

# Carnegie Mellon University

CARNEGIE INSTITUTE OF TECHNOLOGY

## THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF Doctor of Philosophy

TITLE Formation and Chemical Aging of Atmospheric Carbonaceous Aerosol

PRESENTED BY Antonios Tasoglou

ACCEPTED BY THE DEPARTMENT OF

Chemical Engineering

S. PANDIS

8/29/16

S. PANDIS, ADVISOR

DATE

L. BIEGLER

8/29/16

LORENZ BIEGLER, DEPARTMENT HEAD

DATE

APPROVED BY THE COLLEGE COUNCIL

VIJAYAKUMAR BHAGAVATULA

8/29/16

DEAN

DATE

# **FORMATION AND CHEMICAL AGING OF ATMOSPHERIC CARBONACEOUS AEROSOL**

**Antonios Tasoglou**

Center for Atmospheric Particle Studies

Department of Chemical Engineering

Carnegie Mellon University

Pittsburgh, Pennsylvania

August 2016

*In partial fulfillment of the requirements for the Ph.D. degree in Chemical Engineering*

*To*  
*Spyridon and Aikaterini*  
*and*  
*Ioannis*

## Abstract

Atmospheric aerosols can cause serious human health problems and are also affecting the energy balance of our planet contributing to climate change. Organic aerosol (OA) is the most diverse and least understood component of submicron aerosols, in part because of a wide variety of biogenic and anthropogenic sources as well as contributions from both direct emission and secondary formation in the atmosphere. Air quality models often seriously under-predict the concentration of OA in the atmosphere due mainly to our lack of understanding of the atmospheric chemical and physical processing of the emitted organic compounds. A series of experimental studies were performed to address some of the major questions regarding atmospheric OA.

In the first phase of the work, the secondary organic aerosol (SOA) production during the oxidation of  $\beta$ -caryophyllene by ozone ( $O_3$ ) and hydroxyl radicals (OH) and the subsequent chemical aging of the products during reactions with OH were investigated. Experiments were conducted with ozone, hydroxyl radicals at low  $NO_x$  (zero added  $NO_x$ ) and at high  $NO_x$  (100s of ppb). The SOA mass yield at  $10 \mu g m^{-3}$  of organic aerosol was 27% for the ozonolysis, 20% for the reaction with OH at low  $NO_x$  and 38% at high  $NO_x$  under dry conditions,  $20^\circ C$ , and ozone excess. Parameterizations of the fresh SOA yields have been developed. The average fresh SOA atomic O:C ratio varied from 0.24 to 0.34 depending on the oxidant and the  $NO_x$  level, while the H:C ratio was close to 1.5 for all systems examined. An average density of  $1.06 \pm 0.1 \mu g m^{-3}$  of the  $\beta$ -caryophyllene SOA was estimated. The exposure to UV-light had no effect on the  $\beta$ -caryophyllene SOA concentration and Aerosol Mass Spectrometer (AMS) mass spectrum. The chemical aging of the produced  $\beta$ -caryophyllene SOA was studied by exposing the fresh SOA to high concentrations ( $10^7$  molecules  $cm^{-3}$ ) of OH for several hours. These additional reactions

increased the SOA concentration by 15-40% and the O:C by approximately 25%. A limited number of experiments suggested that there was a significant impact of the relative humidity on the chemical aging of the SOA. The evaporation rates of  $\beta$ -caryophyllene SOA were quantified by using a thermodenuder allowing us to estimate the corresponding volatility distributions and effective vaporization enthalpies.

In the second step the accuracy of continuous black carbon measurements of a series of commercially available instruments was assessed for biomass burning particulate matter. Black carbon-containing particles are the most strongly light absorbing aerosols in the atmosphere. They are emitted during the combustion of fossil fuels, biofuels, and biomass. Measurements of black carbon are challenging because of its semi-empirical definition based on physical properties and not chemical structure, the complex and continuously changing morphology of the corresponding particles, and the effects of other particulate components on its absorption. In this study we compare six available commercial continuous BC instruments using biomass burning aerosol. The comparison involves a Soot Particle Aerosol Mass Spectrometer (SP-AMS), a Single Particle Soot Photometer (SP2), an aethalometer, a Multiangle Absorption Photometer (MAAP), and a blue and a green photoacoustic extinctions (PAX). An SP-AMS collection efficiency equal to 0.35 was measured for this aerosol system. The SP-AMS was then compared to all the other commercial instruments. Two regimes of behavior were identified corresponding to high and low organic/black carbon ratio. New mass absorption cross sections (MAC) were calculated for the optical instruments for the two regimes. The new MAC values varied from 30% to 2.3 times the instrument default values depending on the instrument and the regime. This comparison of the optical instruments suggests a stronger discrepancy among the BC measurements as the organic carbon content of the BC-containing particles increases.

In the next step we focused on the chemical aging of combustion emissions. Smog chamber experiments were conducted to study the changes of the physical properties and chemical composition of biomass burning particles as they evolve in the atmosphere. A Soot Particle Aerosol Mass Spectrometer (SP-AMS) and a Single Particle Soot Photometer (SP2) were used for the chemical characterization of the particles. An Aethalometer as well as a green and a blue photoacoustic extinctionmeter (PAX) were used for the study of the aerosol optical properties. As the biomass burning smoke aged, exposed to UV light, ozone, or OH radicals, organic material condensed on the preexisting particles. This coating led to an increase of the absorption of the black carbon-containing particles by as much as a factor of two. The absorption enhancement of biomass burning particles due to their coating with aromatic secondary organic aerosol (SOA) was also studied. The resulting absorption enhancement was determined mainly by the changes in the SOA mass concentration and not the changes of its oxidation state. The enhancement of the absorption of the aging biomass burning particles was consistent with the predictions of a core-shell Mie theory model assuming spherical particles and non-absorbing coating.

In the last phase of the work emissions from cooking activities were studied. Cooking organic aerosol (COA) is a significant fraction of the total fine aerosol in urban areas around the world. COA chemical aging experiments took place in a smog chamber in the presence of UV light or in excess of ozone. Positive matrix factorization was used to characterize the changes in the chemical composition of the COA during the chemical aging. The chemical composition of the produced aged COA was similar for both aging methods. The chemical aging processes cause an increase of the organic mass and its oxidation state. The fresh COA particles have a low CCN activity but their activity increases significantly as they chemically age.

## Acknowledgements

This thesis is dedicated to my parents, Spyridon Tasoglou and Aikaterini Kantiotou, for their unconditional love and support, and to my grandfather Ioannis Kantiotis who urged me to follow my dream and pursue a PhD degree in the United States.

I owe my deepest gratitude to my advisor, Prof. Spyros Pandis, for all his support and mentorship during my undergraduate and graduate studies. This dissertation would not have been possible without him.

I would like to acknowledge my advisory committee members, Professors Neil Donahue, Allen Robinson, Ignacio Grossmann and Ryan Sullivan who guided me during my PhD research. I would also like to thank Prof. Peter Adams for his great air pollution classes that gave me valuable insights into atmospheric chemistry.

I would like to thank my friends and colleagues Eleni Karnezi and Ningxin Wang who supported me all these years and shared their wisdom with me.

I was honored to collaborate with many members of the Center of Atmospheric Particulate Studies (CAPS) who trained me and advised me on different research problems that I had to solve as a PhD student. I had inspiring and helpful discussions and collaborations with Prof. Albert Presto, Prof. Eric Lipsky, Prof. Yanwei Li, Dr. R Subramanian, Dr. Rawad Saleh, Dr. Ellis Robinson, Dr. Daniel Tkacik, Dr. Heber Chacon-Madrid, Dr. Andrea Paciga, Dr. Penglin Ye, Georges Saliba, Peishi Gu and Leif Jahn.

It was a great honor for me to collaborate with members of the Laboratory of Air Quality Studies (LAQS) in the University of Patras. I would like to acknowledge Dr. Evangelia Kostenidou, Dr. Michael Pikridas, Dr. Christos Kaltsonoudis, Kalliopi Florou, Evangelos Louvaris, David Patoulas, Ksakousti Skyllakou, and Aikaterini Liangou.

I am grateful to all the graduate students, staff and faculty members of the Chemical Engineering department at Carnegie Mellon University for their help during my studies.

Finally, I would like to thank the US Environmental Protection Agency for the funding of my research.



## Table of contents

|                                                                                                                                       |        |
|---------------------------------------------------------------------------------------------------------------------------------------|--------|
| <b>List of tables</b>                                                                                                                 | ix     |
| <b>List of figures</b>                                                                                                                | x      |
| <b>Chapter 1: Introduction</b>                                                                                                        | 1      |
| 1.1 Atmospheric aerosol                                                                                                               | 2      |
| 1.2 Carbonaceous aerosol                                                                                                              | 3      |
| 1.2.1 Primary organic aerosol (POA)                                                                                                   | 3      |
| 1.2.2 Black carbon (BC)                                                                                                               | 3      |
| 1.2.3 Secondary organic aerosol (SOA)                                                                                                 | 4      |
| 1.3 Chemical aging of OA                                                                                                              | 6      |
| 1.4 Optical properties of aerosol                                                                                                     | 7      |
| 1.5 Cloud condensation nuclei                                                                                                         | 8      |
| 1.6 Overview of the thesis                                                                                                            | 8      |
| 1.7 References                                                                                                                        | 9      |
| <br><b>Chapter 2: Formation and chemical aging of secondary organic aerosol during the <math>\beta</math>-caryophyllene oxidation</b> | <br>14 |
| Abstract                                                                                                                              | 15     |
| 2.1 Introduction                                                                                                                      | 16     |
| 2.2 Experimental methods                                                                                                              | 19     |
| 2.3 Results and discussion                                                                                                            | 24     |
| 2.3.1 Ozonolysis                                                                                                                      | 24     |
| 2.3.2 Oxidation via OH                                                                                                                | 31     |
| 2.3.3 Chemical aging of fresh $\beta$ -caryophyllene SOA                                                                              | 34     |
| 2.3.4 Vaporization enthalpy of $\beta$ -caryophyllene SOA                                                                             | 39     |
| 2.4 Conclusions                                                                                                                       | 40     |
|                                                                                                                                       | vi     |

|                |    |
|----------------|----|
| 2.5 References | 42 |
|----------------|----|

## **Chapter 3: An inter-comparison of black carbon related instruments in a laboratory study of biomass burning aerosol**

|                                          |    |
|------------------------------------------|----|
| Abstract                                 | 50 |
| 3.1 Introduction                         | 51 |
| 3.2 Experimental setup                   | 55 |
| 3.2.1 eBC measurements                   | 55 |
| 3.2.2 rBC measurements                   | 57 |
| 3.2.3 Additional measurements            | 58 |
| 3.3 Experimental results and discussion  | 59 |
| 3.3.1 SP-AMS collection efficiency       | 59 |
| 3.3.2 Inter-comparison of BC instruments | 62 |
| 3.4 Comparison with previous studies     | 67 |
| 3.5 Conclusions                          | 68 |
| 3.6 References                           | 69 |

## **Chapter 4: Absorption of chemically aged biomass burning carbonaceous aerosol**

|                                                              |    |
|--------------------------------------------------------------|----|
| Abstract                                                     | 78 |
| 4.1 Introduction                                             | 79 |
| 4.2 Experimental methods                                     | 82 |
| 4.3 Results and discussion                                   | 86 |
| 4.3.1 Fresh biomass burning emissions                        | 86 |
| 4.3.2 Chemical aging of fresh bbOA                           | 89 |
| 4.3.3 Coating of biomass burning particles with aromatic SOA | 94 |
| 4.3.3.1 Coating with D-Toluene SOA                           | 94 |
| 4.3.3.2 Coating with a mixture of aromatic SOA               | 99 |

|                                                                                                                  |     |
|------------------------------------------------------------------------------------------------------------------|-----|
| 4.3.4 Theoretical analysis                                                                                       | 100 |
| 4.4 Conclusions                                                                                                  | 102 |
| 4.5 References                                                                                                   | 103 |
| <b>Chapter 5: The chemical composition and CCN activity of fresh and chemically aged cooking organic aerosol</b> | 111 |
| Abstract                                                                                                         | 112 |
| 5.1 Introduction                                                                                                 | 112 |
| 5.2 Experimental methods                                                                                         | 114 |
| 5.3 Results and discussion                                                                                       | 116 |
| 5.3.1 SP-AMS collection efficiency and shape of the particles                                                    | 117 |
| 5.3.2 Chemical aging of COA                                                                                      | 118 |
| 5.3.3 COA composition                                                                                            | 122 |
| 5.3.4 CCN activity                                                                                               | 124 |
| 5.4 Conclusions                                                                                                  | 127 |
| 5.5 References                                                                                                   | 128 |
| <b>Chapter 6: Summary and suggestions for future work</b>                                                        | 136 |
| 5.4 Summary                                                                                                      | 137 |
| 5.5 Suggestions for future work                                                                                  | 140 |
| <b>Appendix</b>                                                                                                  | 142 |

## List of Tables

|                                                                                                                                                                                  |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| <b>Table 2.1:</b> Initial conditions and results of the $\beta$ -caryophyllene oxidation experiments                                                                             | 25  |
| <b>Table 2.2:</b> Initial conditions and results of the aging experiments                                                                                                        | 26  |
| <b>Table 2.3:</b> Product mass yields for the three different reactions using a four product volatility basis set                                                                | 30  |
| <b>Table 3.1:</b> Inter-comparison experiments of the BC instruments                                                                                                             | 59  |
| <b>Table 3.2:</b> Initial concentrations of the biomass burning emissions                                                                                                        | 60  |
| <b>Table 3.3:</b> The calculated mass absorption cross-section (MAC) for the two systems                                                                                         | 66  |
| <b>Table 3.4:</b> Comparison of eBC measurements                                                                                                                                 | 66  |
| <b>Table 4.1:</b> Composition of the fresh biomass burning emissions                                                                                                             | 87  |
| <b>Table 4.2:</b> Conditions before and after the chemical aging of the organic aerosol                                                                                          | 94  |
| <b>Table 4.3:</b> Measurements during the chemical aging of the bbOA (first period), formation of the aromatic SOA (second period), and chemical aging of the SOA (third period) | 95  |
| <b>Table 5.1:</b> Composition of the fresh and aged cooking emissions                                                                                                            | 116 |
| <b>Table A.1.1:</b> Initial mode diameters of the biomass burning particles                                                                                                      | 143 |

## List of figures

- Figure 1.1:** Schematic of the direct and indirect cooling effects of atmospheric aerosols. 2
- Figure 1.2:** Schematic of the processing of emissions from biomass burning and the changing BC morphology. 4
- Figure 1.3:** Global average radiative forcing in 2005 (best estimates and 5 to 95% uncertainty ranges) with respect to 1750 (IPCC, 2007). 7
- Figure 2.1:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) for Experiment 1. Also shown, the time when the temperature inside the chamber room was increased. 27
- Figure 2.2:** The SOA yield versus the total mass produced (for  $w=1$ ). The red dots are the results of this study from the unseeded experiments and the black dots are results from the experiments that ammonium sulfate seeds were used. The open symbols are the results of Chen et al. (2012). The solid line is the fitting of the data from both studies using the volatility basis set (VBS) framework. 28
- Figure 2.3:** The SOA yield versus the total mass aerosol produced. The red dots represent the experiments when photolysis of HONO was used as a source of hydroxyl radicals and the black dots are for the photolysis of  $\text{H}_2\text{O}_2$ . The dashed line corresponds to the SOA yield from the ozonolysis of  $\beta$ -caryophyllene. 31
- Figure 2.4:** Comparison of the organic mass spectra of the  $\beta$ -caryophyllene SOA produced from the three reaction systems: 33
- a) From ozonolysis and OH at low  $\text{NO}_x$  ( $\theta=12^\circ$ )
  - b) From OH at high and low  $\text{NO}_x$  ( $\theta=15^\circ$ ).

