</td>
<td>MetOne 090</td>
<td>1.5 mbar</td>
<td>Capacitance Monometer</td>
</tr>
<tr>
<td>Solar radiation</td>
<td>LICOR LI-200</td>
<td>&lt;10 W m$^{-2}$</td>
<td>Pyranometer</td>
</tr>
</tbody>
</table>
Table 4.S3. The time intervals for each fog processing periods of four nights

<table>
<thead>
<tr>
<th>Fog Type</th>
<th>Day19-20</th>
<th>Day20-21</th>
<th>Day21-22</th>
<th>Day22-23</th>
</tr>
</thead>
<tbody>
<tr>
<td>fog_before_forming (F-B)</td>
<td>18:45-00:10</td>
<td>18:30-23:55</td>
<td>18:50-01:00</td>
<td>18:35-01:10</td>
</tr>
<tr>
<td>fog_forming (F-F)</td>
<td>00:15-02:40</td>
<td>00:00-02:05</td>
<td>01:05-06:30</td>
<td>01:15-07:50</td>
</tr>
<tr>
<td>fog_scavenging (F-S)</td>
<td>02:45-08:20</td>
<td>02:10-08:15</td>
<td>06:35-08:00</td>
<td>N/A</td>
</tr>
<tr>
<td>F-S-L (light fog)</td>
<td>02:45-06:30</td>
<td>02:10-06:40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F-S-H (heavier fog)</td>
<td>06:35-08:20</td>
<td>06:45-08:15</td>
<td></td>
<td></td>
</tr>
<tr>
<td>fog_dissipating (F-D)</td>
<td>08:25-09:25</td>
<td>08:20-11:55</td>
<td>08:05-08:50</td>
<td>N/A</td>
</tr>
<tr>
<td>fog_post_dissipating (F-P)</td>
<td>09:30-10:00</td>
<td>12:00-12:30</td>
<td>08:55-09:25</td>
<td>07:55-08:25</td>
</tr>
</tbody>
</table>
The value for each parameters and compounds concentration used in Eq. (1) and (2)

<table>
<thead>
<tr>
<th></th>
<th>value</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>0.57 µg m⁻³</td>
<td>The half value of the averaged total enhanced C_{BSOA} in Fig. 3b</td>
</tr>
<tr>
<td>((\alpha_1 K_1 \alpha_2 K_2)_1)</td>
<td>(1.187 0.004546 0.496 0.880)</td>
<td>Boyd et al., 2015⁶</td>
</tr>
<tr>
<td>((\alpha_1 K_1 \alpha_2 K_2)_2)</td>
<td>(1.464 0.0158 0 0)</td>
<td>Griffin et al., 1999⁴</td>
</tr>
<tr>
<td>(\kappa_{\text{No}_3+\text{β-pin}})</td>
<td>(-2.51\times10^{-12}) molecules⁻¹ cm⁻³ s⁻¹</td>
<td>Fry et al., 2009⁹</td>
</tr>
<tr>
<td>C_{NO}_3</td>
<td>(2.4\times10^8) molecules cm⁻³</td>
<td>Fry et al., 2009⁹</td>
</tr>
<tr>
<td>C_{β-pin}</td>
<td>(7.2\times10^9) molecules cm⁻³</td>
<td>Xu et al., 2015⁸</td>
</tr>
</tbody>
</table>

References


Chapter 5: The interaction between Aerosol and Clouds
“Observed below-cloud and cloud interstitial submicron aerosol chemical and physical properties at Whiteface Mountain, New York during August 2017”

In this section, below-cloud and cloud interstitial submicron aerosols were characterized in real-time using an Aerodyne High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) and other instruments deployed in the Atmospheric Sciences Research Center (ASRC) sprinter van mobile laboratory at Whiteface Mountain in Wilmington, NY. These measurements allowed the direct comparison of interstitial aerosol and below-cloud aerosol, and provided a baseline for more detailed measurements of cloud formation and processing, as well as additional information for atmospheric models to better simulate cloud processing.

5.1 Introduction

Clouds and aerosols play important roles in the climate system and affect radiation and ecosystems.¹ Individual cloud droplets start from aerosols.²³ Hygroscopic ambient particles act as cloud condensation nuclei (CCN) at sufficient water vapor supersaturation to form cloud droplets, which may dissolve more water-soluble organic compounds, which can then undertake chemical reactions within the aqueous phase including the formation of higher molecular weight organic aerosols (OA).⁴ With the evaporation of cloud droplets, the OA remain in the atmosphere and continue to affect climate, visibility, and human health.⁵⁶ Below-cloud aerosol, cloud sample residues, interstitial aerosol and cloud water composition are often characterized separately as a means for evaluating chemical processing in the aqueous phase.

Many localized studies have investigated the physical and chemical characterization of ambient
aerosols, cloud droplet residues, interstitial particles and clouds to better understand these types of cloud-aerosol interactions using aircraft and mountain field measurements, spanning North America7-13, Europe2-3, 14-17, East Asia18-21, and other geographic locations22-25. In these types of studies, the Aerodyne Aerosol Mass Spectrometer (AMS) is one of the most widely used instruments to evaluate: (1) accumulation of secondary compounds within wet aerosols and cloud droplets, and (2) changes to the oxidation state of organics via cloud processing11,15, both of which can impact the aerosol hygroscopicity26-28. The former includes enhancement of particle nitrate (NO$_3$), sulfate (SO$_4$) and ammonium (NH$_4$) via dissolution of soluble gases (HNO$_3$, SO$_2$ and NH$_3$) within cloud droplets and subsequent acid-base reactions10,15. Likewise, enhanced concentrations of organic acids and other oxygenated organic compounds have been found in wet aerosols, fog and cloud droplets, as compared to aerosols at lower humidity (<70%)3,14, 29, 30, suggesting a similar formation pathway for secondary organic aerosol (SOA) via partitioning of volatile organic compounds to the aqueous phase and subsequent reactions31-33. Organic compounds are more complex than inorganic compounds, with an extremely diverse array of natural and anthropogenic sources, chemical properties and potential reaction pathways5,34-36. Organic compounds can also enter the aqueous phase as soluble gases or as pre-existing aerosol (of both primary and secondary origin), adding to this complexity37. The aerosol aqueous phase as a chemical reactor is thought to be distinctly different from cloud droplets, due to large differences in gas phase partitioning and ionic strength, which can also impact the dominant oxidants at play38. For some organic reactions, interstitial aerosols rather than cloud droplets may be the dominant aqueous SOA formation pathway39. However, interstitial particles and cloud droplet residues both have significantly greater water content than aerosols at < 100% RH and these two different aerosol classes can be found to have very similar characteristics, in which case they are contrasted with aerosols found under cloud
free (clear) conditions. Hill-tops and mountain-tops are desirable locations for studying aerosol-cloud interactions and for evaluation of chemical models, since: (1) the measurements can extend for long time periods, allowing for an abundant dataset that spans all times of day and can capture seasonal and episodic events like forest fire plumes; (2) high elevation sites can be frequently in-cloud, allowing for significant duration of in-cloud sampling; (3) high elevation sites are often representative of regional air quality, and back trajectory analysis can be used to identify the sources of airmasses upwind of clouds. Several major field campaigns have been conducted within the past 25 years specifically to investigate cloud processing from high elevation sites, such as the Great Dun Fell experiments (1995 in northern England), the FEBUKO project (2001-2002 in Germany), and the HCCT experiment (2010 in Germany). Coordinated high elevation studies like these that focus on multiphase (reactive trace gas, aerosol and cloud) chemical interactions have not been conducted in the northeastern United States in recent years, though the region is rich with historical precedent in the study of chemical processes occurring within clouds. Intense renewed interest in aqueous chemical reactions as a potential pathway to bridge the gap between observed and modeled SOA was an important science driver for three major field campaigns within the U.S. in the past decade: Deep Convective Clouds and Chemistry (DC3), Southeast Atmosphere Studies (SAS) and Studies of Emissions and Atmospheric Composition, Clouds and Climate Coupling by Regional Surveys (SEAC4RS). These campaigns primarily operated within the central and southeastern U.S., which is chemically and meteorologically distinct from other areas of the U.S. and may be unique in manifesting a large SOA source from isoprene emissions. The forested and humid environment of the northeastern U.S., frequently downwind of Midwestern urban and industrial centers, was the focus of major field campaigns more than 10
years ago such as International Consortium for Atmospheric Research on Transport and Transformation (ICARTT)\textsuperscript{55}, but there have been significant advancements in measurement capabilities with respect to organic compounds in both the gas and particle phase since then\textsuperscript{56-61}, largely in response to science questions about SOA formation that came later. Furthermore, regional chemistry in the northeastern U.S. has been rapidly evolving over the past several decades, in parallel with the southeast, as states have implemented national air quality standards\textsuperscript{62,63}. The growing importance of organic aerosols in the northeastern U.S. due to reduced sulfate and nitrate mass loadings\textsuperscript{64} may manifest differently in the northeast than in the southeast, due in part to regional differences in biogenic emissions\textsuperscript{65}.