**Figure 2.5:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) (Experiment 31). The shaded part indicates the period where the UV light was off and the period and the white one when the UV light was on. Also shown, the time when HONO was injected in the chamber. 35

**Figure 2.6:** a) The time series of fragments 43 and 44. b) The ratio of the two fragments as a function of time. c) The oxygen over carbon ratio of the particles as a function of time for Experiment 31. The shaded part indicates the period where the UV light was off and the white one the period when the UV light was on. Also shown, the time when HONO was injected in the chamber. 36

**Figure 2.7:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) (Experiment 35). The shaded part indicates the period where the UV light was off and the white one the period when the UV light was on. Also shown, the time when HONO was injected in the chamber. 38

**Figure 2.8:** The thermograms (mass fraction remaining, MFR as a function of temperature) of the three different reaction systems. The circles represent the experimental data while the lines are the fitting of the model. 40

**Figure 3.1:** a) SP-AMS rBC signal transmission as a function of the wire position during the beam width probe measurements for Experiment 10. The black circles represent the average signal transmission, for 5 different position of the wire compared to the center of the vaporizer, for 1.5 hours of sampling. The red line represents the fitting of the measurements using a 2-D Gaussian distribution. b) Cumulative 2-D Gaussian probability density function. These fractions represent the particles that impact the vaporizer. For distance equal to the radius of the vaporizer the fraction is equal to the  $E_s$ . 61

|                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| <b>Figure 3.2:</b> rBC measurements by the SP-AMS and the SP2 and OA measured by the SP-AMS during Experiment 1. A CE=0.35 is assumed for rBC and CE=1 for the OA.                                                                                                                                                                                                                                  | 62 |
| <b>Figure 3.3:</b> Average size distributions of the biomass burning particles during the first 30 min of the measurements.                                                                                                                                                                                                                                                                         | 63 |
| <b>Figure 3.4:</b> The inter-comparison of the measurements of the rBC by the SP2 and the SP-AMS for Experiments 1 to 5.                                                                                                                                                                                                                                                                            | 64 |
| <b>Figure 3.5:</b> Inter-comparison of the rBC measured by the SP-AMS (corrected for CE=0.35) and the measured eBC from all the optical BC related instruments.                                                                                                                                                                                                                                     | 65 |
| <b>Figure 4.1:</b> The organic AMS spectra of the fresh emissions from the burning of white birch bark (red) and longleaf pine (black).                                                                                                                                                                                                                                                             | 88 |
| <b>Figure 4.2:</b> The measured organic aerosol and black carbon mass concentration in the chamber as a function of time for Experiment 1. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on.                                                                                     | 89 |
| <b>Figure 4.3:</b> The red line represents the oxygen to carbon ratio of the organic aerosol as a function of time for Experiment 1. The black line represents the absorption cross section at 532 nm for the same experiment. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on. | 90 |
| <b>Figure 4.4:</b> The absorption enhancement of the black carbon at 532 nm as a function of time for Experiment 1. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on.                                                                                                            | 91 |

**Figure 4.5:** The mass absorption cross-section (MAC) values as a function of the wavelength for the fresh and aged bbOA emissions. Also shown, the absorption angström exponent (AAE) for the two periods. 92

**Figure 4.6:** Measured organic aerosol and black carbon, and D-toluene concentrations during Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when HONO was injected in the chamber and the UV light was turned on. 96

**Figure 4.7:** The oxygen over carbon ratio of the organic aerosol as a function of time for Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when D-toluene and HONO were injected in the chamber and the UV light was turned on. 97

**Figure 4.8:** The absorption enhancement of the black carbon as a function of time for Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when D-toluene and HONO were injected in the chamber and the UV light was turned on. 98

**Figure 4.9:** The timeseries of the measured organic aerosol and the aromatic VOCs concentration in the chamber for Experiment15. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when HONO was injected in the chamber and the UV light was turned on. 99

**Figure 4.10:** The comparison between the measured  $E_{Abs}$  and the  $E_{Abs}$  predicted by Mie theory for Experiments 1 to 10. 101

**Figure 4.11:** The comparison between the measured  $E_{Abs}$  and the  $E_{Abs}$  predicted by Mie theory for Experiment 11, for all the periods of the experiment. 102



|                                                                                                                                                                                                                                                                                                                                                             |     |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| <b>Figure 5.1:</b> The timeseries of the organic aerosol, black carbon, and ozone concentrations for Experiment 1. The shaded region indicates the period during which the chamber was dark                                                                                                                                                                 | 119 |
| <b>Figure 5.2:</b> The timeseries of the elemental ratios of COA for Experiment 1 calculated using a) Aiken et al. (2008) and b) Canagaratna et al. (2015) methods. The red line represents the oxygen over carbon ratio and the black the hydrogen over carbon ratio of the COA. The shaded region indicates the period during which the chamber was dark. | 120 |
| <b>Figure 5.3:</b> The average mass spectra for the fresh and aged COA.                                                                                                                                                                                                                                                                                     | 122 |
| <b>Figure 5.4:</b> The timeseries of the aged COA fraction of the total COA for all experiments                                                                                                                                                                                                                                                             | 123 |
| <b>Figure 5.5:</b> The average mass spectra of the aged COA retrieved from the PMF analysis for the systems where UV light and ozone injection initiated the chemical aging.                                                                                                                                                                                | 124 |
| <b>Figure 5.6:</b> The activation ratios timeseries for Experiments 1-4 for a) supersaturation equal to 0.2% and b) supersaturation equal to 0.4%.                                                                                                                                                                                                          | 125 |
| <b>Figure 5.7:</b> The activation diameter timeseries for Experiments 1-4 for a) supersaturation equal to 0.2% and b) supersaturation equal to 0.4%.                                                                                                                                                                                                        | 126 |
| <b>Figure 5.8:</b> Average activation diameter before and after the chemical aging of COA for Experiments 1-4 for a) supersaturation equal to 0.2% and b) supersaturation equal to 0.4%.                                                                                                                                                                    | 127 |
| <b>Figure A.2.1:</b> a) The concentration of the VOCs of the pine wood emissions and the white birch bark emission. b) The difference of the VOCs concentration between the emissions from the burning of the two fuels. The emissions from the pine wood have higher organic vapor concentrations with the highest peak at $m/z$ 79 (toluene).             | 144 |

**Figure A.2.2:** The aerosol number size distributions as a function of time for Experiment 11. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber. 145

**Figure A.2.3:** The oxygen over carbon (O:C) ratio of the organic aerosol as a function of time for Experiment 15. The shaded parts indicate the periods when the UV light was off and the white ones the periods when the UV light was on. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber. 146

**Figure A.2.4:** The absorption enhancement of the black carbon as a function of time for Experiment 15. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber. 147

**Figure A.2.5:** Predicted (Mie theory) and observed absorption enhancement,  $E_{Abs}$ , for all three periods of Experiment 12. 148

**Figure A.2.6:** Predicted (Mie theory) and observed absorption enhancement,  $E_{Abs}$ , for all three periods of Experiment 13. 149

**Figure A.3.1:** Comparison of the OA concentration measured using filters (with the OM:OC calculated according to the Aiken et al. (2008) and Canagaratna et al. (2015) algorithms) and the online measurement of the SP-AMS for Experiment 5. 150

**Figure A.3.2:** SEM photographs of COA collected during Experiment 5. 151

**Figure A.3.3:** Measured organic aerosol and black carbon, and ozone concentrations for Experiment 5. 152

**Figure A.3.4:** The timeseries of the elemental ratios of COA for Experiment 5 calculated 153  
using the: a) Aiken et al. (2008) and b) Canagaratna et al. (2015) methods. The red line  
represents the oxygen over carbon ratio and the black the hydrogen over carbon ratio of  
the COA. Also shown the time of ozone injection in the chamber.

**Figure A.3.5:** Number size distributions of the fresh and aged (after 5 hrs of aging) 154  
cooking organic aerosol for Experiments 1-4. Also shown the mode diameters of the  
distributions.

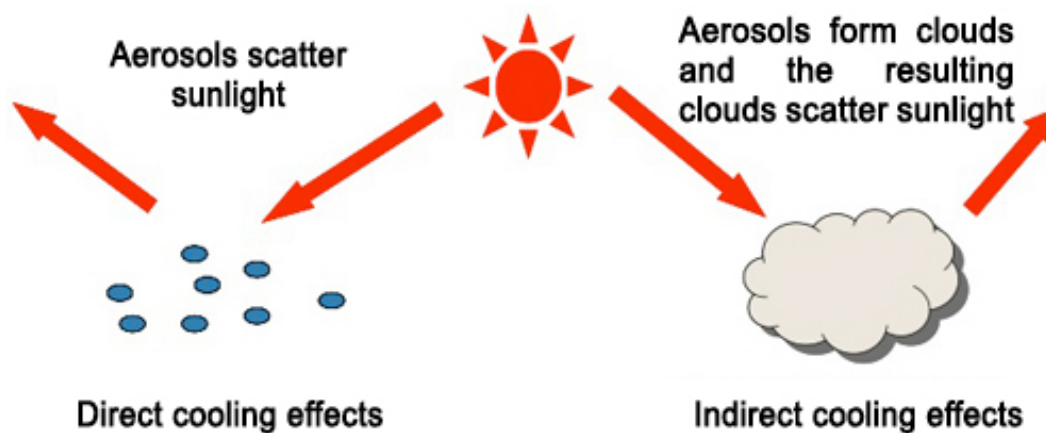
# **Chapter 1**

## **Introduction**

## 1.1 Atmospheric aerosol

The term atmospheric aerosol refers to a collection of airborne solid or liquid particles suspended in air, with a typical size between 0.001 and 100  $\mu\text{m}$ . These particles may be of either natural or anthropogenic origin. Aerosols may influence climate in two ways: directly through scattering and absorbing radiation, and indirectly through acting as cloud condensation nuclei (Figure 1.1) (IPCC, 2011). Long-term exposure of humans to high mass concentrations of suspended particles increases their mortality (Dockery et al., 1993; Laden et al., 2006; Pope et al., 2009). High levels of fine particles (diameter  $\leq 2.5 \mu\text{m}$ ) also cause respiratory problems and heart attacks (Davidson et al., 2005).

The chemical composition of atmospheric particles depends on their source. They are mainly composed of sulfate, nitrate, ammonium, sodium, chloride as well as dust, water, metals, organic compounds and elemental (or black) carbon.



**Figure 1.1:** Schematic of the direct and indirect cooling effects of atmospheric aerosols.

## **1.2 Carbonaceous aerosol**

Carbonaceous aerosol includes organic and black carbon (BC) containing particles. The organic component of fine sub-micrometer aerosol particles comprises about one half of their mass on average (Kanakidou et al., 2005). From a source perspective, organic aerosol can be classified as primary (POA) or secondary (SOA). POA refers to the organic mass that is emitted in the particle phase. SOA is formed in the atmosphere when volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone ( $O_3$ ), hydroxyl radical (OH) or nitrate radical ( $NO_3$ ). These reactions form low volatility products that can condense on preexisting particles in the atmosphere. Both POA and SOA have biogenic and anthropogenic sources. Organic aerosol (OA) is the most diverse and least understood component of submicron aerosols because of its chemical complexity, its numerous sources, and continuous chemical processing in the atmosphere.

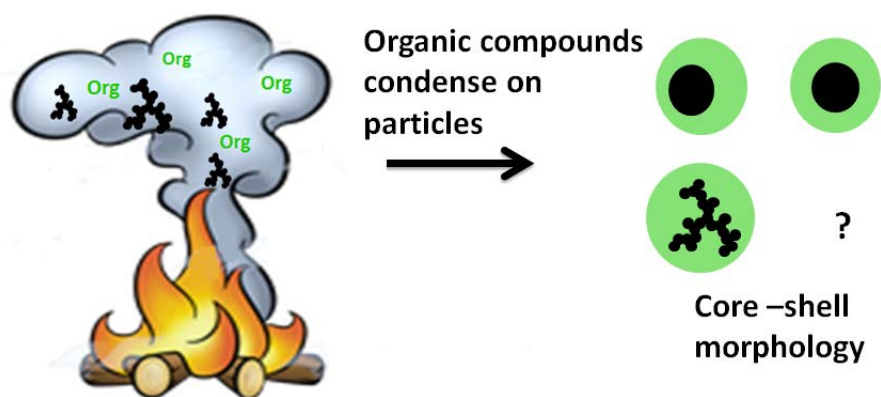
### **1.2.1 Primary organic aerosol (POA)**

POA is directly emitted into the atmosphere from a range of combustion sources including diesel and gasoline vehicle exhaust, biomass burning, meat cooking, etc. On a global scale biomass burning is responsible for almost 90% of primary OA emissions (Bond et al., 2004). Combustion particles consist of both BC and organic compounds and are known as soot.

### **1.2.2 Black carbon (BC)**

BC is a distinct type of carbonaceous material that is formed during incomplete combustion processes. BC is refractory with vaporization temperature near 4000 K and has a strong ability to absorb light (Schwarz et al., 2006). All sources that emit BC also emit POA, as

well as vapors that can be precursors of secondary organic aerosol (SOA) in the atmosphere. The fresh emitted BC-containing particles have aggregate morphology (Medalia et al., 1969), are hydrophobic (Weingartner et al., 1997) and always include organic compounds. These organic compounds usually condense on the BC as the emissions cool down, usually creating a core-shell morphology. This organic coating can affect the morphology of the BC (Figure 1.2) and can also increase the ability of the BC to absorb light.



**Figure 1.2:** Schematic of the processing of emissions from biomass burning and the changing BC morphology.

### 1.2.3 Secondary organic aerosol (SOA)

Secondary organic aerosol is formed in the atmosphere by the mass transfer of low volatility products of the oxidation of organic gases to the particulate phase. As the organic gases are oxidized in the gas phase their products can accumulate. Some of these products have low volatility and condense on the available particles in an effort to establish equilibrium between the gas and particle phases.

A range of anthropogenic and biogenic Volatile organic compounds (VOCs) can serve as SOA precursors in the atmosphere. Anthropogenic SOA precursors include benzene, toluene,

xylenes, large (>C<sub>15</sub>) alkanes, etc. Their emission is connected to biomass burning and fossil fuel combustion. Biogenic VOCs, whose emissions exceed anthropogenic emissions on a global scale, play an important role in atmospheric chemistry at both regional and global scales (Kanakidou et al., 2005). Biogenic VOCs include monoterpenes (C<sub>10</sub>H<sub>16</sub>), sesquiterpenes (C<sub>15</sub>H<sub>24</sub>), and isoprene (C<sub>5</sub>H<sub>8</sub>) as well as oxygenated compounds like methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, etc. (Atkinson and Arey, 2003). Although isoprene and the monoterpenes have higher emission rates, the sesquiterpenes (C<sub>15</sub>H<sub>24</sub>) are of special importance due to their high reactivity towards atmospheric oxidants and their large aerosol formation potential (Griffin et al., 1999). The emissions of sesquiterpenes and the chemical properties of the resulting SOA remain poorly known (Kanakidou et al., 2005).

The SOA contribution of given an organic species is mostly determined by its volatility. The mass fraction  $\xi$  of a species partitioning to the aerosol is (Donahue et al., 2006):

$$\xi = \frac{SOA}{c_{total}} = \frac{SOA}{SOA + c^*} = \left(1 + \frac{c^*}{SOA}\right)^{-1} \quad (1)$$

where  $c_{total}$  is the total mass concentration of the species (gas and particles), SOA is the organic aerosol concentration, and  $c^*$  is its effective saturation mass concentration or volatility.

The SOA mass yield ( $Y$ ) is used in order to quantify the ability of a gaseous precursor to form SOA. The yield is defined as the ratio of organic aerosol mass concentration produced, SOA, to the amount of total precursor reacted,  $\Delta VOC$ :

$$SOA Yield = SOA / \Delta VOC \quad (2)$$

Parameterizations of the SOA yield are used in chemical transport models (CTMs) to predict atmospheric SOA concentrations. One framework used for such parameterizations is the volatility basis set (VBS) which describes the OA volatility distribution using logarithmically



spaced effective saturation concentrations bins (Donahue et al., 2006). The volatility bins shift with temperature according to the Clausius-Clapeyron equation.

### **1.3 Chemical aging of OA**

During the atmospheric life of OA chemistry continuous to occur in both the gas and particulate phases changing its concentration, size, physical and chemical properties. The fresh mildly oxidized aerosol is usually converted to more oxidized, more water soluble, highly oxidized, aerosol. These processes are often called chemical aging and involve later generation reactions that continue to change the original organic compounds. The most common methods that have been used in experimental studies in order to chemically age the particles include exposure to sunlight, ozone, OH, NO<sub>3</sub> or a combination of these.

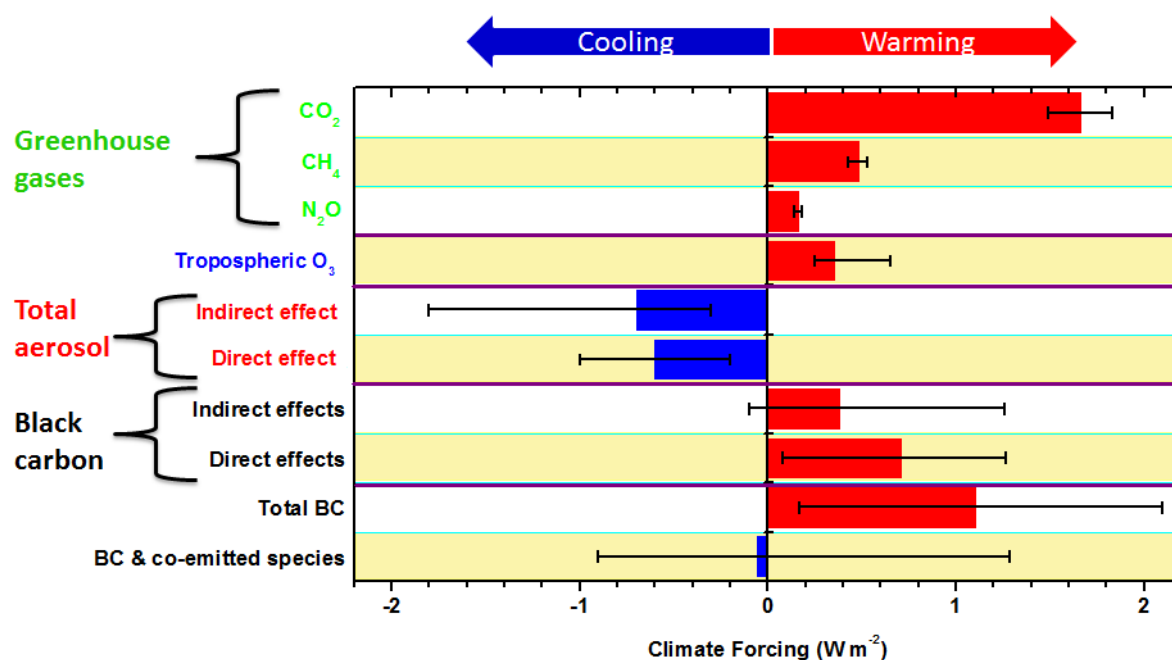
CTMs predict OA concentrations based on results from smog chamber experiments and emission studies (Lane et al., 2008). CTMs neglecting the effect of aging and simulating only the first generation of reactions usually under predict ambient SOA concentrations (Zhang et al., 2007).

The aging reactions can take place in the gas phase (homogeneous), particle phase (heterogeneous) or even in cloud water. Initially, attention was given to the heterogeneous aging reactions of the aerosol surface with OH radicals or other oxidants (Rudich et al., 2007; Smith et al., 2009; George et al., 2010). Later studies focused on homogeneous aging reactions (Henry et al., 2012; Donahue et al., 2011; Hildebrandt et al., 2016). In these reactions atmospheric oxidants react with the low volatility organic vapors resulting frequently in an SOA mass increase (Robinson et al., 2007). Homogeneous gas-phase OH reactions are generally faster than diffusion-limited heterogeneous reactions (Lambe et al., 2009).

## 1.4 Optical properties of aerosols

Atmospheric particles contribute to the sunlight extinction (direct effect). The term “extinction” means the loss of light in the atmosphere from a directly transmitted beam. Light extinction by particles depends on their chemical composition as well as their size, shape, and concentration. Two different mechanisms contribute to extinction: scattering and absorption. The light extinction coefficient ( $b_{\text{ext}}$ ), is the sum of the scattering ( $b_{\text{scat}}$ ) and absorption ( $b_{\text{abs}}$ ) coefficients.