With these reasons in mind, a pilot study was conducted at Whiteface Mountain in August 2017 Wilmington, NY, to lay the groundwork for better understanding of “Chemical Processing of Organics within Clouds” (CPOC) within the northeastern U.S. in the “post acid rain” era\textsuperscript{66-68}. Whiteface Mountain (WFM) was chosen because (1) as the fifth-highest peak in New York State (summit: 1483 m a.s.l.), its summit is in-cloud 25-60% of the time during summer\textsuperscript{66}, (2) there is an air quality monitoring site on the mountain’s summit, with decades of aerosol and summertime cloud water chemical speciation measurements\textsuperscript{64} and reactive trace gas measurements\textsuperscript{69}, providing valuable context for intensive measurement efforts; and (3) deployment of a mobile lab for below-cloud measurements is possible alongside the road to the mountain’s summit. The CPOC Pilot study was comprised of several coordinated measurements, including below-cloud and in-cloud measurements from the mobile lab, cloud water, aerosol and trace gas measurements from the WFM summit, and wind LiDAR and radiosonde observations based at an upwind site near Lake Placid (https://www.asrc-research.com/cpoc). This paper reports results from the mobile lab real-time measurement for interstitial aerosol and below-cloud aerosol, focusing on the aerosol physical
and chemical properties.

**5.2 Experimental procedures**

**5.2.1 Sampling location and period**

The mobile lab measurements were carried out at the “Lake Placid Turn” (hereafter LPT, about 1250 m a.s.l.) alongside the Whiteface memorial highway below the summit of WFM as a part of the CPOC Pilot Study from August 15-23, 2017. During the measurement periods, August 15, 18, 19, and 23 were defined as “In-Cloud” days, when the LPT was engulfed in cloud during the morning and the mobile lab sampled cloudy air. Since the mobile lab was parked at LPT for all measurements reported in this study, with the lifting of cloud base as the day progressed, the instruments captured different types of aerosols: interstitial aerosols when the van was in-cloud and ambient aerosols when below-cloud (Fig. 5.S1). August 20 was a cloudy day, but the mobile lab was not deployed early enough to sample interstitial aerosols on this day. August 17, 21, and 22 are all marked as “Clear” days and were treated as reference days. The key instruments used for this study are briefly described in the following section.

**5.2.2 Aerosol measurements**

The ASRC mobile measurement platform (a modified 2007 Dodge Sprinter van) was used during the CPOC Pilot study, and included an Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS) that measured submicron non-refractory aerosol chemical component mass concentration and size distribution; a TSI Scanning Mobility Particle Sizer Spectrometer (SMPS) that measured the ambient aerosol size distribution; and a single column Cloud Condensation Nuclei counter (CCNc, Droplet Measurement Technologies) for the CCN number concentration. Power to the instruments was supplied by an 8-battery system, which ran
for about 4 (7) hours with (without) air conditioning. A URG PM cyclone followed the aerosol sample inlet to remove large aerosol/cloud droplets (> 2 µm) at a flow rate of 56 LPM. After the cyclone, a silica dryer was used to dry the aerosol (RH < 40%) upstream of the instruments’ inlets. The cutoff of the PM cyclone and of the instruments themselves did not allow direct measurement of most cloud droplets, but smaller cloud droplets (e.g. within the transition layer) could still pass through the PM cyclone and evaporate at the silica gel dryer to form residual aerosols. During measurements in-cloud, the instruments measured interstitial particles, which were not activated into cloud droplets, and residual particles from the smallest cloud droplets (< 2 um) after evaporating in the silica dryer. For simplicity, these forms of aerosols are collectively defined as interstitial aerosols in this study.

For future intensive field campaigns at WFM, a counterflow virtual impactor (CVI)\textsuperscript{20,70} for sampling cloud droplet residuals would be a desirable addition to our measurements of interstitial and below-cloud aerosol composition and cloud water composition. A full accounting of the chemical evolution of aerosols also requires real-time collocated measurements of relevant gas phase precursors, including volatile organic compounds (VOCs) and oxidants. These measurements capabilities (i.e. droplet residuals and VOCs) were not available for the CPOC pilot study, however, and reactive trace gas measurements were confined to the summit (and therefore will be discussed in a separate paper). However, very few field studies to date have been able to include every one of these relevant measures of the multiphase system involved in aerosol-cloud interactions. The main purpose of the LPT measurements during the pilot study was to characterize the below-cloud aerosol. However, we found that the interstitial aerosol measured from the LPT yielded additional interesting observations when compared to below-cloud aerosol measured at the same location, and both sets of observations are described here.
Meteorological data (including temperature, wind direction, wind speed, relative humidity (RH), precipitation and solar radiance) with a 1-minute time resolution were collected by an ASRC portable weather station (HOBO RX3000) from August 17-23. The weather station was deployed at the LPT approximately 5 meters from the ASRC mobile measurement platform.

The basic working principle of the HR-ToF-AMS can be found in detail previously. The CCN activation spectra were obtained by splitting the electrostatic classifier (EC) flow between the condensation particle counter (CPC, TSI 3785) and the CCNc, with a controlled and filtered dilution flow after the EC to maintain 0.6 LPM sample flow through the EC while providing sufficient flow to both the CPC and CCNc (1.0 and 0.5 LPM, respectively). The EC sheath flow was set to 4.5 LPM to obtain sufficient particle counting statistics and to obtain a consistent 7.5:1 sheath to aerosol ratio (SAR) as a SMPS operating concurrently at the WFM summit. Particle size scans 13-749 nm were acquired in 5-minute intervals. The CCNc was operated with 10:1 SAR and cycled through five supersaturations each hour (20 minutes at 0.2% followed by 10 minutes at 0.4%, 0.6%, 0.8% and 1.0% setpoints). Calibrations at the LPT with ammonium sulfate aerosol (assuming dynamic shape factor of 0.98 and van’t Hoff factor of 2.5) showed that the actual supersaturations were: 0.23%, 0.37%, 0.51%, 0.65% and 0.78%. Only time periods when the mobile lab sampled below-cloud were included in the CCN measurements shown here.