The major aerosol components sulfate and OA scatter solar radiation back to space and as a result cool the planet (Charlson et al., 1991; Charlson et al., 1992; Kiehl and et al., 1993; Pósfai et al., 1999) (Figure 1.3). BC on the other hand heats the atmosphere by absorbing solar and thermal radiation (Jacobson, 2002; Menon et al., 2002; Andreae et al., 2006; Bond et al., 2013).



**Figure 1.3:** Global average radiative forcing in 2005 (best estimates and 5 to 95% uncertainty ranges) with respect to 1750 (IPCC, 2007).

## 1.5 Cloud condensation nuclei

Atmospheric particles have the potential to impact climate through their ability to act as cloud condensation nuclei (CCN) (Lohmann and Feichter, 2005; Solomon et al., 2007; Rosenfeld et al., 2008). Water condenses on CCN at the low water supersaturations (usually less than 1%) present in the atmosphere forming cloud droplets. At a given mass of soluble material in the particle there is a critical value of the ambient water vapor supersaturation below which the particle exists in a stable state and above which it spontaneously grows to become a cloud droplet of 10  $\mu\text{m}$  or more diameter. The number of particles from a given aerosol population that can act as CCN is thus a function of the water supersaturation. Depending on particle size, composition, and mixing state, aerosol particles are activated as CCN at different water vapor supersaturations (e.g., Köhler, 1936; Dusek et al., 2006; McFiggans et al., 2006; Andreae et al., 2008; Su et al., 2010).

## 1.6 Overview of the thesis

This thesis presents experimental investigations of the formation and chemical aging of organic aerosol. The effects of the chemical aging of OA on different properties of the particles, such as their ability to absorb light and to act as CCN is quantified.

In Chapter 2 the aerosol concentration produced by the reaction of  $\beta$ -caryophyllene with  $\text{O}_3$  or OH radicals is measured and SOA yield parameterizations are developed. The volatility and effective vaporization enthalpy of  $\beta$ -caryophyllene SOA are estimated. Finally, the chemical aging of the SOA as it continues reacting with OH radicals is investigated.

In Chapter 3 the newly developed Soot Particle Aerosol Mass Spectrometer (SP-AMS) is evaluated and compared with 5 other BC instruments. For the inter-comparison we use emissions

from biomass burning. Two regimes of high and low organic to BC concentration are examined to investigate the effect of the OA concentration on the BC measurement.

A laboratory study of the chemical aging of biomass burning emissions is presented in Chapter 4. The chemical aging of the biomass burning emissions leads to coating of the BC particles with aged OA. We investigate how the changes of the properties of the bbOA during chemical aging affect the absorption of the BC particles.

In Chapter 5, the cooking emissions from grilled burgers are characterized. Cooking organic aerosol (COA) is chemically aged by exposure to UV and/or ozone. The composition of the fresh and aged COA is characterized by aerosol mass spectrometry. The CCN activity of the fresh and aged emissions is also quantified.

## 1.7 References

Andreae, M. O., and Gelencsér, A.: Black carbon or brown carbon? The nature of light-absorbing carbonaceous aerosols, *Atmos. Chem. Phys.*, 6, 3131–3148, 2006.

Andreae, M. O., and Rosenfeld, D.: Aerosol-cloud-precipitation interactions. Part 1. The nature and sources of cloud-active aerosols, *Earth-Sci. Rev.*, 89, 13–41, 2008.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, *J. Geophys. Res.*, 109, D14203, 2004.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P.,

Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, *J. Geophys. Res.*, 118, 5380–5552, 2013.

Charlson, R. J., Langner, J., Rodhe, H., Leovy, C. B., and Warren, S. G.: Perturbation of the Northern Hemisphere radiative balance by backscattering from anthropogenic sulfate aerosols, *Tellus*, 43AB, 152–163, 1991.

Charlson, R. J., Schwartz, S. E., Hales, J. H., Cess, R. D., Coakley Jr., J. A., Hansen, J. E., and Hofmann, D. J.: Climate forcing by anthropogenic aerosols, *Science*, 255, 423–430, 1992.

Davidson, C. I., Phalen, R. F., and Solomon, P. A.: Airborne Particulate Matter, and Human Health: A Review, *Aerosol Sci. Technol.*, 39, 737–749, 2005.

Dockery, D.W., Pope, C.A., Xu, X., Spengler, J.D., Ware, J.H., Fay, M.E., Ferris, B.G., Speizer, F.E.: An association between air pollution and mortality in six US cities. *N Engl J Med*, 329, 1753–1759, 1993.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635–2643, 2006.

Donahue, N. M., Henry, K. M., Mentel, T. F., Saathoff, H., Hoffmann, T., Salo, K., Tritscher, T., Barmet, P. B., Hallquist, M., DeCarlo, P. F., Dommen, J., Prevot, A. S. H., and Baltensperger, U.: Aging of Secondary Organic Aerosol: Connecting Chambers to the Atmosphere, *Proc. Natl. Acad. Sci. USA*, 109(34), 13503–13508, 2011.

Dusek, U., Frank, G. P., Hildebrandt, L., Curtius, J., Schneider, J., Walter, S., Chand, D., Drewnick, F., Hings, S., Jung, D., Borrmann, S., and Andreae, M. O.: Size matters more than chemistry for cloud-nucleating ability of aerosol particles, *Science*, 312, 1375–1378, 2006.

George, I. J., and Abbatt, J. P. D.: Chemical evolution of secondary organic aerosol from OH-initiated heterogeneous oxidation, *Atmos. Chem. Phys.*, 10, 5551–5563, 2010.

Griffin, R. J., Cocker, D. R., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 2721–2724, 1999.

Henry, K. M., and Donahue, N.M.: Photochemical aging of  $\alpha$ -pinene secondary organic aerosol: Effects of OH radical sources, and photolysis, *J. Phys. Chem.*, 116, 5932 – 5940, 2012.

Hildebrandt Ruiz, L., Paciga, A. L., Cerully, K. M., Nenes, A., Donahue, and N. M., Pandis, S. N.: Formation and aging of secondary organic aerosol from toluene: changes in chemical composition, volatility, and hygroscopicity, *Atmos. Chem. Phys.*, 15, 8301–8313, 2016.

Jacobson, M. Z.: Control of fossil-fuel particulate black carbon and organic matter, possibly the most effective method of slowing global warming, *J. Geophys. Res.*, 107, 2002.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E. J., Putaud, P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005.

Kiehl, J. T., and Briegleb, B. P.: The relative role of sulfate aerosols and greenhouse gases in climate forcing, *Science*, 260, 311–314, 1993.

Köhler, H.: The nucleus in and the growth of hygroscopic droplets, *Trans. Faraday Soc.*, 32, 1152–1161, 1936.

Laden, F., Schwartz, J., Speizer, F. E., and Dockery, D. W.: Reduction in Fine Particulate Air Pollution and Mortality: Extended Follow-up of the Harvard Six Cities Study, *Am. J. Respir. Crit. Care Med.*, 173, 667–672, 2006.

Lambe, A. T., Miracolo, M. A., Hennigan, C. J., Robinson, A. L., and Donahue, N. M.: Effective rate constants and uptake coefficients for the reactions of organic molecular markers (n-alkanes, hopanes, and steranes) in motor oil, and diesel primary organic aerosols with hydroxyl radicals, *Environ. Sci. Technol.*, 43, 8794–8800, 2009.

McFiggans, G., Artaxo, P., Baltensperger, U., Coe, H., Facchini, M. C., Feingold, G., Fuzzi, S., Gysel, M., Laaksonen, A., Lohmann, U., Mentel, T. F., Murphy, D. M., O'Dowd, C. D., Snider, J. R., and Weingartner, E.: The effect of physical and chemical aerosol properties on warm cloud droplet activation, *Atmos. Chem. Phys.*, 6, 2593–2649, 2006.

Medalia, A. I., and Heckman, F. A.: Morphology of aggregates—II. Size, and shape factors of carbon black aggregates from electron microscopy, *Carbon*, 7, 569–582, 1969.

Menon, S., DelGenio, A. D., Koch, D., and Tselioudis, G.: GCM Simulations of the Aerosol Indirect Effect: Sensitivity to Cloud Parameterization and Aerosol Burden, *J. Atmos. Sci.*, 59, 692–713, 2002.

Overpeck, J., Rind, D., Lacis, A., and Healy, R.: Possible role of dust-induced regional warming in abrupt climate change during the last glacial period. *Nature*, 384 447–449, 1996.

Pope, C. A., Ezzati, M., and Dockery, D. W.: Fine-particulate air pollution, and life expectancy in the United States, *New Engl. J. Med.*, 360, 376–386, 2009.

Pósfai, M., Anderson, J. R., Buseck, P. R., and Sievering, H.: Soot and sulfate aerosol particles in the remote marine troposphere, *J. Geophys. Res.*, 104, 21685–21693, 1999.

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., and Pandis, S. N.: Rethinking organic aerosols: semivolatile emissions and photochemical aging, *Science*, 315, 1259–1262, 2007.

Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of organic aerosol: Bridging the gap between laboratory and field studies. *Annu.Rev. Phys. Chem.*, 58, 321–352, 2007.

Smith, J. D., Kroll, J. H., Cappa, C. D., Che, D. L., Liu, C. L., Ahmed, M., Leone, S. R., Worsnop, D. R., and Wilson, K. R.: The heterogeneous reaction of hydroxyl radicals with submicron squalane particles: a model system for understanding the oxidative aging of ambient aerosols, *Atmos. Chem. Phys.*, 9, 3209–3222, 2009.

Su, H., Rose, D., Cheng, Y. F., Gunthe, S. S., Massling, A., Stock, M., Wiedensohler, A., Andreae, M. O., and Pöschl, U.: Hygroscopicity distribution concept for measurement data analysis and modeling of aerosol particle mixing state with regard to hygroscopic growth, and CCN activation, *Atmos. Chem. Phys.*, 10, 7489–7503, 2010.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Baumgardner, D. G., Kok, G. L., Chung, S., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Lowenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, *J. Geophys. Res.*, 111, D16207, 2006.

Weingartner, E., Burtscher, H., and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot particles, *Atmos. Environ.*, 31, 2311–2327, 1997.

Zhang, Q., Jimenez, J. L., Canagaratna, M. R., Allan, J. D., Coe, H., Ulbrich, I., Alfarra, M. R., Takami, A., Middlebrook, A. M., Sun, Y. L., Dzepina, K., Dunlea, E., Docherty, K., De Carlo, P. F., Salcedo, D., Onasch, T., Jayne, J. T., Miyoshi, T., Shimojo, A., Hatakeyama, S., Takegawa, N., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Williams, P., Bower, K., Bahreini, R., Cottrell, L., Griffin, R. J., Rautiainen, J., Sun, J. Y., Zhang, Y. M., and Worsnop, D. R.: Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes, *J. Geophys. Res. Lett.*, 34, L13801, 2007.



## **Chapter 2**

### **Formation and chemical aging of secondary organic aerosol during the $\beta$ -caryophyllene oxidation<sup>1</sup>**

---

<sup>1</sup> Published as: Tasoglou, A. and Pandis, S. N.: Formation and chemical aging of secondary organic aerosol during the  $\beta$ -caryophyllene oxidation, Atmos. Chem. Phys., 15, 6035–6046, 2015.

## Abstract

The secondary organic aerosol (SOA) production during the oxidation of  $\beta$ -caryophyllene by ozone ( $O_3$ ) and hydroxyl radicals (OH) and the subsequent chemical aging of the products during reactions with OH were investigated. Experiments were conducted with ozone, hydroxyl radicals at low  $NO_x$  (zero added  $NO_x$ ) and at high  $NO_x$  (100s of ppb). The SOA mass yield at  $10 \mu g m^{-3}$  of organic aerosol was 27% for the ozonolysis, 20% for the reaction with OH at low  $NO_x$  and 38% at high  $NO_x$  under dry conditions,  $20^\circ C$ , and ozone excess. Parameterizations of the fresh SOA yields have been developed. The average fresh SOA atomic O:C ratio varied from 0.24 to 0.34 depending on the oxidant and the  $NO_x$  level, while the H:C ratio was close to 1.5 for all systems examined. An average density of  $1.06 \pm 0.1 \mu g m^{-3}$  of the  $\beta$ -caryophyllene SOA was estimated. The exposure to UV-light had no effect on the  $\beta$ -caryophyllene SOA concentration and Aerosol Mass Spectrometer (AMS) mass spectrum. The chemical aging of the produced  $\beta$ -caryophyllene SOA was studied by exposing the fresh SOA to high concentrations ( $10^7$  molecules  $cm^{-3}$ ) of OH for several hours. These additional reactions increased the SOA concentration by 15-40% and the O:C by approximately 25%. A limited number of experiments suggested that there was a significant impact of the relative humidity on the chemical aging of the SOA. The evaporation rates of  $\beta$ -caryophyllene SOA were quantified by using a thermodenuder allowing us to estimate the corresponding volatility distributions and effective vaporization enthalpies.

## 2.1 Introduction

Organic compounds represent approximately half of the total mass of sub-micrometer aerosol particles (Kanakidou et al., 2005). From a source perspective, organic aerosol is often classified as primary (POA) or secondary (SOA). POA refers to the organic mass that is emitted in the atmosphere in the particle phase. SOA is formed in the atmosphere when volatile organic compounds (VOCs) react with atmospheric oxidants such as ozone ( $O_3$ ), hydroxyl radical (OH) or nitrate radical ( $NO_3$ ). These reactions form low volatility products that can condense on preexisting particles in the atmosphere. Both POA and SOA have biogenic and anthropogenic sources.

The initial products of oxidation of VOCs in the atmosphere can undergo subsequent reactions in the gas and particulate phases leading to changes in their volatility and thus phase partitioning. This series of processes is called chemical aging and can be a significant source of SOA in the atmosphere (Donahue et al., 2012).

Biogenic VOCs, whose emissions exceed anthropogenic emissions on a global scale, play an important role in atmospheric chemistry at both regional and global scales (Kanakidou et al., 2005). Biogenic VOCs include monoterpenes ( $C_{10}H_{16}$ ), sesquiterpenes ( $C_{15}H_{24}$ ), and isoprene ( $C_5H_8$ ) as well as oxygenated compounds like methanol, 2-methyl-3-buten-2-ol, 6-methyl-5-hepten-2-one, etc. (Atkinson and Arey, 2003). Although isoprene and the monoterpenes have higher emission rates, the sesquiterpenes ( $C_{15}H_{24}$ ) are of special importance due to their high reactivity towards atmospheric oxidants and their large aerosol formation potential (Griffin et al., 1999b).

Sesquiterpenes are mostly emitted by conifers, deciduous trees, and flowers (Knudsen et al., 1993).  $\beta$ -caryophyllene is often one of the most abundant sesquiterpenes (Helmig et al.,

2007). It has two double bonds so its oxidation occurs in two steps. The reaction rate constants for the two reactions steps are  $k_1=1.2\pm0.4\times10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Shu and Atkinson, 1995) and  $k_2=1.1\pm0.4\times10^{-16}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$  (Winterhalter et al., 2009) respectively. Assuming an  $\text{O}_3$  mixing ratio of 40 ppb, the atmospheric lifetime of  $\beta$ -caryophyllene is 1.5 min and the lifetime of the first generation products is approximately 2.5 hours. The first and second generation oxidation products of  $\beta$ -caryophyllene that have been detected in the particle phase include  $\beta$ -caryophyllonic acid,  $\beta$ -caryophyllinic acid,  $\beta$ -caryophyllon aldehyde,  $\beta$ -nocaryophyllon aldehyde, etc. (Jaoui et al., 2003; Winterhalter et al., 2009; Li et al., 2011). The ambient concentrations of most of these have not been quantified due to the lack of suitable standards. The lifetime of  $\beta$ -caryophyllene due to the reaction with OH radicals (assuming an OH concentration of  $2\times10^6\text{ molecule cm}^{-3}$ ) is approximately 40 min (Atkinson and Arey, 2003).

A number of earlier studies have measured the SOA yield of  $\beta$ -caryophyllene ozonolysis. The SOA yield does increase with increasing OA levels as predicted by Odum et al. (1996). Winterhalter et al. (2009) reported SOA yields from 6 to 41% for 50-440  $\mu\text{g m}^{-3}$  of SOA. Chen et al. (2012) found that the SOA yield is sensitive to the  $\text{O}_3$  concentration, especially for SOA levels higher than 10  $\mu\text{g m}^{-3}$ . They measured SOA yields from 8 to 46 % for 0.5 – 170  $\mu\text{g m}^{-3}$  of SOA for the reaction of  $\beta$ -caryophyllene with 50 ppb of  $\text{O}_3$ , 15.8 to 60 % for 2.1 – 230  $\mu\text{g m}^{-3}$  of SOA for 100 ppb of  $\text{O}_3$ , and 14.6 to 69.5 % for 1.9 – 77.4  $\mu\text{g m}^{-3}$  of SOA for 200 ppb of  $\text{O}_3$ . Lee et al. (2006a) (also reported in Ng et al., 2006) found a yield of 45% for 336  $\mu\text{g m}^{-3}$  SOA while Jaoui et al. (2013) measured an SOA yield of 53% for 55.4  $\mu\text{g m}^{-3}$  SOA. These results are quite inconsistent with relatively low values suggested by Winterhalter et al. (2009) and Lee et al. (2006a; b) and higher for the other studies.

Oxidation of  $\beta$ -caryophyllene by OH radicals in the presence of light has also been studied. Lee et al. (2006b) produced OH radicals by the photolysis of HONO and measured an SOA yield of 68% for  $212 \mu\text{g m}^{-3}$  SOA. Other studies investigated the photo-oxidation of  $\beta$ -caryophyllene/ $\text{NO}_x$  mixtures. Griffin et al. (1999a) found an SOA yield of 37-79% for  $18\text{-}82 \mu\text{g m}^{-3}$  SOA while Hoffmann et al. (1997) found an SOA yield of 103-125% for  $845\text{-}998 \mu\text{g m}^{-3}$ , Alfarra et al. (2012) reported an SOA yield of 9.5-26.7% for  $35.6\text{-}128.8 \mu\text{g m}^{-3}$  and Jaoui et al. (2013) measured an SOA yield of 30% for  $54 \mu\text{g m}^{-3}$  SOA. Jaoui et al. (2013) also reported an effective enthalpy of vaporization of  $43.9 \text{ kJ mol}^{-1}$  for aerosol generated from  $\beta$ -caryophyllene ozonolysis and  $41.1 \text{ kJ mol}^{-1}$  for aerosol generated from  $\beta$ -caryophyllene photo-oxidation. Finally, Chan et al. (2011) and Offenberg et al. (2009) found that the SOA yield during  $\beta$ -caryophyllene photooxidation is enhanced by aerosol acidity. Chan et al. (2011) showed that increased acidity leads to increased concentration of organosulfates and other particle-phase reaction products formed via hydration. This acidity effect has not been investigated in the current work.

There are significant discrepancies among the results of previous studies regarding the SOA yield in the system. Potential reasons for the differences include the absence, in some of the studies, of correction of the mass of the particles that is lost on the walls of the smog chamber reactor. Other reasons include challenges with the injection and measurement of  $\beta$ -caryophyllene (Jaoui et al., 2013; Lee et al., 2006a; Helmig et al., 2004). Jaoui et al. (2013) did not use an OH scavenger and therefore OH radicals were produced in their system potentially leading the system to different reaction pathways. Winterhalter et al. (2009) did not use excess  $\text{O}_3$  while in some experiments Criegee intermediates scavengers were used. Winterhalter et al. (2009), Lee et al. (2006a, b), Alfarra et al. (2012) and Hoffman et al. (1997) calculated the SOA assuming an

effective density ranging from 1 to 1.3  $\mu\text{g m}^{-3}$  depending on the study. Chen et al. (2012) estimated effective density values from 1.23 to 1.81  $\mu\text{g m}^{-3}$  for their experiments. Relative humidity and temperature might also affect the yield. All the previous studies were conducted at temperatures 20-26°C apart from Hoffman et al. (1997) who used much higher temperatures ranging from 43 to 49°C. Finally the relative humidity ranged from 5% to 72% in the studies making the comparison of their results even more challenging.

The objective of this work is to measure the amount of aerosol produced by the reaction of the  $\beta$ -caryophyllene with  $\text{O}_3$  or OH radicals and suggest aerosol yield parameterizations for atmospheric chemical transport models. We also examine the effect that UV light and temperature has on the  $\beta$ -caryophyllene SOA. The volatility and the effective vaporization enthalpy of  $\beta$ -caryophyllene SOA are estimated. Finally, the chemical aging of the SOA as it continues reacting with OH radicals is investigated.

## 2.2. Experimental methods

Experiments were carried out in the smog chamber of Carnegie Mellon University Center for Atmospheric Particle Studies (CAPS). The smog chamber is a 12  $\text{m}^3$  Teflon reactor (Welch Fluorocarbons). The chamber was suspended inside a temperature-controlled room. The walls of the smog chamber room were lined with UV lights (General Electric model 10526 black). Prior to an experiment, the chamber was flushed with purified air for 12-48 h. Air was purified by passing through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity to <10%.

Ozone was added to the chamber using an electrical discharge generator (AZCO, model HTU-500ACPS). 0.5 ml of 2-butanol (Sigma-Aldrich, ReagentPlus,  $\geq 99\%$ ) was also introduced

into the chamber before selected experiments as an OH-scavenger to avoid the oxidation of the precursor by the OH produced during the ozonolysis experiments. We tested the possibility of formation of aerosol from the reaction of OH and 2-butanol in the presence of ammonium sulfate seeds. There was no detectable organic aerosol formation for the conditions used in our experiments. For the photooxidation experiments we used HONO and H<sub>2</sub>O<sub>2</sub> (Sigma-Aldrich, 50-50% solution) photolysis as the source of OH radicals. A fresh solution of HONO was produced and used in each experiment. HONO was produced by mixing a 4.9 g L<sup>-1</sup> sulfuric acid solution with a 6.9 g L<sup>-1</sup> sodium nitrite with a volumetric ratio of 2:1. HONO or H<sub>2</sub>O<sub>2</sub> were injected in the chamber using a bubbler. After the injection, the UV lights were turned on to initiate the production of OH radicals. We tested the injection method by measuring the concentration of the OH radicals using 2-butanol as a tracer and a GC/FID (Chromatotec airmoBTX) with 15 min time resolution. The estimated concentration of OH radicals was approximately 10<sup>7</sup> molecules cm<sup>-3</sup> for HONO photolysis and 10<sup>6</sup> molecules cm<sup>-3</sup> for H<sub>2</sub>O<sub>2</sub> photolysis. We did not add any NO<sub>x</sub> in the chamber for the ozonolysis experiments and the low NO<sub>x</sub> experiments. The measured NO<sub>x</sub> level was of the order of a few ppb for these experiments. For the high NO<sub>x</sub> experiments the corresponding NO<sub>x</sub> concentrations due the dissociation of HONO were more than 1 ppm.

β-caryophyllene (Sigma-Aldrich, ≥98.5 %) was injected through a heated septum injector in which clean air was passed over the injected liquid to vaporize and transfer it to the chamber via Teflon tubing. The concentration of the β-caryophyllene that reacted in the chamber was calculated based on injected mass. Previous studies have reported tubing losses during the injection of “sticky” compounds like the sesquiterpenes (Jaoui et al., 2013; Lee et al., 2006a; Helmig et al., 2004). To overcome this problem, we tested the injection by gently purging the Teflon tubing with clean air (5 L min<sup>-1</sup>) for 1 hour after the injection. The signal of m/z 81 of a

Proton-Transfer Reactor Mass spectrometer (PTR-MS, Ionicon Analytic GmbH), which has been found to be a strong signal for  $\beta$ -caryophyllene (Lee et al., 2006a, b), was measured. During the tests the initial signal of  $m/z$  81 was zero and after the injection and the purging of the line the signal increased and reached a plateau. We found that 10-20 min of purging was sufficient for the complete  $\beta$ -caryophyllene injection into the chamber. The accuracy of the estimated concentration based on the injected  $\beta$ -caryophyllene amount was checked in selected experiments using the PTR-MS. The total amount of air added in the chamber during the purging was less than  $0.3 \text{ m}^{-3}$  (less than 3% of the chamber volume)

A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3772 or 3010) was used for the measurement of the number and the volume distributions of aerosols. The mass concentration and the chemical composition of the particles were monitored using a High Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-ToF-AMS, Aerodyne Research, Inc.). For the HR-ToF-AMS data analysis SQUIRREL 1.51H and PIKA 1.10H were used. In our analysis we used the fragmentation table of Aiken et al. (2008). The HR-ToF-AMS was operated alternatively between V-mode and W-mode with 1 min of measurement time for each mode. In this paper the V-mode data are presented. The elemental ratios of the SOA were calculated using the HR-ToF-AMS data without including the organonitrate fragments in the analysis. The concentration of  $\text{O}_3$  was measured using a continuous  $\text{O}_3$  analyzer (Dasibi 1008-PC) and the concentration of nitrogen oxides was measured using a Teledyne chemiluminescence  $\text{NO}/\text{NO}_2/\text{NO}_x$  analyzer (Model 200A).

The reported SOA mass concentration was calculated by using the volume distribution and the density of the  $\beta$ -caryophyllene SOA. In each experiment we used the algorithm of Kostenidou et al. (2007) to estimate the effective density of the SOA and the collection



efficiency (CE) of the HR-ToF-AMS. This algorithm combines the volume and mass distributions of the aerosol measured, respectively, by the SMPS and HR-ToF-AMS

A major complication in smog chamber experiments is that particles and potentially vapors are lost to the walls of the reactor. As a result the number and the mass concentration of the particles decrease continuously. The particle wall loss rate in general depends on particle size, the geometry of the smog chamber, the turbulence and electric fields within the chamber, and the charge distribution of the particles (Crump and Seinfeld, 1981). A semi-empirical approach for calculating the particle wall losses (Pathak et al., 2007) involves measuring an average mass wall-loss rate constant in the chamber after the reactions are completed and then applying this constant to the entire experiment. This method assumes that the wall loss rate is first order and independent of particle size for the particle size range in the chamber. To ensure that the rate constants were estimated during periods in which the reactions rate were very low or zero we used three different criteria. The first was the theoretical estimates of the reaction times. For example in all the ozonolysis experiments in which the  $O_3$  concentration was in excess of 300 ppb the time required for the first reaction step at 293 K is approximately 12 seconds while the second requires around 20 minutes. To ensure that these reactions were completed the particle wall loss rate constants were estimated by using the mass concentration decay at least after one hour from the beginning of the reactions. The second criterion was the testing of sub-periods after the reaction completion to ensure that there was no change in the corresponding constant from period to period. For example in Experiment 6 we calculated a wall loss rate constant  $0.29 \text{ hr}^{-1}$  for the 50-100 min period (with  $R^2=0.98$ ),  $0.29 \text{ hr}^{-1}$  for 100-150 min (with  $R^2=0.99$ ) and  $0.28 \text{ hr}^{-1}$  for 150-200 min (with  $R^2=0.99$ ). Similar results were obtained for other experiments during periods in which the reactions in the system were assumed to be completed.

The third criterion was the use of periods in which the SOA O:C ratio was stable. The wall loss rate constants at 293 K estimated for all the ozonolysis experiment were equal to  $0.27 \pm 0.13 \text{ hr}^{-1}$ .

The use of a time-independent value for the correction of the wall losses (even if sub-100 nm particles are lost in general faster than larger particles in our system) is justified by the fact that particles in our experiments grew to sizes above 100 nm in less than 20 minutes. Therefore the period during which losses may have been different was small and the resulting uncertainty also small. We are estimating for this fast reacting system that the uncertainty in the yields introduced by the particle wall loss correction is of the order of 20%.

Changes in temperature do result in significant changes of the loss rate constants in our chamber. In Experiment 1 in which the temperature was increased from 20 to 40 °C the particle loss rate constant increased from 0.26 to  $0.46 \text{ h}^{-1}$ . This increase is due to the increased ventilation outside the chamber which leads to increased turbulence inside the chamber and thus increased particle losses. We have estimated and used different loss rate constants for periods with different temperatures in the same experiment.

Most previous studies have neglected the losses of organic vapors on the particles deposited on the reactor walls. Hildebrandt et al. (2011) developed a method that calculates SOA yields in two extreme cases: when there are no vapor losses on the particles deposited on the walls ( $w=0$ ) similar to Pathak et al. (2007), and also the case in which organic vapors condense on the particles on the walls in a way similar to the suspended particles in the reactor ( $w=1$ ). We have corrected for vapor losses to the particles deposited on the chamber walls using both the  $w=0$  and the  $w=1$  approaches.

Matsunaga and Ziemann (2010) and Zhang et al. (2014) have also reported loss of organic vapors directly onto the Teflon walls. Measurement of these losses during SOA

formation is challenging. To quantify the magnitude of these losses we have performed four additional experiments using ammonium sulfate seeds. The use of the seeds increases the surface area of the aerosol in the chamber and should reduce any artifact related to vapor losses to the Teflon wall. The results of these experiments are discussed in a subsequent section.

The oxidation of  $\beta$ -caryophyllene took place at a constant temperature of  $20\pm 2^\circ\text{C}$  and at  $\text{RH} < 10\%$  in most experiments. Two experiments were conducted at higher relative humidity equal to 50% and 90% respectively. No high RH experiments were conducted in the presence of ammonium sulfate particles. The interactions of aerosol water, inorganic ions, and the SOA compounds in this system require additional detailed studies.

After the reactions were completed the chamber was heated to  $40^\circ\text{C}$  to investigate the evaporation of the particles produced. For investigation of the behavior of the SOA at higher temperatures we used the thermodenuder of An et al. (2007). The temperatures in the thermodenuder were in the range of  $25\text{--}120^\circ\text{C}$  with a centerline residence time of 26 s. Table 2.1 and Table 2.2 list the initial conditions and the calculated SOA yields for all experiments.

## **2.3 Results and discussion**

### **2.3.1 Ozonolysis**

The results of a typical ozonolysis experiment (Experiment 1) are shown in Figure 2.1. Initially, we injected 2-butanol and  $\text{O}_3$  in the chamber followed by the injection of  $\beta$ -caryophyllene. The reaction started at time zero with the presence of both reactants in the smog chamber. The mass of the aerosol started increasing right away and 30 min later the SOA concentration reached  $32\ \mu\text{g m}^{-3}$ . 2.5 hours after the beginning of the experiment, the temperature

was increased to 40°C. Approximately  $6 \mu\text{g m}^{-3}$  of suspended SOA evaporated in 20 min (Figure 2.1).

**Table 2.1:** Initial conditions and results of the  $\beta$ -caryophyllene oxidation experiments

| Exp                                          | VOC<br>(ppb) <sup>a</sup> | O <sub>3</sub><br>(ppb) | Seeds<br>(μg m <sup>-3</sup> ) | SOA<br>density<br>(g cm <sup>-3</sup> ) | SOA mass<br>(μg m <sup>-3</sup> ) <sup>b</sup> |       | SOA<br>yield (%) <sup>c</sup> |
|----------------------------------------------|---------------------------|-------------------------|--------------------------------|-----------------------------------------|------------------------------------------------|-------|-------------------------------|
|                                              |                           |                         |                                |                                         | w=0                                            | w=1   |                               |
| Ozonolysis (in the presence of OH scavenger) |                           |                         |                                |                                         |                                                |       |                               |
| 1                                            | 13                        | 300                     | -                              | 1.01                                    | 41.2                                           | 45    | 41.7                          |
| 2                                            | 14                        | 300                     | -                              | 0.97                                    | 47.6                                           | 50.7  | 43.3                          |
| 3                                            | 5                         | 600                     | -                              | 0.93                                    | 10.9                                           | 11    | 24.2                          |
| 4                                            | 32                        | 300                     | -                              | 0.97                                    | 89.2                                           | 95.1  | 34.8                          |
| 5                                            | 2                         | 600                     | -                              | 0.97                                    | 0.3                                            | 0.3   | 1.9                           |
| 6                                            | 4                         | 300                     | -                              | 0.95                                    | 8.9                                            | 9.4   | 29.4                          |
| 7                                            | 21                        | 300                     | -                              | 0.98                                    | 108                                            | 119   | 65.2                          |
| 8                                            | 11                        | 300                     | -                              | 0.96                                    | 44.8                                           | 52    | 57.1                          |
| 9                                            | 27                        | 300                     | -                              | 0.95                                    | 88.6                                           | 97.7  | 42.8                          |
| 10                                           | 19                        | 300                     | -                              | 1.03                                    | 84.6                                           | 96.2  | 58.6                          |
| 11                                           | 30                        | 300                     | -                              | 0.96                                    | 140                                            | 163   | 63.7                          |
| 12                                           | 13                        | 300                     | -                              | 0.96                                    | 56                                             | 65.4  | 59.7                          |
| 13                                           | 24                        | 300                     | -                              | 0.99                                    | 162                                            | 194   | 96.1                          |
| 14                                           | 3                         | 300                     | -                              | 0.99                                    | 12.4                                           | 13.2  | 48.2                          |
| 15                                           | 23                        | 300                     | 26.7                           | 1.17                                    | 108.3                                          | 113.2 | 59.1                          |
| 16                                           | 25                        | 300                     | 53                             | 1.00                                    | 175.9                                          | 180.6 | 86.1                          |
| 17                                           | 16                        | 300                     | 30.1                           | 1.01                                    | 113.5                                          | 119   | 86.9                          |
| 18                                           | 11                        | 300                     | 22.3                           | 1.02                                    | 89.5                                           | 94.4  | 103.4                         |
| OH radicals at high NO <sub>x</sub>          |                           |                         |                                |                                         |                                                |       |                               |
| 19                                           | 11                        | -                       | -                              | 1.12                                    | 78.1                                           | 81.2  | 89                            |
| 20                                           | 24                        | -                       | -                              | 1.25                                    | 223                                            | 229   | 113.9                         |
| 21                                           | 32                        | -                       | -                              | 1.21                                    | 303                                            | 311   | 113.5                         |
| 22                                           | 5                         | -                       | -                              | 1.12                                    | 43.2                                           | 44.4  | 97.4                          |
| 23                                           | 3                         | -                       | -                              | 1.06                                    | 7.8                                            | 8.4   | 30.7                          |
| 24                                           | 4                         | -                       | -                              | 1.34                                    | 20.1                                           | 20.1  | 55.2                          |
| 25                                           | 19                        | -                       | -                              | 1.22                                    | 222.1                                          | 226.3 | 137.8                         |
| OH radicals at low NO <sub>x</sub>           |                           |                         |                                |                                         |                                                |       |                               |
| 26                                           | 32                        | -                       | -                              | 1.02                                    | 156                                            | 193   | 70.3                          |
| 27                                           | 16                        | -                       | -                              | 1.08                                    | 55.7                                           | 56.9  | 41.6                          |
| 28                                           | 11                        | -                       | -                              | 1.07                                    | 47.2                                           | 49.0  | 53.7                          |
| 29                                           | 5                         | -                       | -                              | 0.99                                    | 8                                              | 8.8   | 19.3                          |
| 30                                           | 21                        | -                       | -                              | 1.09                                    | 97.8                                           | 97.7  | 53.5                          |

**Table 2.2:** Initial conditions and results of the aging experiments

| Exp | VOC<br>(ppb) <sup>a</sup> | O <sub>3</sub><br>(ppb) | RH<br>(%) | SOA<br>density<br>(g cm <sup>-3</sup> ) | Fresh SOA                                      |      |      |      |                                  | Aged SOA                                       |      |      |      |                                  |
|-----|---------------------------|-------------------------|-----------|-----------------------------------------|------------------------------------------------|------|------|------|----------------------------------|------------------------------------------------|------|------|------|----------------------------------|
|     |                           |                         |           |                                         | SOA mass<br>(μg m <sup>-3</sup> ) <sup>b</sup> |      | O:C  | H:C  | SOA<br>yield<br>(%) <sup>c</sup> | SOA mass<br>(μg m <sup>-3</sup> ) <sup>b</sup> |      | O:C  | H:C  | SOA<br>yield<br>(%) <sup>c</sup> |
|     |                           |                         |           |                                         | w=0                                            | w=1  |      |      |                                  | w=0                                            | w=1  |      |      |                                  |
| 31  | 3                         | 300                     | <10       | 1.12                                    | 17                                             | 17.6 | 0.26 | 1.48 | 64.4                             | 18.6                                           | 20.6 | 0.32 | 1.48 | 75.4                             |
| 32  | 5                         | 300                     | <10       | 1.09                                    | 60.4                                           | 64.4 | 0.31 | 1.51 | 141.2                            | 65.2                                           | 72.5 | 0.35 | 1.51 | 159                              |
| 33  | 3                         | 300                     | <10       | 1.12                                    | 30.7                                           | 31.1 | 0.26 | 1.47 | 113.5                            | 39.8                                           | 41   | 0.29 | 1.46 | 149.7                            |
| 34  | 3                         | 300                     | ~50       | 1.15                                    | 32.8                                           | 33.7 | 0.28 | 1.43 | 123.3                            | 44                                             | 47.2 | 0.35 | 1.43 | 140                              |
| 35  | 3                         | 300                     | ~90       | 1.21                                    | 22.7                                           | 23   | 0.21 | 1.47 | 84.2                             | 29.4                                           | 32.1 | 0.28 | 1.45 | 117.5                            |
| 36  | 5                         | 500                     | <10       | 1.00                                    | 28.6                                           | 30.5 | 0.28 | 1.44 | 66.9                             | 28.8                                           | 30.8 | 0.29 | 1.44 | 67.6                             |
| 37  | 3                         | 400                     | <10       | 1.13                                    | 16                                             | 16.3 | 0.31 | 1.46 | 59.6                             | 16.2                                           | 16.7 | 0.31 | 1.46 | 61.1                             |

<sup>a</sup> This concentration was calculated based on the amount of β-caryophyllene injected into the chamber.