5.2.3 Data analysis

For the HR-ToF-AMS data, the default relative ionization efficiency (RIE) values were used (4 for ammonium, 1.1 for nitrates, 1.2 for sulfate, 1.3 for chloride, and 1.4 for organics) along with the standard analysis software, SQUIRREL v1.59D and PIKA v1.19, with a collection efficiency (CE) of 0.5 for all aerosol chemical compounds. The elemental analysis (oxygen-to-carbon (O:C) and hydrogen-to-carbon (H:C) ratio) is calculated using the original method proposed by Aiken et
al. (2009)\textsuperscript{73} and the improved method proposed by Canagaratna et al. (2015)\textsuperscript{74}. Organonitrates were evaluated based on the ratio of measured NO\textsubscript{2}\textsuperscript{+} and NO\textsuperscript{+} signals\textsuperscript{75,76}. The average CCN activation spectra for each day of the pilot study at each of the five supersaturations were obtained by averaging 2-11 (most frequently 3-5) particle size scans. The first half of the size scans at each supersaturation were discarded to allow time for temperature and humidity in the CCNc to stabilize. Scans were also discarded when spikes were observed in the particle number concentration and CCN concentration, most likely due to a passing car, or when a given particle size scan was significantly different from the other size scans. A Scanning Mobility CCN Analysis (SMCA) package was used to analyze the CCN activation spectra (http://nenes.eas.gatech.edu/Experiments/SMCA.html)\textsuperscript{77}. Calibrations were performed both in a steady state mode (waiting 30 seconds after each size setting) and in the size scanning mode described above, with no change in the CCNc or SMPS setup between calibrations and ambient measurements to ensure that time lags between the CCNc and CPC were accurately accounted for. The CCNc thermal resistance (1.5 K W\textsuperscript{-1}) and ΔT offset (0.5 K)\textsuperscript{78} were calibrated using the steady state calibrations, and the CCNc flow model parameterization developed by Lance et al. (2006)\textsuperscript{79} was used to interpolate between the calibrated supersaturations (with R\textsuperscript{2} value of 0.994 when plotted versus ΔT) and to correct for changes in ambient temperature on different days. The aerosol hygroscopicity (κ) was calculated based on the measured d\textsubscript{50} for a given instrument supersaturation\textsuperscript{80}. The inferred hygroscopicity of the organic fraction (κ\textsubscript{org}) was calculated based on the measured volume fractions (as reported in Table 5.S1) and linear mixing rules, assuming an organic density of 1.4 g mL\textsuperscript{-1}.\textsuperscript{81} The κ\textsubscript{org} calculated in this way may be an underestimate, since we did not measure refractory material such as black carbon (which typically does not contribute significant soluble matter, but can make up a significant fraction of the particle volume, thereby
skewing the volume fractions of the soluble components).

To help determine the sources of the ambient aerosol at Whiteface Mountain, 24-hour air mass back trajectories were calculated using the NOAA ARL Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT) model, based on GDAS meteorological data. Ending heights of 1000 m, 1250 m, and 1500 m ASML (above mean sea-level) were chosen to investigate the influence of different transport layers.

5.3 Results and Discussion

Figure 5.1 shows the time series of the aerosol component mass concentrations and the mass fractions during the CPOC Pilot study period measured by the HR-ToF-AMS. During the study period, the average aerosol mass concentration was about 4.4 µg m$^{-3}$, consistent with other remote areas. Organics were the main aerosol component, with a mass fraction of 58-94%. Higher mass fractions of organics occurred on Aug. 17 (93%), Aug. 20 (91%) and Aug. 23 (85%) simultaneously with lower aerosol number concentrations (1796 # cm$^{-3}$, 974 # cm$^{-3}$, and 1228 # cm$^{-3}$, respectively) than the adjacent days. These three days were characterized by flows mainly from the northwest, which transported cleaner air containing mainly biogenic organic aerosols to Whiteface Mountain, while other days were more likely influenced by air that passed over urban areas. More detailed discussion regarding the relationship between mass concentration and mass fraction with wind direction will be presented below.
**Figure 5.1.** The time series of (a) the aerosol component mass concentrations, (b) the aerosol components mass fractions and number concentration (half-filled diamonds) during the CPOC Pilot study period measured by HR-ToF-AMS.

The four In-Cloud days (August 15, 18, 19, and 23) were characterized by relatively lower aerosol mass concentrations (organics, SO$_4$, NH$_4$), and higher NO$_3$ mass concentration/fraction at the beginning of the measurement periods compared to later in the day as the clouds lifted (Fig. 5.1a). As cloud base lifted, the evolution of interstitial aerosols was characterized as discussed in following sections. A complication to this uniform cloud lifting picture occurred on August 19, during which the aerosol compound mass concentrations first increased (from 0.7 to 2.1 µg m$^{-3}$), then decreased to 0.1 µg m$^{-3}$ in about 20 minutes, followed by a second increase over the next several hours (Fig. 5.1a), behavior similar to the variation in the height of the cloud base (Fig. 5.2c). This cloud base height was estimated using webcam images (https://www.wildcenter.org/cams/whiteface_live_view/) and a schematic showing the altitude of different landmarks on Whiteface Mountain (Fig. 5.3). The August 19 cloud event will be discussed in detail as a case study.
5.3.1 Cloud layer classification

![Graph showing aerosol compounds mass concentration and NO\(^+\)/NO\(_2^+\) ratio](image)

**Figure 5.2.** The classification of cloud layers, as well as the variation of aerosol compounds mass concentrations, number concentration (black half-filled diamonds), and NO\(^+\)/NO\(_2^+\) ratio (purple open circles and line) for each layer during the August 19 cloud event.

To better characterize the aerosol properties in/below cloud, three cloud layers were identified for the four In-Cloud days: the below-cloud layer (hereafter “BL”), the transition layer (hereafter “TL”), and the in-cloud layer (hereafter “IL”), as detailed in Table 5.S2 (different time periods for each day) with Fig. 5.2 as the most striking example. Figure 5.2 shows the variability of the aerosol component mass concentrations and the NO\(^+\)/NO\(_2^+\) ratio (an indicator of the ratio of the inorganic NO\(_3\) to the total HR-ToF-AMS NO\(_3\))\(^{75,76}\) during the August 19 cloud event, in addition to the boundary lines determined for each cloud layer. The three different cloud layers were identified based on the variation of the aerosol properties, rather than the measured metrological parameters (such as RH, which were all very near to 100 during the periods in Table 5.S2). We defined the separation of the below-cloud layer from the transition layer based on the variation of NO\(_3\) and the
NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratio. Namely, NO\textsubscript{3} was observed to increase with decreasing NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratio at the boundary of the below-cloud to transition layer (Fig. 5.2). Furthermore, the boundary between the transition layer and the in-cloud layer (Fig. 5.2) was defined where aerosol components (organics, SO\textsubscript{4}, NH\textsubscript{4}) mass concentration and number concentration began rapidly decreasing (Fig. 5.2), which was likely related to the activation of aerosols to form cloud droplets. This classification of layers was used for three other In-Cloud days, namely August 15, 18, and 23, as shown in Fig. 5.S4. The time point for separating the TL layers and IL layers matched the point of the visual cloud base cutting the LPT, as shown in Fig. 5.S5a, 5.S5c, 5.S5e, and 5.S5g. At the same time, the time points for separating the TL layers and BL layers matched the point of the visual cloud base cutting the castle (about 1405m a.s.l., Fig. 5.S3a), as shown in Fig. 5.S5b, 5.S5d, 5.S5f, 5.S5h, indicating the transition layer was about 160 m deep on the four cloud days, and can be considered as the edge of the cloud appearing to act as a reaction chamber for the wetted aerosol to experience liquid reaction under saturated conditions (RH~100%).