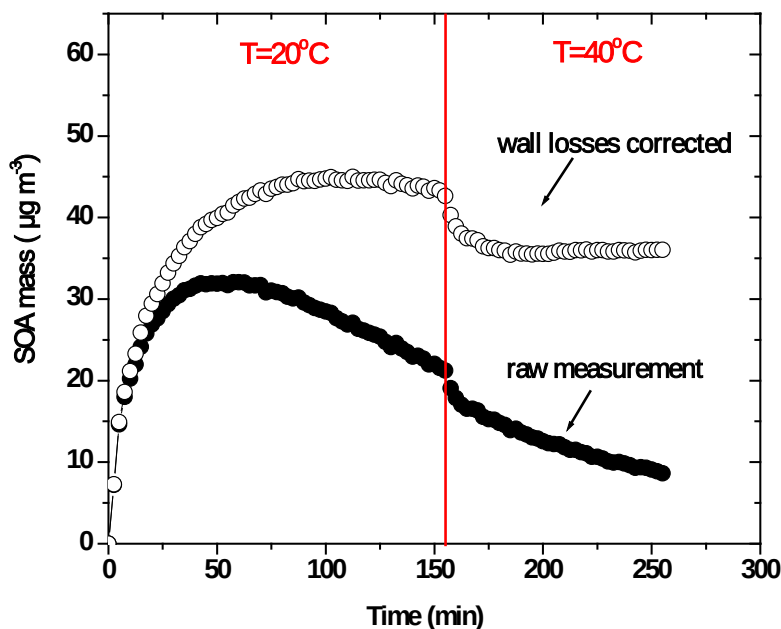
<sup>b</sup> This is the wall losses corrected mass concentration measured by the SMPS.

<sup>c</sup> The SOA yields are calculated using the wall losses corrected SOA mass concentration for w=1.

The wall loss- corrected SOA mass decreased 15% due to evaporation. After 20 minutes the system appeared to reach equilibrium and the suspended mass decreased again slowly due to wall losses.

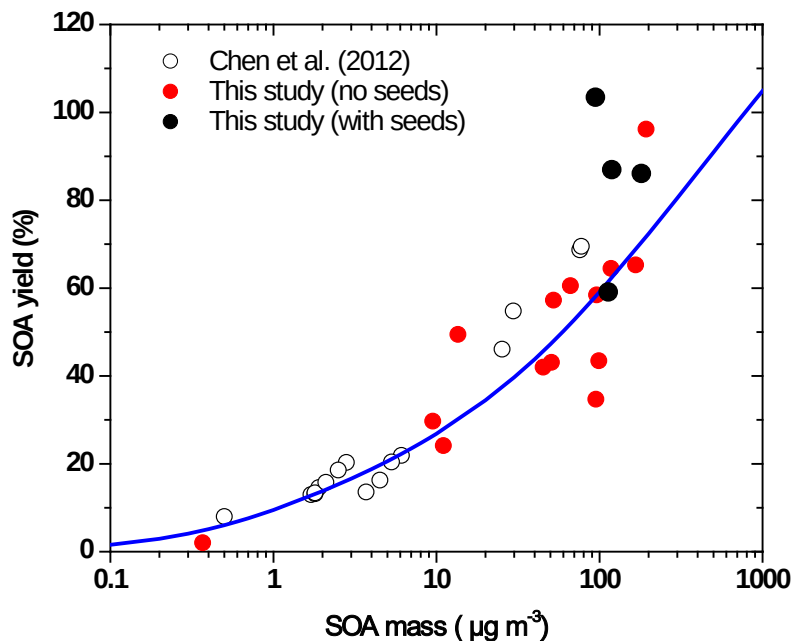
In Experiment 2 (not shown) the β-caryophyllene SOA produced in the dark during ozonolysis was exposed to UV-light. The SOA formed had a wall-loss corrected mass of 50.7 μg m<sup>-3</sup> and O:C=0.38. Approximately 1.5 hours after the mass of the SOA started decreasing in the smog chamber we turned on the UV lights. After one hour of exposure the wall loss-corrected SOA concentration was 50.1 μg m<sup>-3</sup> and the O:C was 0.38. We compared the mass spectra in these two periods using the angle θ between the corresponding vectors as described in Kostenidou et al. (2009). The θ angle was less than 2 degrees suggesting that there were no

noticeable effects of chemical aging or photolysis of the SOA at least from the point of view of the AMS.



**Figure 2.1:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) for Experiment 1. Also shown, the time when the temperature inside the chamber room was increased.

The wall-loss corrected aerosol mass concentrations are presented in Table 2.1 for two extreme cases: assuming there are no vapor losses on the particles deposited on the walls ( $w=0$ ), and also for the case in which organic vapors condense on the particles on the walls in a way similar to the suspended particles in the reactor ( $w=1$ ) (Hildebrandt et al., 2011). Because reactions are fast in this system the  $w=1$  case results are at most 20% higher than that the  $w=0$  ones. In Experiments 15-18 we used ammonium sulfate seeds to test for direct losses of vapors to the Teflon wall. The yields of these experiments (Figure 2.2) are not different from the rest of the yields. This suggests that the magnitude of losses of vapors to the walls for this fast reacting



**Figure 2.2:** The SOA yield versus the total mass produced (for  $w=1$ ). The red dots are the results of this study from the unseeded experiments and the black dots are results from the experiments that ammonium sulfate seeds were used. The open symbols are the results of Chen et al. (2012). The solid line is the fitting of the data from both studies using the volatility basis set (VBS) framework.

system is of the same order as the variability of the yields calculated in the rest of the experiments with artifacts of the order of 20-30%.

The average density of the SOA formed in the ozonolysis experiments was  $0.99 \pm 0.05 \mu\text{g m}^{-3}$  (Table 2.1) a value lower than the Chen et al. (2012) calculated values. The approaches that were used for the density estimation are different; we matched the full distributions while Chen et al. (2012) relied on the mass mode diameters. The variation of composition with size (seeds were used in the Chen et al. (2012) and there could be more organics condensing on the smaller

and less on the larger particles) could introduce some additional uncertainty in approaches that use one particle size and the average particle composition.

For the ozonolysis experiments under dry conditions (RH=1-5%) the corresponding average HR-ToF-AMS collection efficiency was  $CE = 0.59 \pm 0.12$ . Docherty et al. (2013) reported an even lower AMS CE of  $0.36 \pm 0.01$  for  $\beta$ -caryophyllene ozonolysis SOA under dry conditions while Chen et al. (2012) found a  $CE=1$  for moderate relative humidity (RH=40 $\pm$ 1%) experiments. The CE in our higher RH experiments described later (Experiment 34 and Experiment 35) was around 0.5 similar to the experiments under dry conditions. The CE differences between our study and Chen et al. (2012) are probably due to AMS instrument differences.

The average O:C ratio of the fresh SOA produced was  $0.31 \pm 0.04$  and the H:C ratio was  $1.5 \pm 0.03$ . There was no difference in the elemental ratios between the seeded and unseeded experiments. Chen et al. (2012) reported higher O:C values ranging from 0.33 to 0.54. The difference in O:C between this study and Chen et al. (2012) is partially due to the use of the Aiken et al. (2008) fragmentation table in our study while the Chen et al. (2011) approach was used in the latter. To investigate the sensitivity of our estimated O:C to the algorithm used for its calculation we also used the Canagaratna et al. (2015) O:C estimation approach for two of our experiments. For Experiment 6 we estimated O:C= 0.25 and H:C=1.45 and after the correction we obtained O:C= 0.44 and H:C=1.69. For Experiment 12 we estimated O:C= 0.35 and H:C=1.49 and after the correction we got O:C= 0.53 and H:C=1.7. These results do underline the sensitivity of the O:C ratio to the specifics of the fragmentation table used for its calculation.

The SOA yields for the ozonolysis experiments were similar to the “ultimate yields” (no data above  $10 \mu\text{g m}^{-3}$  and  $\text{O}_3$  concentration less than 200 ppb) reported by Chen et al. (2012)



**Table 2.3:** Product mass yields for the three different reactions using a four product volatility basis set

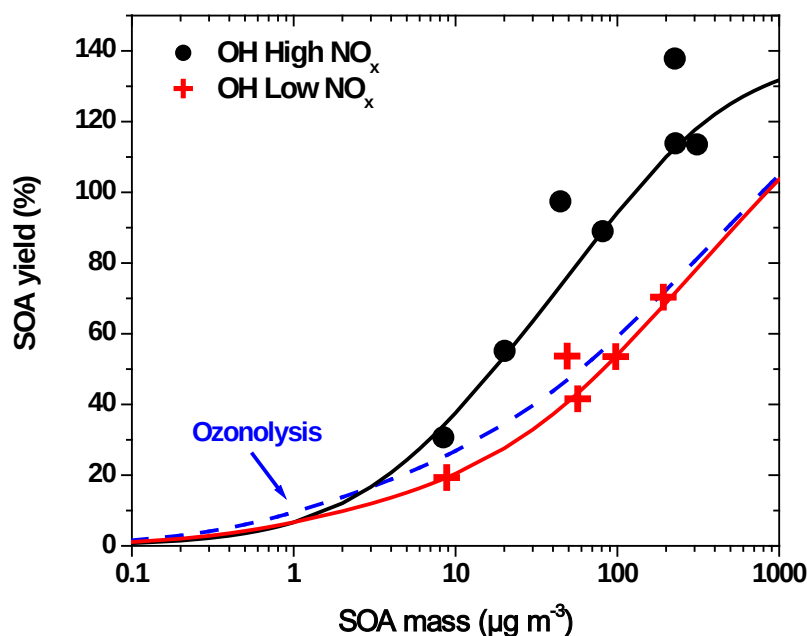
| Reaction                          | Saturation concentration ( $\mu\text{g m}^{-3}$ ) |      |      |      |
|-----------------------------------|---------------------------------------------------|------|------|------|
|                                   | 1                                                 | 10   | 100  | 1000 |
| Ozonolysis                        | 0.15                                              | 0.17 | 0.47 | 0.61 |
| OH radicals at high $\text{NO}_x$ | 0.01                                              | 0.59 | 0.79 | 0.01 |
| OH radicals at low $\text{NO}_x$  | 0.1                                               | 0.11 | 0.57 | 0.62 |

(Figure 2.2). Given that all our experiments covered periods much longer than the reaction timescales, potentially incomplete reactions cannot explain the observed scatter in the yields. We performed a few experiments at higher RH and the yields did not appear to be substantially different from the low RH experiments (described later). Finally the small temperature difference between our experiments and those of Chen et al. (2012) can only explain a few percent of the yield difference. Uncertainties in losses of vapors and particles and the reacted VOC are probably responsible for most of the scatter in Figure 2.2. The dashed line in Figure 2.2 represents the fitting of the data from the two studies using the volatility basis set framework (Donahue et al., 2006). The resulting parameters (mass yields of the products of the various volatilities) are shown in Table 2.3. This fitting suggests that 15 % of the SOA had relatively low volatility ( $C^*=1 \mu\text{g m}^{-3}$ ). For comparison, the mass yields for the ozonolysis products of sesquiterpenes that have been used in CTMs (Lane et al., 2008) for  $C^* = \{1, 10, 100, 1000\} \mu\text{g m}^{-3}$  are  $\alpha_1=0.05$ ,  $\alpha_2= 0.1$ ,  $\alpha_3= 0.5$ ,  $\alpha_4= 0.6$  respectively. This parameterization is a fit of the experimental studies of Griffin et al. (1999a), Hoffmann et al. (1997), and Ng et al. (2006). Chen et al. (2012) reported mass-based stoichiometric yields  $\alpha_1=0.17$ ,  $\alpha_2= 0.11$  and  $\alpha_3= 1.03$  for corresponding saturation concentrations of 1, 10, and 100  $\mu\text{g m}^{-3}$ . These results suggest that

practically all the products of the  $\beta$ -caryophyllene ozonolysis have effective saturation concentrations less or equal than  $1000 \mu\text{g m}^{-3}$ .

### 2.3.2 Oxidation via OH

In a second series of experiments  $\beta$ -caryophyllene was oxidized by OH radicals produced by HONO photolysis. NO and NO<sub>2</sub> were formed when HONO was injected in the chamber. Thus, in these experiments the oxidation happened under high NO<sub>x</sub> conditions (NO<sub>x</sub>/VOC= 0.17 ppb/ppbC). The initial reactant concentrations and the results of these experiments are listed in Table 2.1. The average density of the SOA formed in these experiments was  $1.19 \pm 0.1 \mu\text{g m}^{-3}$ .



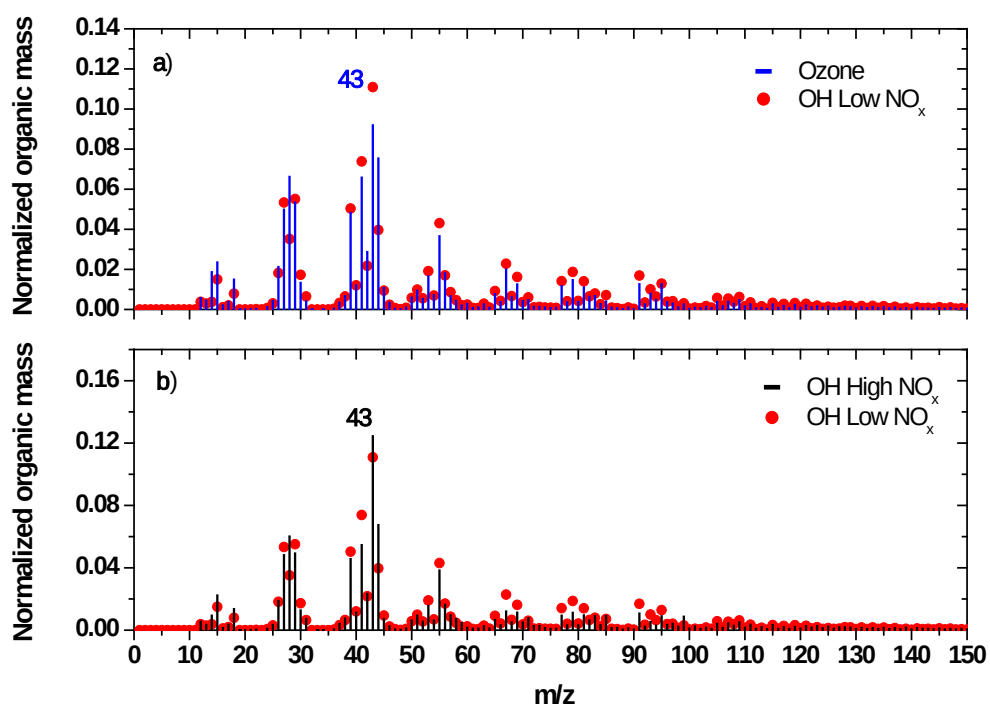
**Figure 2.3:** The SOA yield versus the total mass aerosol produced. The red dots represent the experiments when photolysis of HONO was used as a source of hydroxyl radicals and the black dots are for the photolysis of H<sub>2</sub>O<sub>2</sub>. The dashed line corresponds to the SOA yield from the ozonolysis of  $\beta$ -caryophyllene.

The average collection efficiency of the HR-ToF-AMS was  $0.38 \pm 0.11$ . Figure 2.3 depicts the measured SOA yields as a function of SOA mass concentration. The SOA yields in these experiments were higher than the yields of ozonolysis experiments. The average O:C ratio was  $0.34 \pm 0.07$  and the H:C ratio was  $1.5 \pm 0.07$ . The elemental ratios of the SOA were calculated using the HR-ToF-AMS without considering the presence of organonitrates. The  $O_3$  produced during the oxidation was always less than 10 ppb.

Similar experiments were performed using OH radicals produced by  $H_2O_2$  photolysis. The SOA yields for these experiments were similar to the yields of  $\beta$ -caryophyllene ozonolysis (Table 2.1). The average density of the SOA formed in these series of experiments was  $1.05 \pm 0.04 \mu g m^{-3}$ . The average O:C ratio was  $0.24 \pm 0.02$  and the H:C ratio was  $1.52 \pm 0.03$ . The average collection efficiency of the HR-ToF-AMS was  $0.67 \pm 0.1$ . The SOA yields at low  $NO_x$  conditions were lower than the ones at high  $NO_x$  conditions. These results are consistent with Ng et al. (2007) who found that SOA yield increases with increasing  $NO_x$  levels during the formation of SOA from sesquiterpenes (longifolene and aromadendrene) oxidation by OH. These authors suggested that the formation of low volatility organonitrates might be one reason for the higher SOA yields. Before the reaction started the HR-ToF-AMS nitrate signal was zero. After the SOA formation the ratio of the nitrate over the organic signal was  $0.15 \pm 0.04$  at the high  $NO_x$  experiments, while for the low  $NO_x$  experiments it was less than 0.01. Another potential reason for the difference in the SOA yield is the concentration of the oxidant. HONO photolysis produced one order of magnitude higher levels of OH than  $H_2O_2$  photolysis. We estimate that the exposure of the organics to OH was 10 times higher in the HONO experiments compared to the  $H_2O_2$  ones for the period until the maximum yield was achieved. The existence of nitrated organosulfates can also affect the SOA yield (Chan et al., 2011). The  $O_3$  formed in these

experiments was a few ppb so its contribution to the SOA formed was small. This is consistent with the differences in the AMS spectra of the SOA formed during the ozonolysis and the OH experiments.

Our results suggest that there are substantial differences in  $\beta$ -caryophyllene SOA produced under different  $\text{NO}_x$  conditions. The density of the SOA produced under high  $\text{NO}_x$  conditions is approximately 20% higher than the one produced under low  $\text{NO}_x$  conditions. Furthermore, during the oxidation of  $\beta$ -caryophyllene under high  $\text{NO}_x$  conditions less volatile compounds are produced (Table 2.3).



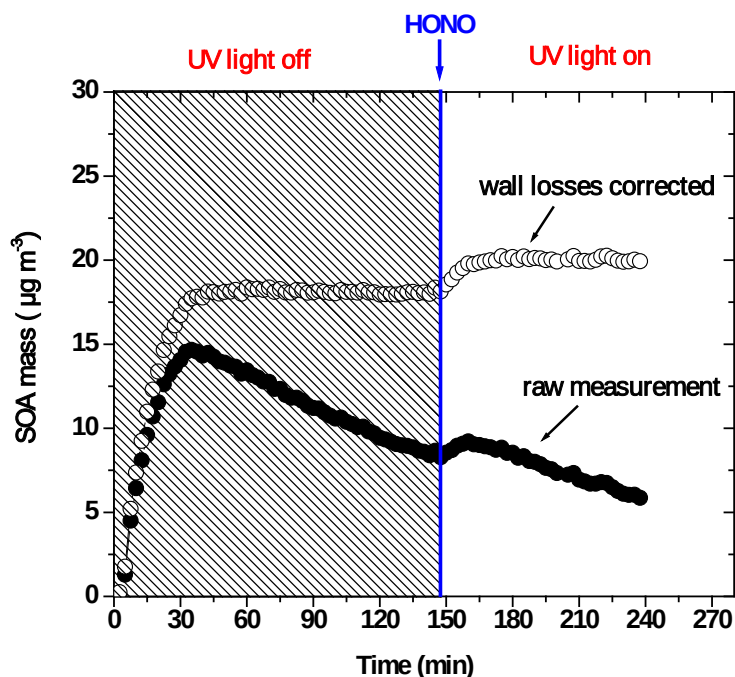
**Figure 2.4:** Comparison of the organic mass spectra of the  $\beta$ -caryophyllene SOA produced from the three reaction systems:

- a) From ozonolysis and OH at low  $\text{NO}_x$  ( $\theta=12^\circ$ )
- b) From OH at high and low  $\text{NO}_x$  ( $\theta=15^\circ$ ).

In Figure 2.4 we compare the average mass spectra of the  $\beta$ -caryophyllene SOA produced by ozonolysis, reaction with OH at high NO<sub>x</sub>, and low NO<sub>x</sub>. The ozonolysis SOA spectra had significant differences from those produced by the OH reaction (lower  $f_{43}$ , higher  $m/z$   $f_{44}$ , etc.) and  $\theta$  angles of 12° with the high NO<sub>x</sub> SOA and 17.1° for the low NO<sub>x</sub> case. For the high and low NO<sub>x</sub> spectra (without accounting for the nitrate) the  $\theta$  angle was 15°.

### 2.3.3 Chemical aging of fresh $\beta$ -caryophyllene SOA

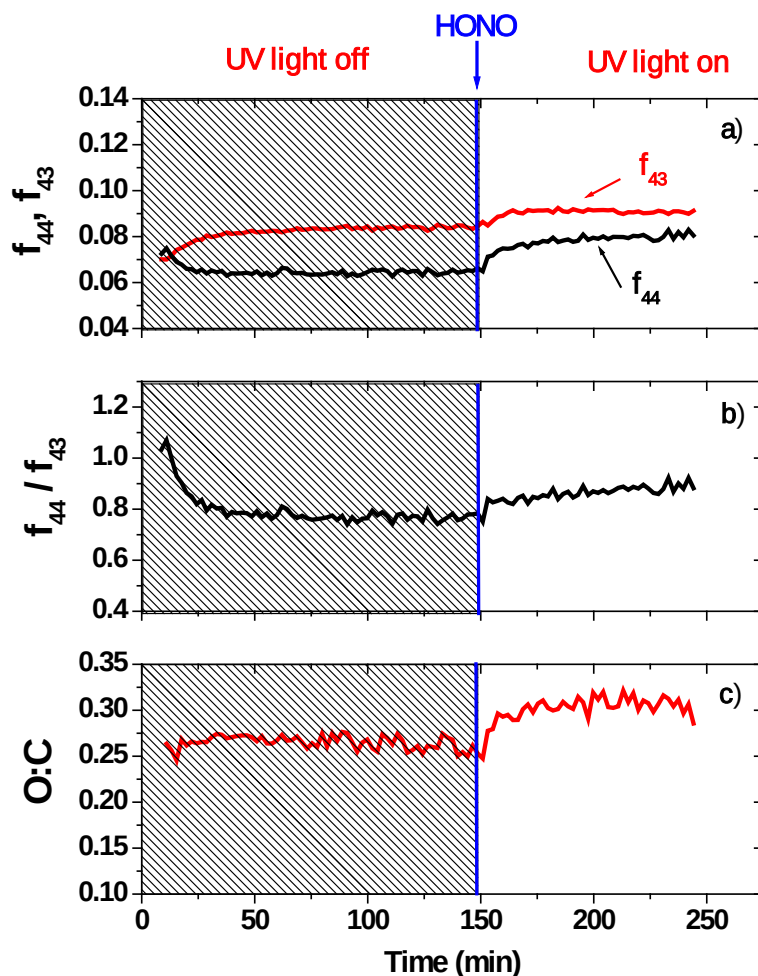
In another series of experiments we studied the chemical aging of the  $\beta$ -caryophyllene SOA produced in this first set of reactions. The SOA in these experiments was produced by the oxidation of the  $\beta$ -caryophyllene with O<sub>3</sub> in the presence of OH radicals (without the addition of OH scavenger). The SOA yield of this reaction is higher than the yields of the reactions of  $\beta$ -caryophyllene with the individual oxidants. The reason is probably the synergism between the two oxidants reacting with the first generation products of the oxidation of  $\beta$ -caryophyllene. In experiments 31-37 (Table 2.2) we investigated the effect of the subsequent exposure to OH radicals on  $\beta$ -caryophyllene SOA. In experiments 31-35 the OH radicals were produced by HONO photolysis while in experiments 36 and 37 they were produced by H<sub>2</sub>O<sub>2</sub> photolysis. The SOA mass concentration time series of Experiment 31 is presented in Figure 2.5. SOA was formed by the reaction of 300 ppb of O<sub>3</sub> and 3 ppb of  $\beta$ -caryophyllene. Approximately 1.5 hours after the mass of the SOA started decreasing in the smog chamber, HONO was injected in the chamber and the UV lights were turned on resulting in the production of significant levels of OH radicals (around 10<sup>7</sup> molecules cm<sup>-3</sup>). This resulted in an immediate increase of the aerosol corrected mass concentration by approximately 3  $\mu\text{g m}^{-3}$  (17%).



**Figure 2.5:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) (Experiment 31). The shaded part indicates the period where the UV light was off and the white one the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

The time series of the HR-ToF-AMS signals at  $m/z$  43 and  $m/z$  44 for the same experiment (Experiment 31) are shown in Figure 2.6. Chemical aging resulted in an increase of  $f_{43}$  from 0.08 to 0.09 and  $f_{44}$  from 0.065 to 0.08. Also, the ratio  $f_{44}/f_{43}$  increased approximately 10% when OH was introduced into the chamber. The O:C ratio increased from 0.26 to 0.32, after the production of the OH radicals in the chamber indicating chemical aging of  $\beta$ -caryophyllene SOA (Figure 2.6c). The results of all aging experiments are summarized in Table 2.2. The SOA yields increased 10-30% because of the aging reactions.

Matsunaga and Ziemann (2010) and Zhang et al. (2014) have stressed the possibility of losses of vapors to the Teflon chamber walls. During chemical aging these compounds could be



**Figure 2.6:** a) The time series of fragments 43 and 44. b) The ratio of the two fragments as a function of time. c) The oxygen over carbon ratio of the particles as a function of time for Experiment 31. The shaded part indicates the period where the UV light was off and the white one the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

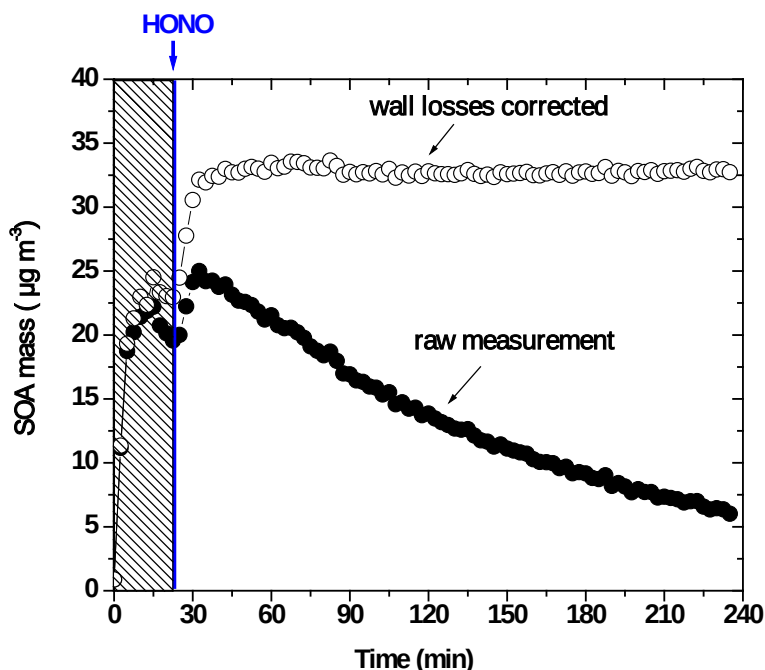
transformed to SOA and therefore these vapor losses may be introducing significant negative artifacts in chemical aging experiments. In order to test this hypothesis, we conducted experiments in which chemical aging of the SOA was initiated immediately after the SOA was formed. In Experiment 33 we initiated chemical aging of the  $\beta$ -caryophyllene SOA

approximately 10 min after the maximum SOA mass concentration was reached instead of around 1.5 hours in other experiments. The chemical aging of the SOA resulted in a wall-loss corrected SOA mass concentration increase from  $31 \mu\text{g m}^{-3}$  to  $41 \mu\text{g m}^{-3}$ , approximately 32%. The O:C ratio increased from 0.26 to 0.29. Gas-phase oxidation and transfer of the corresponding later generation products to the particulate phase can probably explain the increase in SOA mass concentration and the change in O:C. However, we cannot eliminate the possibility of existence of heterogeneous processes that also contribute to this increase. Studies in which the gas phase organic compounds were not present (or were present at much lower levels) are needed to separate the effects of homogeneous and heterogeneous reaction in the system. The results in Experiment 33 do support the wall loss of organic vapors to the walls.

To test the role of RH reaction between 3 ppb of  $\beta$ -caryophyllene and 300 ppb  $\text{O}_3$  two experiments occurred under higher relative humidity conditions, 50% and 90% (Experiments 34, 35). The SMPS sheath air flow was not dried and therefore the SMPS measurements were at a RH similar and a little lower of that in the smog chamber. The hygroscopic growth of  $\beta$ -caryophyllene SOA has been investigated by Alfarra et al. (2012). The corresponding water uptake even at RH=90% was low (diameter growth factor of 1.03 on average) and therefore any increase in the volume of the particles should be less than 10%. The high relative humidity did not affect the SOA production and their chemistry; the SOA yield and the O:C for this set of experiments were similar to the low relative humidity experiments of these series. Our results are not consistent with those of Winterhalter et al. (2009). However, there are numerous experimental differences in the two studies so it is difficult to draw any firm conclusions about what is causing this discrepancy. Figure 2.7 depicts the SOA mass concentration time series of



Experiment 35. Ten minutes after the maximum SOA mass concentration was reached, the OH concentration in the chamber was increased by injecting HONO. The earlier maximum in



**Figure 2.7:** The measured aerosol mass concentration in the chamber as a function of time and the wall losses corrected SOA mass concentration (for  $w=1$ ) (Experiment 35). The shaded part indicates the period where the UV light was off and the white one the period when the UV light was on. Also shown, the time when HONO was injected in the chamber.

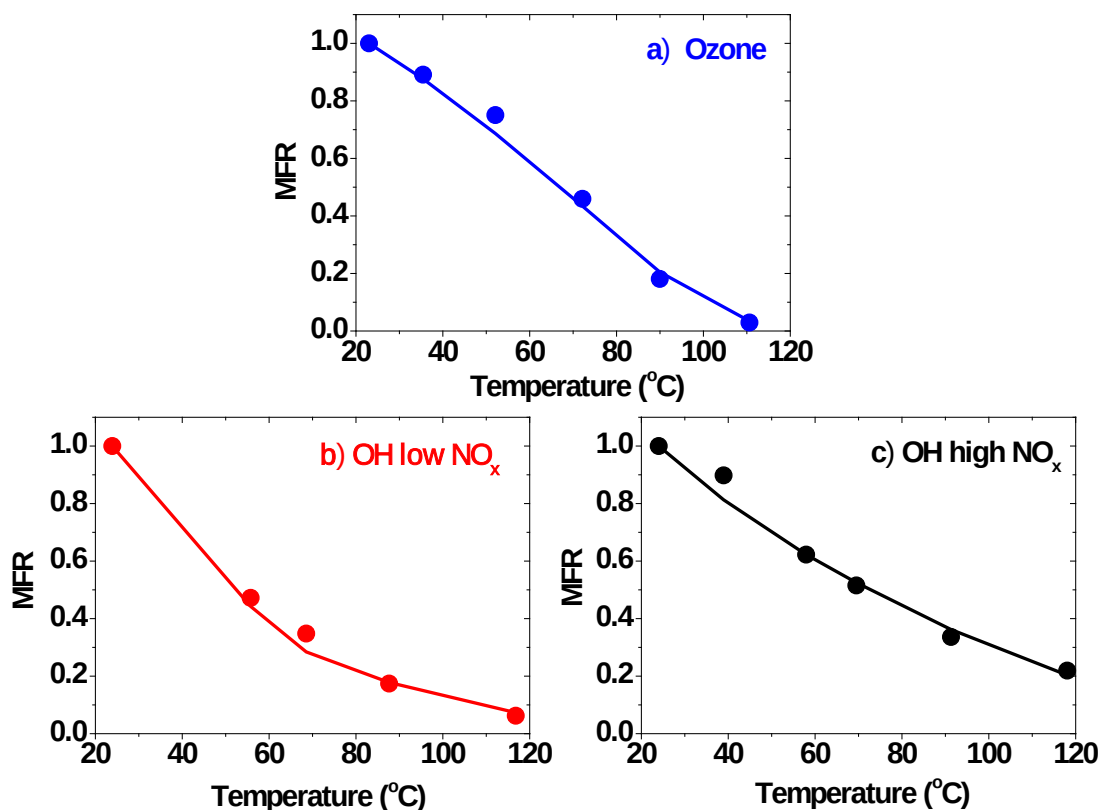
Experiment 35 is mainly due to a much higher wall loss rate constant for this experiment compared to the others. It was  $0.42 \text{ h}^{-1}$  compared to  $0.28 \text{ h}^{-1}$  for Experiment 1. These faster losses led to an earlier decline of the concentrations by 15 min or so compared to other experiments. In both experiments 34 and 35 the chemical aging resulted in a 40% increase of the wall-loss corrected mass concentration. The chemical aging of the  $\beta$ -caryophyllene SOA under high relative humidity resulted in the largest additional SOA mass production.

In experiments 36 and 37 we investigated the chemical aging of the  $\beta$ -caryophyllene SOA in the presence of OH radicals when photolysis of  $\text{H}_2\text{O}_2$  was used as a source of OH. In Experiment 36 the wall-loss corrected SOA mass concentration of the fresh SOA was  $30 \mu\text{g m}^{-3}$ , and the O:C was approximately 0.28. Approximately 1.5 hours after the mass of the SOA had started decreasing in the smog chamber the photolysis of  $\text{H}_2\text{O}_2$  was initiated. The exposure of the SOA to OH radicals was one order of magnitude lower than in the previous aging experiments (Experiment 31-35). After the production of OH radicals the mass concentration of the SOA remained stable and the O:C was 0.29. The corresponding mass spectra of the organic aerosol mass at the periods before and after the OH radical production were practically the same ( $\theta=3^\circ$ ). Experiment 37 led to similar results.