The different cloud layers have unique characteristics. For example, a near-constant mass concentration of organics, SO\textsubscript{4}, and NH\textsubscript{4} was present in the transition layer and below-cloud layer (Fig. 5.2 and 5.S4). However, the NO\textsubscript{3} mass concentration was higher in the transition layer compared to the below-cloud layer. Accordingly, the NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratio decreased from the below-cloud layer to the transition layer (Fig. 5.2 and 5.S4), implying that the enhanced NO\textsubscript{3} was mainly derived from inorganic compounds. Using the organic nitrate calculation method\textsuperscript{75,76}, the NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratio for ammonium nitrate (value of 2.1 based on IE calibration) and organic nitrate (value taken to be 7), the organic and inorganic nitrate were calculated, and the results are depicted in Fig. 5.S6. According to Fig. 5.S6, the contribution of organic nitrate to the total nitrate decreases from 35% (below-cloud layer) to about 18% (transition layer), indicating the most of enhancement
of NO$_3$ was inorganic nitrate. Assuming full neutralization of NO$_3$ and SO$_4$ for aerosol-phase NH$_4$ in the TL and IL layers on cloud days, the NH$_4$ mass concentration was compared to the measured NH$_4$ mass concentration by HR-ToF-AMS, as shown in Fig. 5.S7. The slope of 1.03 indicates that (1) there was little difference between the two NH$_4$ mass concentrations, and (2) the measured aerosol particles in the TL and IL layers were fully neutralized. Based on the full neutralized property, the formation of inorganic NO$_3$ would likely follow the uptake of nitric acid, which was subsequently neutralized by ammonium under saturated high-RH conditions.$^{10,15}$

Under supersaturated conditions (RH > 100%, in-cloud layer), aerosols are activated to form cloud droplets or incorporated into existing droplets, which causes significant overall mass concentration decrease of organics, SO$_4$ and NH$_4$ (Fig. 5.2 and 5.S4). However, the NO$_3$ decrease was much slower, which may have been due to the formation of inorganic NO$_3$ under high RH conditions.

On Aug. 19, as the cloud base descended and sample inlet became deeper into the cloud, the aerosol total mass and number concentration decreased significantly to only 10% and 52%, respectively, compared to their values at the edge of the transition layer. The different relative reductions for aerosol mass and number concentrations implies that activation/incorporation favors larger diameter aerosol as expected. However, it is not clear if our deepest in-cloud conditions represent the innermost regions of the cloud. For simplicity, the lowest total aerosol mass concentration in the in-cloud layer during the August 19 cloud event was defined as the center of cloud (hereafter “IL$_{center}$”). For three other In-Cloud days (Aug. 15, 18, 23), as shown in Fig. 5.S4, the measurement depths were shallower than Aug. 19, which implies these in-cloud layers likely sampled nearer the cloud bases, instead of the regions nearer the center of the clouds.

### 5.3.2 Aerosol properties comparison

Based on the above cloud layer classification, the physical and chemical properties of aerosols in
the three layers (BL layer, TL layer, and IL layer) were compared. The properties include (1) the mass concentrations and mass fractions of the HR-ToF-AMS detected compounds, (2) number and mass size distributions, (3) oxidation state of the organic aerosol component, and (4) CCN activity.

5.3.2.1 Compounds mass concentrations and fractions

![Figure 5.3.](image)

**Figure 5.3.** The total mass concentration (ug m$^{-3}$) and the average mass concentration (ug m$^{-3}$)/fraction of aerosols of each layer during urban influenced In-Cloud days, Aug 15, 18, 19.

Based on the backward air mass trajectories (Fig. 5.S8) and aerosol compound mass concentrations/fractions (Table 5.S3), the measurement days were classified into two groups, similar to the classification method of Cook et al. (2017). First, August 15, 18, 19, 21, and 22 were classified as days influenced by urban sources (defined as urban influence periods) because air masses passed through metropolitan areas in the Great Lakes region before arriving at Whiteface Mountain (Fig. 5.S5). Second, on August 17, 20, and 23, the air mass originated from boreal forests in Canada (Fig. 5.S5), so those three days were defined as biogenic influence periods. As expected, the measurements during four of the urban influence periods – August 15, 18, 21, and 22 – yielded (1) elevated total BL aerosol mass concentrations ranging from 4.8 to 6.7 µg m$^{-3}$ vs. 2.3 to 3.4 µg m$^{-3}$ during biogenic influence periods, Table S3, (2) elevated SO$_4$/NH$_4$ mass concentrations and mass fractions in the BL layer aerosol (0.8-1.6 µg m$^{-3}$/0.4-0.7 µg m$^{-3}$ vs.
0.1-0.2 µg m$^{-3}$/0.07-0.1 µg m$^{-3}$ for mass concentration, and 15-24%/7-9% vs. 4-10%/2-4% for mass fraction), and (3) lower organic compound mass fraction (66-78% vs. 85-93%). The extreme high mass fraction (85-93%) of organics during the biogenic-influenced periods in this study was near the value reported in Drewnick et al. (2007) when the air masses passed over Southern Finland forests$^2$, and these values may represent the aerosol organic properties in air masses originating from boreal forests. An exception for the urban-influenced periods was Aug. 19, where the total mass concentration was only about 2.65 µg m$^{-3}$ for the BL layer, even though the mass fractions of each aerosol component measured on August 19 were similar to other days (Table 5.S3). The lower total mass concentration in the BL layer on August 19 compared to other urban-influenced periods was likely due in part to wet removal resulting from a heavy rain event that occurred on the evening of August 18 (Fig. 5.S9). It is worth noting that the Ozone Mapping Profiler Suite (OMPS) images showed measurable smoke aerosol in the air column above Whiteface on August 21, and that day yielded the highest measured mass concentrations of the campaign (Fig. 5.S10).

Figure 5.3 shows the average aerosol mass concentration and mass fraction for each layer during the urban-influenced In-Cloud days (Aug. 15, 18 and 19). As Fig. 5.3 shows, the average aerosol mass concentrations of TL and BL were similar (3.96 vs. 3.90 µg m$^{-3}$), and larger than the average aerosol mass concentration of IL (1.76 µg m$^{-3}$), consistent with the activation/incorporation of the ambient aerosol into cloud droplets in IL. The mass fractions of organics and NH$_4$ were stable over all three cloud layers, with average values of 73% and 7%, respectively, while SO$_4$ had the highest mass fraction in the BL layer (18%) (Fig. 5.3 and Table 5.S3). Meanwhile, NO$_3$ had a greater mass fraction in the IL and TL layers (about 6%) compared to the BL layer (about 2%) (Fig. 5.3 and Table 5.S3). Additionally, the NO$_3$ mass concentration of the IL layers during urban-influenced periods were higher than those during biogenic-influenced periods (0.11 µg m$^{-3}$ vs. 0.05 µg m$^{-3}$, 219
Table 5.3). This may be partially attributable to (1) elevated NO$_x$ concentrations resulting from the air masses passing through the urban areas, and (2) NO$_x$ reacting to form additional NO$_3$ under high RH conditions.

### 5.3.2.2 Size distributions

Figure 5.4a shows the average aerosol number size distribution in each layer (IL, TL, and BL) during urban-influenced periods corresponding to two In-Cloud days (August 15 and August 18) and one clear day (August 22). The TL and BL aerosols show a bi-modal size distribution, with a larger (accumulation) mode of about 150 nm and a smaller (Aitken) mode of about 60 nm (Fig. 5.4a). These two size modes are comparable to those reported by several previous mountaintop cloud experiments$^{16,18}$. Here, August 19 was not included in the size distribution averaging due to its unusual BL size distribution, as shown in Fig. 5.4b. Specifically, the August 19 BL size distribution shows a sharp decrease in accumulation-mode aerosol. Such a reduction in accumulation-mode aerosol was likely due in part to wet removal resulting from the aforementioned August 18 evening rain event.