#### **2.3.4 Vaporization enthalpy of $\beta$ -caryophyllene SOA**

Using a thermodenuder we examined the behavior of the SOA at high temperatures. The mass fraction remaining (MFR) of SOA for the thermodenuder experiments is presented in Figure 2.8. We used the volatility distributions of the reaction products estimated from the measured yields (Table 2.3) as inputs to the thermodenuder model described by Riihimäki et al. (2010) and estimated the vaporization enthalpy and the accommodation coefficient ( $\alpha$ ) of the  $\beta$ -caryophyllene SOA. For the particles that are produced from the ozonolysis of  $\beta$ -caryophyllene (Experiment 3) the calculated effective enthalpy of vaporization was  $70 \pm 21 \text{ kJ mol}^{-1}$  and  $\alpha = 0.03$ . In other sets of simulations, the mass fraction remaining during the ramp of the temperature in the chamber (Experiment 1) was also used as input to the model. Finally, a combination of the two experiments was used. In all cases, the estimated enthalpy of vaporization and accommodation coefficient did not change. For  $\beta$ -caryophyllene reacted with OH in the presence

of high concentrations of  $\text{NO}_x$  (Experiment 25), the SOA formed had an effective enthalpy of vaporization of  $44 \pm 23 \text{ kJ mol}^{-1}$  and  $\alpha = 0.08$ . The SOA produced by the reaction with OH at low  $\text{NO}_x$  concentration (Experiment 26) had an effective enthalpy of  $56 \pm 21 \text{ kJ mol}^{-1}$  and  $\alpha = 0.05$ .



**Figure 2.8:** The thermograms (mass fraction remaining, MFR as a function of temperature) of the three different reaction systems. The circles represent the experimental data while the lines are the fitting of the model.

## 2.4 Conclusions

In this study we examined the formation of secondary organic aerosol from the reaction of  $\beta$ -caryophyllene with  $\text{O}_3$  and OH radicals. The SOA yield for the ozonolysis of  $\beta$ -caryophyllene was 27% at  $10 \mu\text{g m}^{-3}$  SOA. The measured yields are generally consistent with

those reported by Chen et al. (2012). The average density of the SOA formed in the ozonolysis experiments was  $0.99 \pm 0.05 \mu\text{g m}^{-3}$ . The average O:C ratio of the SOA produced was  $0.31 \pm 0.04$  and the H:C ratio was  $1.5 \pm 0.03$ . These values were calculated with the Aiken et al. (2008) approach. Use of the Canagaratna et al. (2015) corrections increases the O:C by approximately 0.2 units. The exposure of the  $\beta$ -caryophyllene SOA in UV light had no effect in the SOA.

The reaction of  $\beta$ -caryophyllene with OH at low  $\text{NO}_x$  gave an SOA yield equal to 20% at  $10 \mu\text{g m}^{-3}$  SOA, similar to the SOA yield measured for the ozonolysis experiments. The average density of the SOA formed in these experiments was  $1.05 \pm 0.04 \mu\text{g m}^{-3}$  and the average O:C ratio was  $0.24 \pm 0.02$  and the H:C ratio was  $1.52 \pm 0.03$ .

The SOA yield at the reaction of  $\beta$ -caryophyllene with OH at high  $\text{NO}_x$  was 38% at  $10 \mu\text{g m}^{-3}$  SOA. The average density of the SOA formed in this series of experiments was  $1.19 \pm 0.1 \mu\text{g m}^{-3}$ , 20% higher than the low  $\text{NO}_x$  experiments. The average O:C ratio was  $0.34 \pm 0.07$  and the H:C ratio was  $1.5 \pm 0.07$ . While the reactions under low  $\text{NO}_x$  conditions had similar SOA yields as the ozonolysis reactions, the presence of high  $\text{NO}_x$  levels leads to the production of less volatile compounds and higher yields.

A series of chemical aging experiments were performed. During these experiments the SOA produced from the reaction of  $\beta$ -caryophyllene and  $\text{O}_3$  was exposed to OH radicals. The addition of OH radicals, under high  $\text{NO}_x$  conditions, led to 13-17% increase of SOA mass concentration at dry conditions, and the O:C increased by 0.04 to 0.06 units. An experiment in which the chemical aging was initiated faster was conducted. The chemical aging of the SOA resulted in a SOA mass increase of 32%, indicating that in this system the vapor losses to the Teflon chamber walls were not negligible. The exposure of the  $\beta$ -caryophyllene SOA to UV light and to hydroxyl radicals under low  $\text{NO}_x$  conditions had little effect on the SOA.

We performed experiments with various amounts of seeds to estimate the magnitude of the vapor wall losses to the Teflon wall. We have also tried different reaction timescales (the longer the timescale the higher the corresponding losses). Our conclusion is that there are such losses in the  $\beta$ -caryophyllene system, but they are modest (less than 30% in most cases).

A limited number of experiments was performed to investigate the role of RH in the SOA formation and chemical aging. Experiments at 50% and 90% RH were conducted in which  $\beta$ -caryophyllene reacted with  $O_3$  in the presence of OH radicals. The high relative humidity did not appear to affect the fresh SOA production and its AMS spectrum. On the contrary, the high RH conditions enhanced the chemical aging of the  $\beta$ -caryophyllene SOA. The exposure of the SOA to OH radicals under high  $NO_x$  and high RH led to an increase of the SOA concentration by 40% and the O:C increased by 0.07 units.

For the particles that are produced by the ozonolysis of  $\beta$ -caryophyllene the calculated effective enthalpy of vaporization was  $70 \pm 21 \text{ kJ mol}^{-1}$ , while for the experiments in which  $\beta$ -caryophyllene reacted with OH at low  $NO_x$  conditions it was  $56 \pm 21 \text{ kJ mol}^{-1}$ , and at high  $NO_x$  conditions  $44 \pm 23 \text{ kJ mol}^{-1}$ . In all cases there was evidence of moderate resistances to mass transfer (mass accommodation coefficient 0.03-0.08).

## 2.5 References

Aiken, A. C. , DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U. and Jimenez, J. L.: O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, 2008.

Alfarra, M. R., Hamilton, J. F., Wyche, K. P., Good, N., Ward, M. W., Carr, T., Barley, M. H., Monks, P. S., Jenkin, M. E., Lewis, A. C., and McFiggans, G. B.: The effect of photochemical ageing and initial precursor concentration on the composition and hygroscopic properties of  $\beta$ -caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, 12, 6417–6436, 2012.

An, J. W., Pathak, K. R., Lee, B. H., and Pandis, S. N.: Aerosol volatility measurement using an improved thermodenuder: Application to secondary organic aerosol, *J. Aerosol Sci.*, 38, 305–314, 2007.

Atkinson, R. and Arey, J.: Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review, *Atmos. Environ.*, 37, 197–219, 2003.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R et al: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15, 253–272, 2015.

Chan, M. N., Surratt, J. D., Chan, A. W. H., Schilling, K., Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., Jaoui, M., Edgerton, E. S., Tanner, R. L., Shaw, S. L., Zheng, M., Knipping, E. M., and Seinfeld, J. H.: Influence of aerosol acidity on the chemical composition of secondary organic aerosol from  $\beta$ -caryophyllene, *Atmos. Chem. Phys.*, 11, 1735–1751, 2011.

Chen, Q., Li, Y. J., McKinney, K. A., Kuwata, M., and Martin, S. T.: Particle mass yield from caryophyllene ozonolysis, *Atmos. Chem. Phys.* 12, 3165–3179, 2012.

Crump, J. G. and Seinfeld, J. H.: Turbulent deposition and gravitational sedimentation of an aerosol in a vessel of arbitrary shape, *J. Aerosol Sci.*, 12, 405–415, 1981.

Docherty, K. S., Jaoui, M., Corse, E., Jimenez, J. L., Offenberg, J. H., Lewandowski, M., and Kleindienst, T.E.: Collection efficiency of the aerosol mass spectrometer for chamber-generated secondary organic aerosols, *Aerosol Sci. Tech.*, 47, 294-309, 2013.

Donahue, N. M., Robinson, A. L., Stanier, C. O., and Pandis, S. N.: Coupled partitioning, dilution and chemical aging of semivolatile organics, *Environ. Sci. Technol.*, 40, 2635-2643, 2006.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K. H., Möhler, O., Leisner, T., Müller, L., Reinnig, M. C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Urs Baltensperger, U: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, *PNAS*, 109, 13503-13508, 2012.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates and implications for atmospheric chemistry *P. Natl. Acad. Sci. USA*, 107, 6670-6675, 2010.

Griffin, R. J., Cocker III, D. R., Flagan R. C., and Seinfeld, J. H.: Organic aerosol from the oxidation of biogenic hydrocarbons, *J. Geophys. Res.*, 104, 3555–3567, 1999a.

Griffin, R. J., Cocker III, D. R., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 2721–2724, 1999b.

Helmig, D., Bocquet, F., Pollmann, J., and Revermann, T.: Analytical techniques for sesquiterpene emission rate studies in vegetation enclosure experiments, *Atmos. Environ.*, 38, 557-572, 2004.

Helmig, D., Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J., and Sakulyanontvittaya, T.: Sesquiterpene emissions from pine trees – identifications, emission rates and flux estimates for the contiguous United States, *Environ. Sci. Technol.*, 41, 1545–1553, 2007.

Hildebrandt, L., Henry, K. M., Kroll, J. H., Worsnop, D. R., Pandis, S. N., and Donahue, N. M.: Evaluating the mixing of organic aerosol components using High-Resolution Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 45, 6329–6335, 2011.

Hoffmann, T., Odum, J. R., Bowman, F., Collins, D., Klockow, D., Flagan, R. C., and Seinfeld, J. H.: Formation of organic aerosol from oxidation of biogenic hydrocarbons, *J. Atmos. Chem.*, 26, 189–222, 1997.

Jaoui, M., Leungsakul, S., and Kamens, R. M.: Gas and particle products distribution from the reaction of  $\beta$ -caryophyllene with ozone, *J. Atmos. Chem.*, 45, 261–287, 2003.

Jaoui, M., Kleindienst, T. E., Docherty, K. S., Lewandowski, M., and Offenberg J. H.: Secondary organic aerosol formation from the oxidation of a series of sesquiterpenes:  $\alpha$ -cedrene,  $\beta$ -caryophyllene,  $\alpha$ -humulene and  $\alpha$ -farnesene with  $O_3$ , OH and  $NO_3$  radicals, *Environ. Chem.*, 10, 178–193, 2013.

Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes I., Dentener, F. J., Facchini, M. C., Van Dingenen, R., Ervens, B., Nenes, A., Nielsen, C. J., Swietlicki, E. J., Putaud, P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5, 1053–1123, 2005.

Knudsen, J. T., Tollsten, L., and Bergström, L. G.: Review Article Number 76: Floral scents-a checklist of volatile compounds isolated by head-space techniques, *Phytochemistry*, 33, 253-280, 1993.



Kostenidou, E., Pathak, R. K., and Pandis, S. N.: An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, *Aerosol Sci. Tech.*, 41, 1002-1010, 2007.

Kostenidou, E., Lee, B. H., Engelhart, G. J., Pierce, J. R., and Pandis, S. N.: Mass spectra deconvolution of low, medium, and high volatility biogenic secondary organic aerosol, *Environ. Sci. Technol.*, 43, 4884–4889, 2009.

Lane, T., Donahue, N. M., and Pandis, S. N.: Simulating secondary organic aerosol formation using the basis-set approach in a chemical transport model, *Atmos. Environ.*, 42, 7439-7451, 2008.

Lee, A., Goldstein, A. H., Keywood, M. D., Gao, S., Varutbangkul, V., Bahreini, R., Ng, N. L., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the ozonolysis of ten different terpenes, *J. Geophys. Res.*, 111, D07302, 2006a.

Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.*, 111, D17305, 2006b.

Li, Y. J., Chen, Q., Guzman, M. I., Chan, C. K., and Martin, S. T.: Second-generation products contribute substantially to the particle-phase organic material produced by  $\beta$ -caryophyllene ozonolysis, *Atmos. Chem. Phys.*, 11, 121–132, 2011.

Matsunaga, A. and Ziemann, P. J.: Gas-wall partitioning of organic compounds in a Teflon film chamber and potential effects on reaction product and aerosol yield measurements, *Aerosol Sci. Tech.*, 44, 881-892, 2010.

Ng, N. L., Kroll, H. J., Keywood, D. M., Bahreini, R., Varutbangkul V., Flagan R. C., and Seinfeld J. H.: Contribution of first- versus second-generation products to secondary organic aerosols formed in the oxidation of biogenic hydrocarbons, *Environ. Sci. Technol.*, 40, 2283–2297, 2006.

Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO<sub>x</sub> level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *Atmos. Chem. Phys.*, 7, 5159-5174, 2007.

Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld J. H.: Gas/particle partitioning and secondary organic aerosol yields, *Environ. Sci. Technol.*, 30, 2580–2585, 1996.

Offenberg, J. H., Lewandowski, M., Edney, E. O., Kleindienst, T. E., and Jaoui, M.: Influence of aerosol acidity on the formation of secondary organic aerosol from biogenic precursor hydrocarbons, *Environ. Sci. Technol.*, 43, 7742-7747, 2009.

Pathak, R. K., Stanier, C. O., Donahue, N. M., and Pandis S. N.: Ozonolysis of  $\alpha$ -pinene at atmospherically relevant concentrations: Temperature dependence of aerosol mass fractions (yields), *J. Geophys. Res.*, 112, D03201, 2007.

Riipinen, I., Pierce, J. R., Donahue N. M., and Pandis S. N.: Equilibration time scales of organic aerosol inside thermodenuders: Kinetics versus equilibrium thermodynamics, *Atmos. Environ.*, 44, 597–607, 2010.

Shu, Y. H. and Atkinson, R.: Atmospheric lifetimes and fates of a series of sesquiterpenes, *J. Geophys. Res.*, 100, 7275–7281, 1995.

Winterhalter, R., Herrmann, F., Kanawati, B., Nguyen, T. L., Peeters, J., Vereeckenb L., and Moortgat G. K.: The gas-phase ozonolysis of  $\beta$ -caryophyllene ( $C_{15}H_{24}$ ). Part I: an experimental study, *Phys. Chem. Chem. Phys.*, 11, 4152–4172, 2009.

Zhang, X., Cappa, D. C., Jathar, S. H., McVay, R. C., Ensberg, J. J., Kleeman, M. J., and Seinfeld, J. H.: Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *PNAS*, 111, 5802-5807, 2014.

## **Chapter 3**

### **An inter-comparison of black carbon related instruments in a laboratory study of biomass burning aerosol**

## **Abstract**

Black carbon-containing particles are the most strongly light absorbing aerosols in the atmosphere. They are emitted during the combustion of fossil fuels, biofuels, and biomass. Measurements of black carbon are challenging because of its semi-empirical definition based on physical properties and not chemical structure, the complex and continuously changing morphology of the corresponding particles, and the effects of other particulate components on its absorption. In this study we compare six available commercial continuous BC instruments using biomass burning aerosol. The comparison involves a Soot Particle Aerosol Mass Spectrometer (SP-AMS), a Single Particle Soot Photometer (SP2), an aethalometer, a Multiangle Absorption Photometer (MAAP), and a blue and a green photoacoustic extinctions (PAX). An SP-AMS collection efficiency equal to 0.35 was measured for this aerosol system. The SP-AMS was then compared to all the other commercial instruments. Two regimes of behavior were identified corresponding to high and low organic/black carbon ratio. New mass absorption cross sections (MAC) were calculated for the optical instruments for the two regimes. The new MAC values varied from 30% to 2.3 times the instrument default values depending on the instrument and the regime. This comparison of the optical instruments suggests a stronger discrepancy among the BC measurements as the organic carbon content of the BC-containing particles increases.

### 3.1 Introduction

BC containing particles are emitted in the atmosphere from a wide variety of combustion processes. Sources that emit high concentrations of BC include diesel engines, industrial processes, residential solid fuel combustion, open burning, etc. (Bond et al., 2013). BC is characterized by its ability to absorb light and is refractory with vaporization temperature near 4000 K (Schwarz et al., 2006). The fresh emitted BC-containing particles have aggregate morphology (Medalia et al., 1969), are hydrophobic (Weingartner et al., 1997) and always include organic compounds usually coating the BC.

The effect of BC on human health and climate remains uncertain (Seinfeld, 2008). BC exerts significant radiative forcing and is believed to be the second most important global warming agent after carbon dioxide (Ramanathan and Caramichael, 2008; Bond et al., 2013). However its importance for the radiative balance of our planet might be even more significant because BC particles also contain other components like organics, sulfate, and nitrate (Adachi et al., 2010, Jacobson 2001) which can enhance their absorption. The magnitude of this enhancement though remains controversial (Cappa et al., 2012; Lack et al., 2012).

The measurement of the BC concentration in the atmosphere is complicated because there is no clear chemical definition of the species. It is also challenging because of the non-spherical, complex morphology of the BC-containing particles (Chakrabarty et al., 2006) which changes as the particles evolve in the atmosphere. The varying thickness of coatings that can be formed through condensation of secondary organic aerosol components on BC-containing particles, presents an additional challenge for the measurement of BC.

Petzold et al. (2013) proposed a terminology for the BC based on the method used for its measurement. A number of commercial instruments (aethalometer, photoacoustic extinctions-

PAX, Multiangle Absorption Photometer-MAAP, Particle Soot/Absorption Photometer-PSAP, Photoacoustic Soot Spectrometer-PASS, Photoacoustic Spectrometer-PAS, continuous soot monitoring system-COSMOS) for the measurement of BC calculate the equivalent BC (eBC) concentration by measuring the absorption coefficient ( $b_{\text{abs}}$ ) of the particles. The aerosol mass absorption cross section (MAC) is then used to convert measured the measured  $b_{\text{abs}}$  to the eBC concentration. Other instruments (Soot Particle Aerosol Mass Spectrometer-SP-AMS, Single Particle Soot Photometer-SP2) measure the refractory BC (rBC) by heating the particles with a laser (Melton, 1984; Snelling et al., 2005; Chan et al., 2011; Stephens et al., 2003; Schwarz et al., 2006). In the SP2 the BC-containing particles are heated to the point of incandescence. At this point the energy emitted by the BC is measured. In the SP-AMS the BC-containing particles are vaporized with the use of the laser. The resulting vapor is ionized and the ions are detected by a high-resolution mass spectrometer (DeCarlo et al., 2006). These instruments are calibrated relating their signal to the rBC mass with the help of BC proxies like Aquadag (Aqueous Deflocculated Acheson Graphite, Achenson Inc.) or fullerene soot (Alfa Aesar) or regal black (REGAL 400R pigment black Cabot Corp.). Finally there are thermal-optical methods that measure elemental carbon (EC). These methods exploit the fact that EC does not evaporate at temperatures below 700°C, but it can be oxidized at temperatures higher than 350°C (Karanasiou et al., 2015; Petzold et al., 2013). The aerosol samples are heated in a helium atmosphere until all the organic compounds are removed. During this process some of organic compounds are converted into pyrolytic carbon, which can be misidentified as EC. There are a number of approaches for the correction for this artifact based on the absorption of light by the sample (Huntzicker et al., 1982). After heating in an inert atmosphere, O<sub>2</sub> is introduced into the system converting the remaining carbonaceous material on the filter to carbon dioxide. The CO<sub>2</sub> is then

reduced to methane by passing through a methanator oven, and the resulting CH<sub>4</sub> is detected by a flame ionization detector (FID). Using the transmission signal and the FID data the EC concentration is finally calculated. This work will not focus on the above thermal–optical techniques.