**Figure 5.4.** The average aerosol number size distribution of each layer (a) for the urban influenced period (August 15 and August 18) and one clear day (August 22) and (b) on August 19, 2017.
The IL and IL_center size distributions on August 19 shows that aerosol number started to sharply decrease at mobility sizes of 50 nm and above (Fig. 5.4b), which suggests that 50 nm may be the minimum size required for the activation of aerosols to cloud droplets under supersaturated conditions on this day at Whiteface Mountain. Additionally, when the height of the cloud base increased, the sample inlet went through IL_center to BL, leading to a shift in the measured aerosol size distribution towards larger particles. Furthermore, a comparison between IL_center (Fig. 5.4b) and IL_urban (Fig. 5.4a) reveals that the sample inlet during the IL_urban period seemed to only capture the interstitial aerosol in the shallow cloud bottom, instead of all aerosols in the inner part of the cloud. This may partly explain why the larger-mode aerosol size distribution measured during the IL_urban period did not decrease to very low values at a larger aerosol size (i.e., 100 nm). Overall, this phenomenon suggests that future mountain cloud study campaigns should consider the relative distance of the sample inlet to the cloud base to better understand the interstitial aerosol characteristics and aerosol/cloud interactions.

![Figure 5.5](image)

**Figure 5.5.** (a) The HR-ToF-AMS aerosol compounds mass size distribution for organic and SO$_4$ on 08/18/2017 and 08/22/2017; (b) The average SMPS aerosol number size distribution for the biogenic influenced periods.
In contrast to the urban-influenced In-Cloud days presented in Fig. 5.4a, the size distribution of the August 22 clear day was unimodal, with a peak of about 150 nm. This peak was almost identical to the larger aerosol size mode in the BL and TL layers on In-Cloud days, which suggests that the smaller aerosol size mode on In-Cloud days was produced under cloudy conditions at either Whiteface Mountain or the surrounding area. This feature of In-Cloud days was also evident in the aerosol compound mass size distributions (Fig. 5.5a). Figure 5.5a shows an enhanced organic particle mode in the size range of 100-300 nm for the below-cloud aerosol on the August 18 In-Cloud day that was not observed on the August 22 clear day, very possibly indicating newly formed organic aerosols at small sizes. For the biogenic-influenced period, all three days showed a bi-modal shape, with a larger number mode of about 150 nm and a smaller number mode of about 60 nm (Fig. 5.5b). However, it is noteworthy that the August 17 clear day was characterized by a third, even smaller number mode of about 30 nm. In addition, the August 20 aerosol number size distribution revealed a much greater concentration for the large mode compared to the small mode, consistent with aerosols on Aug. 20 being more aged than on Aug. 17 and 23, a suggestion also backed up by the higher oxidation state of Aug. 20 aerosols compared to those measured on Aug. 17 and 23, as shown in the next section.

5.3.2.3 Oxidation state
Figure 5.6. The comparison between $f_{44}$ and $f_{43}$ for LPT-measured aerosol in each cloud layer and clear days (the cloudy Aug. 20 was classified into BL)

One commonly used measure of the oxidation state of organic aerosols measured with the HR-ToF-AMS is the measured mass spectral signal fractions at m/z 43 ($f_{43}$, C$_2$H$_3$O$^+$) and m/z 44 ($f_{44}$, CO$_2^+$)\textsuperscript{84,85}, and these ratios will change as a result of atmospheric oxidation reactions, including aqueous oxidation reactions.\textsuperscript{35} When organic aerosols are oxidized, $f_{44}$ increases while $f_{43}$ decreases. Figure 5.6 shows the $f_{44}$ as a function of $f_{43}$ for LPT-measured aerosol in each layer of the In-Cloud days, as well as the cloudy and clear days. The urban-influenced clear days (Aug. 21 and 22) show higher $f_{44}$ and lower $f_{43}$ than the clear day of the biogenic-influenced period (Aug.17), indicating a lower oxidation state of the biogenic-influenced aerosol and matching the results of Drewnick et al. (2007), that the large fraction of organics seemed to be slightly less oxidized due to relatively freshly generated organic aerosol from the forest\textsuperscript{2}. On a given day and among the different layers, the LPT-measured aerosol of IL and TL layers reveal similar $f_{44}$ and $f_{43}$, with slightly higher $f_{44}$ and lower $f_{43}$ for the BL layer aerosols. For the urban-influenced periods, a lower oxidation state was observed for the In-Cloud days (Aug. 15, 18, 19, $f_{44}$: 0.11-0.12) than the clear days (Aug. 21
(f_{44}: 0.17) and 22 (f_{44}: 0.15)), supporting the possibility that there was new organic formation in BL layers under cloudy conditions (Fig. 5.5b). Another possibility is that the larger size aerosols with higher oxidation state (that is, those that have experienced oxidative aging over long distance transport) have been previously cloud-processed. Interestingly, these conditions seem reversed for the biogenic-influenced periods, with higher oxidation state for the In-Cloud days (Aug. 23) and Cloudy (Aug. 20) than the clear day (Aug. 17), which may be related with relatively shorter back trajectories for Aug. 17 (Fig. 5.S8b) which are consistent with fresher ambient aerosol. At the same time, the lowest oxidation state was shown for Aug. 18, whose very low layer (below 1000 AMSL, Fig. 5.S8i) back trajectories were short and stayed in the near-surface layer, consistent with regional, freshly emitted aerosol transported to the WFM area. Excluding the organics of Aug. 21 and 22 with higher f_{44}, the other points were at a medium level of f_{44} and appeared in the upper part of the semi-volatile oxygenated organic aerosol (LV-OOA) region, which represents less oxidized and less photochemically aged organics.84,85

5.3.2.4 Cloud Condensation Nucleus (CCN) activity

Measured size-resolved CCN activation curves showed that the aerosol was internally-mixed with d_{50} ranging from 43nm (at 0.76% SS on Aug 22) to 126nm (at 0.23% SS on Aug 17) for the eight days that the ASRC Sprinter Van was deployed at the LPT. See Fig. 5.S11 for a summary of the full suite of CCN measurements during this period. d_{50} values observed at a given instrument supersaturation are shown in Fig. 7 for comparison to κ-Kohler theory.80 The hygroscopicity parameter κ ranged from 0.13 to 0.33, with the highest values (0.27-0.33) observed on the two urban-influenced days with the highest sulfate mass loadings (Aug 21 and 22, Fig. 5.7a). For the other three urban-influenced days (Aug 15, 18 and 19) κ varied between 0.13 and 0.19. On the three biogenic-influenced days (Fig. 5.7b) κ was between 0.14 and 0.18, except at the lowest
instrument supersaturation on Aug 20 and 23 when $\kappa$ was 0.23-0.25, indicating an increase in hygroscopicity with particle size on those two days.

**Figure 5.7.** Summary of the measured $d_{50}$ versus instrument supersaturation for a) urban-influenced days and b) biogenic-influenced days.

Low $\kappa$ values (< 0.15) as observed during the biogenic-influenced days are expected for the very high organic mass fractions observed (> 0.85), as shown by previous studies in other remote forested environments, e.g. in Germany, Finland and Japan$^{20,86,87}$. The increased $\kappa$ values for particle sizes $> \sim 80$nm (corresponding to critical supersaturations $\sim 0.23\%$) observed during CPOC on two of the biogenic-influenced days (Aug 23 and Aug 20) is also consistent with observations from many other remote sites$^{20,28,87,88}$ and may be attributed to accumulation of secondary inorganic compounds (sulfates and nitrates) in larger particles during cloud processing. This suggests that observations from the other biogenic-influenced day during the CPOC pilot study (Aug 17), which had the highest organic mass fractions (0.93) and lowest $\kappa$ values (0.13), even at the lowest supersaturation probed (0.23%), experienced the least amount of cloud processing of the three biogenic-influenced aerosols sampled during CPOC. The nearly negligible nitrate concentrations and relatively low O:C ratio observed on Aug 17 support this hypothesis (see Tables
Figure 5.8. Average hygroscopicity parameter attributed to the organic fraction ($\kappa_{\text{org}}$) versus a measure for the organic oxidation state for each day of ambient observations at WFM during the CPOC pilot study, using the O:C parameterization from Aiken et al. (2008)\textsuperscript{73} (“Aiken-Ambient”, dark blue) and a modified O:C parameterization from Canagaratna et al. (2015)\textsuperscript{74} (“Improved-Ambient”, red). For comparison, observations from Ontario (light blue), and linear fits to observations from Mexico City and Jungfraujoch (green) and Germany (black) are also included, which were based on the original “Aiken-Ambient” parameterization.

The southeastern U.S. frequently exhibited higher $\kappa$ values (0.1-0.4)\textsuperscript{81} than observed during the CPOC pilot study, but organic mass fractions were also typically higher during CPOC. The average $\kappa_{\text{org}}$ for ambient non-denuded samples in the southeastern U.S. was comparable to the current study at similar O:C ratios (i.e. $\kappa_{\text{org}} \sim 0.15$ at O:C $\sim 0.55$). Cerully et al. (2015) found that $\kappa_{\text{org}}$ increased during the day from $\sim$0.14 in the early morning, peaking at $\sim$0.16 in the early evening\textsuperscript{81}. We were not able to assess diurnal changes in aerosol hygroscopicity in the current study due to the short (2-3 hr) deployments of the mobile laboratory. But, most of the below-cloud observations during CPOC occurring during the late morning and early afternoon, suggesting that our observations of
κorg (0.08-0.22) may have been about average for the day81. Figure 5.8 shows κorg as a function of the measured O:C ratio for the CPOC study (O:C ratio is calculated based on “Aiken-Ambient” method73 and “Improved-Ambient” method74 with values for each day listed in Table S1), in comparison to several previous ambient studies in Germany28, Ontario26, Jungfraujoch and Mexico City27. Using the “Aiken-method”, which was also used for the previous studies26-28, our observations show a steeper slope than most of these previous studies, and a steeper slope than SOA formed in chamber studies27,89, with best agreement found with the observations from Ontario (binned by O:C ratio in increments of 0.25 in Fig. 5.8), suggesting that regional difference in biogenic emissions may be important. It should be noted that values for κorg in most of these previous studies were obtained using measurements of aerosol hygroscopicity at < 100% RH, which have been found to be lower than κorg derived from CCN measurements90. The observations from Ontario were obtained using CCN measurements26. It should also be noted that the observations from Chang et al. (2010)26 were highly variable, with many negative values for κorg, which may suggest an influence from non-hygroscopic refractory material such as black carbon or other measurement biases. The linear fit plotted in Fig. 5.8 for the observations from Ontario includes an offset [κorg = (0.9±0.5)(O/C) −(0.3±0.2)], which Chang et al. (2010) was reluctant to provide due to this uncertainty26. Also note that for two of the urban-influenced days during CPOC (Aug 15 and Aug 19), κorg was zero or slightly less than zero, which also may suggest an influence from non-hygroscopic refractory material in the solute volume fraction calculations for the CPOC pilot study. Linear fits to the κorg versus O:C ratio are provided in Fig. 5.8, which do not include these two days. Co-located observations of black carbon aerosol should be added for future studies, to improve the solute volume fraction calculations and obtain a more robust assessment of κorg. Another hypothesis is that the O:C ratio for these two days (Aug 15 and 19) is better represented
by the original “Aiken-Ambient” parameterization\textsuperscript{73}, while all other days are better represented by the “Improved-Ambient” parameterization\textsuperscript{74}. When combined, these assumptions yield a highly correlated linear fit ($R^2 = 0.98$) for all of the CPOC observations: [$\kappa_{\text{org}} = (0.75\pm0.03)\cdot(O/C) – (0.37\pm0.04)$]. Since negative O:C ratios are unphysical, this may suggest that the organic compounds with O:C ratio $<~0.5$ (as appear to better describe the Aug 15 and 19 organic aerosol) do not contribute significantly to the aerosol hygroscopicity.

Estimates for $\kappa_{\text{org}}$ of 0.11 to 0.13 are used in modeling studies for most of the U.S.\textsuperscript{91}, but $\kappa_{\text{org}}$ may extend to values $>0.15$ and even $>0.2$ at remote sites that receive extremely aged airmasses or when oxidation proceeds rapidly to produce O:C ratios $>0.65$, as during the latter half of the CPOC pilot study (which were characterized both as biogenic-influenced and urban-influenced). Though these differences in $\kappa_{\text{org}}$ are minor when compared to the hygroscopicity of sulfate or nitrate aerosol, the dominance of organic aerosol mass observed during the current study suggests that these differences can be important for water uptake by aerosols and subsequent chemical reactivity, in addition to the optical properties and fate of the aerosol.

5.4. Conclusion

The ASRC mobile lab (containing a HR-ToF-AMS, a SMPS, a CPC, and a CCNc) was used to measure the physical and chemical properties of below-cloud aerosol and interstitial aerosol during the CPOC pilot study carried out at Whiteface Mountain from August 15-23, 2017. Measurements on In-Cloud days (August 15, 18, 19, and 23) revealed a stratified atmosphere with a below-cloud layer, a transition layer, and an in-cloud layer. The transition layer likely represented the edge region of the cloud, with a depth of around 160 meters. The high RH ($\sim100\%$) of the transition layer provided conditions suitable for aqueous reactions, and this transition layer could potentially be incorporated into regional cloud-processing models to better simulate the conditions.
The aerosol’s original sources and subsequent evolution will determine its properties during cloud formation, with clearly enhanced nitrate aerosol in transition layers of urban-influenced clouds compared to the biogenic-influenced periods, the latter showing a much higher organic mass fraction (83-93%). These two clusters of air mass back-trajectories are typical for the Whiteface Mountain area, and these measurements provide useful information for atmospheric models to better simulate the aerosol-cloud interaction and cloud processing applicable to Whiteface Mountain and other mountainous regions in the northeastern U.S. In addition, the methodology presented in this study could be carried out at other mountaintop locations that are frequently in cloud.

ACKNOWLEDGMENTS

This work has been supported by the New York State Energy Research and Development Authority (NYSERDA) contract number 48971 and National Science Foundation (NSF) RAPID grant contact number 1753278. Special thanks go to Paul Casson and the rest of the Whiteface CPOC team, research scientist David Fitzjarrald for providing the ASRC portable weather station data, Guoxing Chen for assistance with the analysis, and Wei-Ting Hung for providing the OMPS Aerosol Index map.
5.5 Reference


5.6 Supplement

Figure 5.S1. The experiment diagram for the mobile lab measurement at LPT.
Figure 5.S2. The time series of the cloud base height for In-cloud days (Aug. 15 (a), 18 (b), 19 (c), 23 (d). The grey dash line indicates the height of LPT)
Figure 5.S3. (a) The original schematic used for identifying the height of the cloud base at Whiteface Mountain and (b) the enlarged schematic.
In contrast to the urban influenced cloud days (August 15, 18, and 19, in section 3.2.1), the biogenic influenced cloud day (August 23) did not show clearly elevated NO$_3^-$ mass concentrations in the transition layer and in-cloud layer. The elevated NO$_3^-$ mass concentrations in the transition and in-cloud layers during the urban-influenced cloud days may be due in part to NO$_x$ reacting to form more particle NO$_3^-$ under high RH.
Figure 5.S5. The webcam images of time points for separating TL layer and IL layer (TL/IL, left) and TL layer and BL layer (TL/BL, right) on the four cloud days.
Figure 5.S6. The time series of organic NO\textsubscript{3} and inorganic NO\textsubscript{3} during the LPT measurement period.

Using the organic nitrate calculation method\textsuperscript{1}, the NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} ratio for ammonium nitrate (value of 2.1 based on IE calibration) and organic nitrate (value taken to be 7), the organic and inorganic nitrate were calculated. Matching the results shown in section 3.2.1 and Fig. S5, the urban influenced periods (August 15, 18, 19, 21, 22) show higher NO\textsubscript{3} and inorganic NO\textsubscript{3} mass concentration than on August 17, 20, and 23 (biogenic influenced periods).
Figure 5.S7. Calculated ammonium (assuming full neutralization of nitrate and sulfate) vs. measured ammonium of aerosol in TL and IL layers on cloud days.
Figure 5.8. The HYSPLIT back trajectories for (a)-(h) the LPT measurement days with ending heights of 1000 m, 1250 m, and 1500 m AMSL (above the mean sea-level); (i) 08/18/2017 with
ending heights of 500m, 750m, and 1000m AMSL. For the HYSPLIT system, the “ground level” of the grid square which contains Whiteface Mountain and the Lake Placid Turn is 474 m AMSL. This means that the AGL altitude of 525 (+/- 3m) corresponds to a height of approximately 1000 m AMSL, etc.
Figure 5.S9. The LPT meteorological parameters, with relative humidity (%), temperature, wind direction, wind speed, and precipitation from 2017/08/17 to 2017/08/24.
Figure 5.S10. The Ozone Mapping Profiler Suite (OMPS) measured aerosol index on 08/21/2017. Positive AI (~2) was observed over northern NYS on Aug 21, which indicated the presence of absorbing aerosols, most likely due to wildfire smoke plumes.
Figure 5.S11. Measured CCN and CN concentrations on all days that the Sprinter Van was deployed for the CPOC pilot study. Biogenic-influenced days are highlighted in green. The measurements shown here do not include any corrections for inlet transmission efficiency or particle charging efficiency that would be necessary to infer the ambient particle size distribution, but rather show the observations used to infer the CCN active fraction as a function of dry particle diameter.
**Table 5.S1.** Measured organic mass fraction ($m_{org}$), hygroscopicity parameter ($\kappa$) at 0.6% nominal supersaturation (~0.51% actual supersaturation), calculated $\kappa_{org}$ based on assumed organic density of 1.44 g/mL, and the measured O:C ratio following Aiken et al. (2008)\(^3\) and Canagaratna et al. (2015)\(^4\). Biogenic-influenced days are signified by green text.

<table>
<thead>
<tr>
<th></th>
<th>$m_{org}$</th>
<th>$\kappa$ (at 0.6% SS)</th>
<th>$\kappa_{org}$</th>
<th>O:C (Aiken)</th>
<th>O:C (Canagaratna)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aug 15</td>
<td>0.68</td>
<td>0.162</td>
<td>0</td>
<td>0.50</td>
<td>0.64</td>
</tr>
<tr>
<td>Aug 17</td>
<td>0.93</td>
<td>0.135</td>
<td>0.11</td>
<td>0.46</td>
<td>0.60</td>
</tr>
<tr>
<td>Aug 18</td>
<td>0.75</td>
<td>0.188</td>
<td>0.08</td>
<td>0.46</td>
<td>0.61</td>
</tr>
<tr>
<td>Aug 19</td>
<td>0.70</td>
<td>0.135</td>
<td>-0.02</td>
<td>0.45</td>
<td>0.66</td>
</tr>
<tr>
<td>Aug 20</td>
<td>0.93</td>
<td>0.173</td>
<td>0.15</td>
<td>0.53</td>
<td>0.68</td>
</tr>
<tr>
<td>Aug 21</td>
<td>0.78</td>
<td>0.289</td>
<td>0.22</td>
<td>0.60</td>
<td>0.78</td>
</tr>
<tr>
<td>Aug 22</td>
<td>0.66</td>
<td>0.284</td>
<td>0.15</td>
<td>0.54</td>
<td>0.69</td>
</tr>
<tr>
<td>Aug 23</td>
<td>0.85</td>
<td>0.154</td>
<td>0.09</td>
<td>0.50</td>
<td>0.62</td>
</tr>
</tbody>
</table>
Table 5.2. The time periods for each layer of the in-cloud days

<table>
<thead>
<tr>
<th>Location</th>
<th>Aug.15</th>
<th>Aug.18</th>
<th>Aug.19</th>
<th>Aug.23</th>
</tr>
</thead>
<tbody>
<tr>
<td>In-Cloud center</td>
<td>n/a</td>
<td>n/a</td>
<td>13:15-14:05</td>
<td>n/a</td>
</tr>
<tr>
<td>(IL_center)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>In-Cloud Layer (IL)</td>
<td>10:40-11:05</td>
<td>12:00-13:05</td>
<td>14:05-15:00</td>
<td>09:20-10:00</td>
</tr>
<tr>
<td>Transition Layer (TL)</td>
<td>11:05-11:30</td>
<td>13:05-13:25</td>
<td>15:00-15:25</td>
<td>10:00-10:30</td>
</tr>
<tr>
<td>Below Cloud Layer (BL)</td>
<td>11:30-12:00</td>
<td>13:25-13:55</td>
<td>15:25-16:00</td>
<td>10:30-11:00</td>
</tr>
</tbody>
</table>
Table 5.S3. The mass concentration (µg m\(^{-3}\)) and mass fraction of the aerosol compounds of each layer of the cloud days (UI: urban influenced days; BI: biogenic influenced days; Cle.: clear day; Cdy: cloudy day)

<table>
<thead>
<tr>
<th>µg m(^{-3}) (µg m(^{-3})) (%)</th>
<th>IL 08/15 (UI)</th>
<th>TL 08/15 (UI)</th>
<th>BL 08/15 (UI)</th>
<th>Cle. 08/17 (UI)</th>
<th>IL 08/18 (UI)</th>
<th>TL 08/18 (UI)</th>
<th>BL 08/18 (UI)</th>
<th>IL 08/19 (UI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org</td>
<td>2.83 (68%)</td>
<td>3.59 (69%)</td>
<td>3.24 (68%)</td>
<td>3.19 (93%)</td>
<td>2.75 (75%)</td>
<td>4.18 (75%)</td>
<td>3.98 (75%)</td>
<td>0.47 (68%)</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>0.24 (6%)</td>
<td>0.16 (3%)</td>
<td>0.08 (2%)</td>
<td>0.02 (1%)</td>
<td>0.26 (7%)</td>
<td>0.23 (4%)</td>
<td>0.11 (2%)</td>
<td>0.06 (9%)</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>0.73 (18%)</td>
<td>1.05 (20%)</td>
<td>1.05 (22%)</td>
<td>0.13 (4%)</td>
<td>0.41 (11%)</td>
<td>0.80 (14%)</td>
<td>0.83 (16%)</td>
<td>0.10 (9%)</td>
</tr>
<tr>
<td>NH(_4)</td>
<td>0.33 (8%)</td>
<td>0.42 (8%)</td>
<td>0.39 (8%)</td>
<td>0.07 (2%)</td>
<td>0.24 (7%)</td>
<td>0.39 (7%)</td>
<td>0.36 (7%)</td>
<td>0.06 (8%)</td>
</tr>
<tr>
<td>Cl</td>
<td>0.02 (~)</td>
<td>0.01 (~)</td>
<td>0.01 (~)</td>
<td>0.01 (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>0.01 (~)</td>
</tr>
<tr>
<td>Total</td>
<td>4.17 5.24</td>
<td>4.77 5.62</td>
<td>3.42 5.30</td>
<td>0.69</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>µg m(^{-3}) (µg m(^{-3})) (%)</th>
<th>TL 08/19 (UI)</th>
<th>BL 08/19 (UI)</th>
<th>Cdy 08/20 (BI)</th>
<th>Cle. 08/21 (UI)</th>
<th>Cle. 08/22 (BI)</th>
<th>IL 08/23 (UI)</th>
<th>TL 08/23 (BI)</th>
<th>BL 08/23 (BI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org</td>
<td>1.54 (70%)</td>
<td>1.60 (71%)</td>
<td>3.10 (93%)</td>
<td>5.20 (78%)</td>
<td>4.31 (66%)</td>
<td>1.46 (83%)</td>
<td>1.96 (85%)</td>
<td>1.94 (85%)</td>
</tr>
<tr>
<td>NO(_3)</td>
<td>0.10 (5%)</td>
<td>0.04 (2%)</td>
<td>0.02 (1%)</td>
<td>0.06 (1%)</td>
<td>0.07 (1%)</td>
<td>0.05 (3%)</td>
<td>0.03 (2%)</td>
<td>0.02 (1%)</td>
</tr>
<tr>
<td>SO(_4)</td>
<td>0.38 (17%)</td>
<td>0.44 (19%)</td>
<td>0.13 (4%)</td>
<td>0.99 (15%)</td>
<td>1.55 (24%)</td>
<td>0.16 (9%)</td>
<td>0.22 (9%)</td>
<td>0.22 (10%)</td>
</tr>
<tr>
<td>NH(_4)</td>
<td>0.18 (8%)</td>
<td>0.18 (8%)</td>
<td>0.07 (2%)</td>
<td>0.41 (6%)</td>
<td>0.57 (9%)</td>
<td>0.08 (5%)</td>
<td>0.10 (4%)</td>
<td>0.09 (4%)</td>
</tr>
<tr>
<td>Cl</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
<td>~ (~)</td>
</tr>
<tr>
<td>Total</td>
<td>2.21 2.28</td>
<td>3.32 3.66</td>
<td>6.50 6.50</td>
<td>1.76 2.31</td>
<td>2.27</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Reference:


Chapter 6: Concluding Remarks
Among ambient aerosols, secondary organic aerosols (SOA) are major constituents, and are generally formed through gas-to-particle conversion. Despite recent advances, there still exists great uncertainty in the understanding of the detailed formation of SOA, as well as its evolution under different atmospheric conditions. From urban to mountain locations, these atmospheric aerosols undergo both simple and more complicated transformation and evolution under a wide variety of physical and chemical conditions, and relatively few detailed observational studies have been carried out in the northeastern US, which has a wide variety of environments.

This dissertation focused on 1) the influence of extreme conditions (including high O$_3$, heat wave, and firework displays) on urban aerosol properties, 2) fog processing on rural forest secondary organic aerosol, and 3) cloud processing on the mountain-top aerosol, and attempts to use these studies to build a more general picture of aerosol formation and characteristics in the northeastern US.

With regards to the urban NYC metro area, it was observed that the sea breeze was able to cause rapid spatial variations in O$_3$ concentration, and contribute to O$_3$ exceedances (with O$_3$ concentrations over 100 ppb) as well as contributing to enhanced aerosol mass concentration with higher oxidation state. This extreme pollution pattern was seen to stagnate at the Long Island southern shore area for several hours, and not regularly reported and therefore prone to be ignored by the public. However, it could be very harmful for people on the beach, and should be a cause for concern. Also, on Long Island in the NYC metro area the co-occurrence of extremes in surface ozone, particulate matter, and temperature during the period from June 29 to July 4, 2018 provided a chance to study the aerosol evolution during this extreme heat wave event. Significantly enhanced aerosol concentrations were observed with maximum daily value of roughly 32 µg m$^{-3}$. Two main influences on this pollution were observed, the first was regional in character and
involved the direct photo-oxidation of anthropogenic VOC, and this influence seemed to dominate the aerosol evolution in the whole upstate area concurrent with the high temperatures. The second influence was unique to the NYC metro area and involved further reaction and formation of in the ocean surface boundary layer (including DMS oxidation), and the transport via sea breeze of these highly oxidized aerosols back onto Long Island and other parts of the metro area. These results revealed detailed aerosol evolution and processing during this heat wave influenced period in NYC, which could provide clues for other urban areas with similar conditions, especially other areas influenced by the sea breeze and anthropogenic emissions. The observations of urban areas and extreme events conclude with a study of aerosol emissions from a fireworks event in Albany, NY in 2017. The strongly elevated potassium (K) signal in the HR-ToF-AMS mass spectra during the FW periods indicated the presence of K-rich materials in the FW aerosol plumes mostly associated with K\textsubscript{2}SO\textsubscript{4}. A FW-related oxidized organic aerosol factor (FW-OOA) was identified during the most intense FW event of the measurement period. The sum of the potassium salts and FW-OOA factor mass concentrations revealed that 77% of the aerosol mass within the FW plume was associated with FW emissions. Pollution from FW events may be more severe and harmful to nearby area residents in communities with larger FW displays under comparatively calm atmospheric conditions, which are usually when these FW events occur, as rain or high winds will typically result in a postponement of the FW displays.

For the rural forested area (PSP) and foggy conditions, our observations and analysis identified two fresh biogenic secondary organic aerosol factors (BSOA: BSOA-1 and BSOA-2); BSOA-1 was hypothesized to have formed through the nighttime reaction of biogenic volatile organic precursors with NO\textsubscript{3} radical, and compounds making up this factor were then further converted to BSOA-2 through fragmentation or greater oxidation. During fog processing, the more oxidized
oxygenated organic aerosol (MO-OOA) showed the highest uptake into fog droplets, or scavenging efficiency (90%), followed by SO$_4^{2-}$ (50%), the less oxidized OOA (LO-OOA) (45%), and BSOAs (BSOA-1+BSOA-2, 24%). At the same time, the post-fog aerosol mass concentration was higher (12%) than the concentration observed during the pre-fog period, with enhanced concentrations of LO-OOA and BSOA more than making up for reductions in MO-OOA. High positive correlation between relative humidity (RH)/or aerosol liquid water (ALW) and BSOA mass concentration suggests the importance of aqueous-phase processing on BSOA formation, and an increase in the ALW mass fraction of 0.1 corresponded to an average increase of 0.2 μg m$^{-3}$ in the BSOA factors.

The work concludes with observations of below cloud and in cloud aerosols very near the ASRC observatory at Whiteface Mountain (WFM) in Wilmington, NY. Measurements on days that included In-Cloud periods (August 15, 18, 19, and 23) revealed a stratified atmosphere with a below-cloud layer, a transition layer, and an in-cloud layer. The transition layer likely represented the edge region of the cloud, with a depth of around 160 meters. The high RH (~100%) of the transition layer provided conditions suitable for aqueous reactions, and this transition layer could potentially be incorporated into regional cloud-processing models to better simulate the conditions. The aerosol’s original sources and its evolution leading up to cloud incorporation will determine its properties during cloud formation, and observations clearly enhanced nitrate aerosol in transition layers of urban-influenced clouds compared to the biogenic-influenced periods, while the latter showed a much higher organic mass fraction (83-93%). These two clusters of air mass back-trajectories (urban and biogenic influenced) are typical for the Whiteface Mountain area, and these measurements provide useful information for atmospheric models to better simulate the aerosol-cloud interaction and cloud processing applicable to Whiteface Mountain and other
mountainous regions in the northeastern U.S. In addition, the methodology presented in this study could be carried out at other mountaintop locations that are frequently in cloud.

Due to reduced sulfate and nitrate mass loadings, the aerosol organic compounds have become more and more important, and this is also reflected in the aerosol mass fraction from different locations, as shown in Fig. 6.1. From urban to rural, and to remote mountain, the aerosol mass concentration is decreasing, while the organic mass fraction is increasing. Long term continuous measurements need to keep focused on these trends. In addition, the influence of the sea breeze circulation and extreme events like heatwaves on the air quality are also cause for attention and concern, and further work along these lines is needed. Finally, additional studies including field measurements in other regions that include more comprehensive suites of target species, air quality simulations and human health studies are warranted, to provide clear guidance on FW aerosol pollution for other U.S. and foreign cities.

![Figure 6.1. The aerosol mass concentration and mass fraction for different locations in NY state.](image)
Appendix