Several inter-comparisons of BC measuring instruments have been previously conducted. Chirico et al. (2010) compared measurements of eBC in diesel exhaust by an aethalometer and a MAAP. The aethalometer eBC was calculated using a MAC of 16.6 m<sup>2</sup> g<sup>-1</sup> at  $\lambda=880$  nm and a multiple scattering correction (Weingartner et al., 2003). The eBC measured by the aethalometer was higher than that of the MAAP by a factor of  $1.46 \pm 0.05$ . This study found that the MAAP measurements were in a better agreement with the total mass of aerosol.

Slowik et al. (2007) compared an SP2, a PAS, and a MAAP using emissions from the combustion of ethylene (uncoated soot). A MAC of 6.2 m<sup>2</sup> g<sup>-1</sup> at  $\lambda=870$  nm was used for the PAS, and a MAC of 5.1 m<sup>2</sup> g<sup>-1</sup> at  $\lambda=870$  nm for the MAAP. For uncoated soot (OA/BC=0.1-0.7), the average ratio of eBC measured by the MAAP to the rBC measured by the SP2 was 0.91. Moreover, the ratio of the PAS to the SP2 BC measurements was 1.36. This study also tested the instruments at higher OA/BC ratios by using oleic acid and anthracene. Two different soot coatings were used: a 50 nm oleic acid coating and 60 nm anthracene one. For the 50 nm coating the ratio of the MAAP to the SP2 BC was 1.15, while the ratio of the PAS to the SP2 BC was 0.77. For the 60 nm coating the ratio of the MAAP to the SP2 increased to 1.8, while the ratio of the PAS to the SP2 decreased to 1.6. Finally, the same authors compared the instruments by sampling glassy carbon spheres with a known density. In these tests they found  $\pm 60\%$  differences among the various BC measurements.



Holder et al. (2014) compared an SP2, a PASS-3 and an aethalometer during on-road and near road measurements. The PASS-3 measures the  $b_{\text{abs}}$  at  $\lambda=405, 532, \text{ and } 781 \text{ nm}$ . For the aethalometer measurements a  $\text{MAC} = 16.6 \text{ m}^2 \text{ g}^{-1}$  at  $880 \text{ nm}$  was used and a  $\text{MAC} = 7.5 \text{ m}^2 \text{ g}^{-1}$  at  $550 \text{ nm}$  for the PASS-3. For the inter-comparison they used 2 seconds and 10 second-averaged measurements. For the 10 seconds-averaged measurements the slope of the regression line relating the PASS to the aethalometer measurements ranged from 0.89 to 1.07 with an intercept ranging from  $-0.17$  to  $0.21 \mu\text{g m}^{-3}$ . The slope of the SP2 as a function of the PASS measurements ranged from 0.52 to 0.64 with an intercept ranging from 0.02 to  $0.15 \mu\text{g m}^{-3}$ .

Onasch et al. (2012) compared the SP-AMS with a MAAP using ambient measurements in an urban area. The two instruments were correlated, with  $R^2=0.76$  for 2 days of measurements.

Massoli et al. (2015) compared the rBC measurements of an SP-AMS and an SP2 during the CalNex 2010 field campaign. The SP-AMS measurements were approximately 55% (20-100%) of the rBC reported by the SP2.

Despite the above studies there are a number of remaining questions related to the performance of different BC measurements. These include the effect of the non-BC to BC ratio on the BC measurements of especially the optical eBC measurements, the MAC values that should be used, and the performance of the newly developed SP-AMS.

In this study we evaluate the SP-AMS and for the first time compare it with 5 other BC instruments. The inter-comparison involve an SP-AMS, a blue PAX ( $\lambda=405 \text{ nm}$ ), a green PAX ( $\lambda=532 \text{ nm}$ ), a MAAP, an aethalometer, and an SP2. The experiments were conducted under controlled conditions, by injecting biomass burning emissions into a smog chamber. Two regimes of high and low organic to black carbon concentration were examined to investigate the effect of the OA concentration on the measurement of the eBC.

## 3.2 Experimental setup

The experiments took place in the smog chamber facility of the Center for Atmospheric Particle Studies (CAPS) at Carnegie Mellon University. The smog chamber is a 12 m<sup>3</sup> Teflon reactor (Welch Fluorocarbons) inside a temperature controlled room. Prior to an experiment, the chamber was flushed with purified air for 12-48 h. Air was passed through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity. All the experiments were carried out at a constant temperature of 20±2°C and at RH<10%.

BC-containing particles were generated by the combustion of white birch using an environmentally efficient cook stove (G3 rocketstove, Envirofit). The emissions were injected in the smog chamber using two Dekati diluters (DI-1000) in a parallel configuration.

The BC instruments used can be separated in to two categories: instruments that measure the eBC concentration and instruments that measure the rBC concentration.

### 3.2.1 eBC measurements

A seven wavelength aethalometer (AE31, Magee Scientific) was used to measure the eBC in seven wavelengths (470, 520, 590, 660, 880, and 950 nm). The instrument collects particles on a quartz filter and simultaneously measures the attenuation of light through the filter at various wavelengths. The AE-31 measures the  $b_{abs}$  and using  $MAC (m^2 g^{-1}) = 14625/\lambda (nm)$  it calculates the eBC. The aethalometer is a filter-based instrument and has multiple artifacts. These artifacts are associated with the absorption enhancement due to multiple scattering in the collection filter (Weingartner et al., 2003) and the decrease of the aethalometer response due to scattering of aerosols embedded in the filter or due to some particles being shadowed by others

(Kirchstetter and Novakov, 2007). Finally, there are artifacts due to the light absorbing particles accumulating in the filter (Lack et al., 2008; Cappa et al., 2008). Our measurements were corrected for the scattering and multiple scattering artifacts following Saleh et al. (2014) and Tasoglou et al. (2016) using the corrections suggested by Weingartner et al. (2003) and Kirchstetter and Novakov (2007).

The MAAP (5012, Thermo Scientific) is also a filter-based instrument in which the particles are deposited on a quartz fiber filter (Petzold et al., 2002; Petzold and Schönlinner, 2004; Petzold et al., 2005). It uses a 670 nm visible light source and a multi angle absorption photometer, to measure the aerosol light absorption. Using a  $MAC=6.6 \text{ m}^2 \text{ g}^{-1}$  it calculates the eBC. The multi-angle absorption photometer quantifies the change of the radiation field caused by deposited particles in the front and the back of a glass-fiber filter, and removes the scattering effects that can interfere with optical absorption methods. Due to this approach the artifacts of the instrument are lower compared to other filter-based instruments (Petzold et al., 2002; Petzold and Schönlinner, 2004; Petzold et al., 2005).

The PAX (Droplet Measurement Techniques) uses photoacoustic spectroscopy to measure the optical properties of aerosol (Arnott et al., 1999). It uses a modulated diode laser to simultaneously measure light scattering and absorption. The modulated laser light illuminates the sample and heats any absorbing particles. The particles heat the surrounding air and cause a pressure/sound wave. The  $b_{abs}$  can then be calculated directly from the amplitude of the sound wave. The PAX does not have any filter-related artifacts and has an uncertainty of less than 5% for the aerosol absorption measurement (Lack et al., 2006). The BC mass can then be calculated using an assumed MAC ( $MAC = 10.18 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 405 \text{ nm}$  and  $MAC = 7.75 \text{ m}^2 \text{ g}^{-1}$  at  $\lambda = 532 \text{ nm}$ ). The light scattering coefficient ( $b_{scat}$ ) is measured by a wide-angle integrating reciprocal

nephelometer. In our comparison experiments a green ( $\lambda=532$  nm) and a blue ( $\lambda=405$  nm) PAX were used. Fullerene soot and PSL spheres were used to calibrate the absorption and the scattering signals respectively. An activated carbon denuder was placed in front of the PAXs to remove  $\text{NO}_2$ .

### 3.2.2 rBC measurements

The SP2 (Droplet Measurement Techniques) measures the BC mass in individual aerosol particles. An intra-cavity, continuous Nd: YAG laser beam (1064 nm) is used to heat the sample. BC particles absorb the energy and are heated to the point of incandescence. The energy emitted during this incandescence is measured, and a quantitative determination of the BC mass of the particle is made. The SP2 also includes a scattering detector, which detects single-particle light-scattering at 1064 nm (Stephens et al., 2003; Schwarz et al., 2006). When sampling at high concentrations ( $>10,000$  particles  $\text{cm}^{-3}$ ) particle coincidence can be a significant measurement artifact. The data were corrected for coincidence using the approach of Holder et al. (2014) leading to a 1-15% increase of the BC mass. The BC particle size range that can be detected is 70 to 500 nm. The SP2 was calibrated for the BC measurements using fullerene soot. The data were analyzed using the Probe Analysis Package for Igor (PAPI). The scattering measurement was calibrated using monodisperse polystyrene latex (PSL) spheres.

The SP-AMS (Aerodyne Inc.) is an instrument similar to the HR-ToF-AMS with the addition of an intracavity laser vaporizer. This instrument can provide information about the size distribution and the chemical composition of both the non-refractory (organics, nitrate, ammonium, sulfate, chloride), and refractory components of the particles (Onasch et al., 2012).

In contrast to all the previously mentioned instruments, the SP-AMS measurements of BC are affected mostly by particle shape.

The particle collection efficiency (CE) of the SP-AMS depends on the particle transmission through the lens ( $E_L$ ), the fraction of particles focusing on the vaporizer ( $E_S$ ), and the fraction of particles vaporized ( $E_b$ ) (Huffman et al., 2005). When the SP-AMS uses only the tungsten vaporizer the CE of the non-refractory species for 60-600 nm particles is mostly affected by the  $E_b$  (Huffman et al., 2005; Mathew et al., 2008; Middlebrook et al., 2012; Docherty et al., 2013). When using the laser vaporizer the CE is mostly affected by the  $E_S$  (Willis et al., 2014). The SP-AMS is equipped with a beam-width probe which allows the calculation of the  $E_S$  (Huffman et al., 2005; Willis et al., 2014). The SP-AMS was operated in two modes: V mode with the tungsten vaporizer on and V mode with both the tungsten and the laser vaporizer on. The measurement time for each mode was 1 min. The non-refractory components of the particles were measured at the laser-off mode and the refractory species at the laser-on mode. For the SP-AMS data analysis SQUIRREL 1.54B and PIKA 1.13B were used. In our analysis we used the fragmentation table suggested by Aiken et al. (2008).

### **3.2.3 Additional measurements**

A number of additional instruments were deployed during these experiments in order to provide additional information about the systems investigated. A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3772 or 3010) was used for the measurement of the number distribution of the particles. A suite of gas monitors was also used. The concentration of  $O_3$  was measured using a continuous  $O_3$  analyzer (Dasibi 1008-PC) and of nitrogen oxides using a Teledyne chemiluminescent  $NO/NO_2/NO_x$  analyzer Model 200A. Also,

a carbon dioxide (CO<sub>2</sub>) gas analyzer (LI-820, LI-Cor Biosciences) and a carbon monoxide (CO) gas analyzer (model 300A, API-Teledyne) were used. Gas-phase instruments were calibrated before each experiment.

### 3.3 Experimental results and discussion

In a typical experiment the emissions from biomass burning were injected in the smog chamber during the flaming phase of combustion. The injection lasted approximately 5 minutes. Table 3.1 summarizes all the inter-comparison experiments and the instruments available in each experiment. Table 3.2 summarizes the initial concentrations of the experiments.

**Table 3.1:** The inter-comparison experiments of the BC instruments

| Exp. | SP2 | SP-AMS | Aethalometer | PAX <sub>blue</sub> | PAX <sub>green</sub> | MAAP |
|------|-----|--------|--------------|---------------------|----------------------|------|
| 1    | ✓   | ✓      |              |                     |                      |      |
| 2    | ✓   | ✓      |              |                     |                      |      |
| 3    | ✓   | ✓      |              |                     |                      |      |
| 4    | ✓   | ✓      |              |                     |                      |      |
| 5    | ✓   | ✓      |              |                     |                      |      |
| 6    |     | ✓      | ✓            | ✓                   | ✓                    | ✓    |
| 7    |     | ✓      | ✓            | ✓                   | ✓                    | ✓    |
| 8    |     | ✓      | ✓            | ✓                   | ✓                    | ✓    |
| 9    |     | ✓      | ✓            | ✓                   | ✓                    | ✓    |
| 10   |     | ✓      |              |                     |                      |      |
| 11   |     | ✓      |              |                     |                      |      |
| 12   |     | ✓      |              |                     |                      |      |

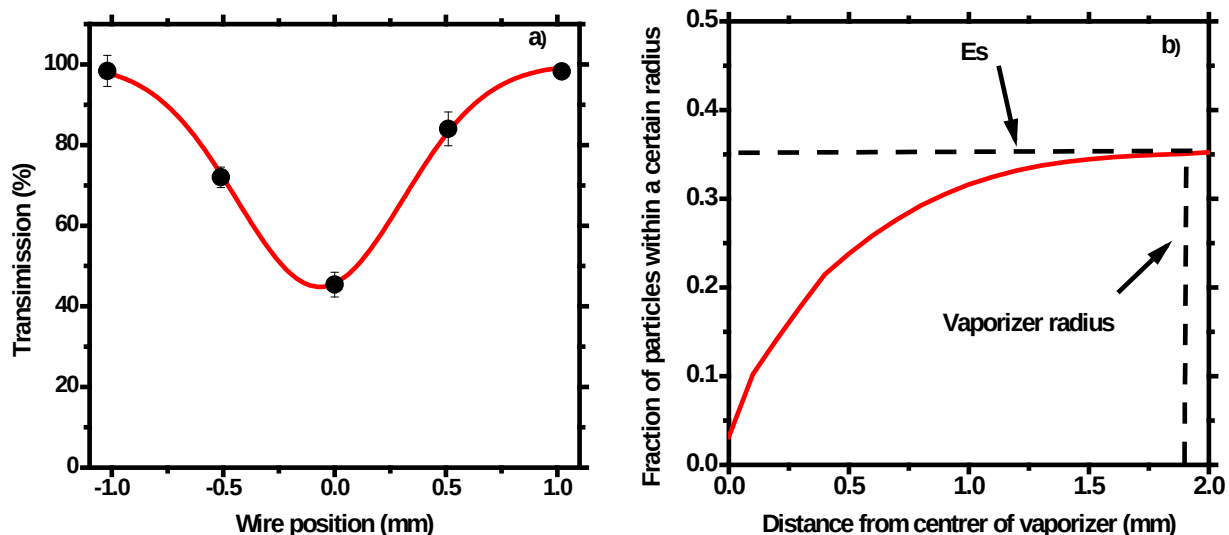
#### 3.3.1 SP-AMS collection efficiency

In Experiments 10-12, rBC measurements were made with the SP-AMS using a beam width-probe while the instrument was sampling in the laser-on mode. The positions of the probe with respect to center of the tungsten vaporizer were -1.02, -0.51, 0, 0.51, 1.02 mm. The sampling lasted for 1.5 hours during each experiment.

**Table 3.2:** Initial concentrations of the biomass burning emissions

| Exp. | SP-AMS                                   |                                              |        | SP2                         |                                 | SMPS                                 |
|------|------------------------------------------|----------------------------------------------|--------|-----------------------------|---------------------------------|--------------------------------------|
|      | OA<br>( $\mu\text{g m}^{-3}$ )<br>(CE=1) | rBC<br>( $\mu\text{g m}^{-3}$ )<br>(CE=0.35) | OA/rBC | rBC<br>( $\text{cm}^{-3}$ ) | rBC<br>( $\mu\text{g m}^{-3}$ ) | Total number<br>( $\text{cm}^{-3}$ ) |
| 1    | 4.4                                      | 121.7                                        | 0.04   | 19500                       | 116.4                           | 32000                                |
| 2    | 5.0                                      | 28.7                                         | 0.17   | 11500                       | 29.6                            | 91100                                |
| 3    | 1.8                                      | 103.0                                        | 0.02   | 13500                       | 91.6                            | 17000                                |
| 4    | 3.8                                      | 56.3                                         | 0.07   | 11000                       | 32.9                            | 32500                                |
| 5    | 15.5                                     | 46.6                                         | 0.33   | 13500                       | 42.6                            | 52500                                |
| 6    | 4.0                                      | 89.8                                         | 0.04   | -                           | -                               | 17000                                |
| 7    | 7.1                                      | 44.5                                         | 0.16   | -                           | -                               | 16000                                |
| 8    | 1.6                                      | 21.1                                         | 0.08   | -                           | -                               | 1600                                 |
| 9    | 28.0                                     | 40.6                                         | 0.69   | -                           | -                               | 13500                                |
| 10   | 12.9                                     | 429.3                                        | 0.03   | -                           | -                               | -                                    |
| 11   | 1.4                                      | 150.6                                        | 0.01   | -                           | -                               | -                                    |
| 12   | 2.3                                      | 262.2                                        | 0.01   | -                           | -                               | -                                    |

For the data analysis a mathematical model was used that assumes that the particle density in the beam can be represented by a 1-D Gaussian probability density function. The  $E_s$  is a function of the particle beam width at the vaporizer relative to the vaporizer radius. More specifically,  $E_s$  is equal to the cumulative 1-D Gaussian probability density function for a distance equal to the radius of the vaporizer (Huffman et al., 2005). Figure 3.1 shows the results of the analysis for Experiment 10. The beam width ranged from 0.34 to 0.4 mm. The  $E_s$  ranged from 0.34 to 0.35. Assuming that the CE of the rBC for the SP-AMS is mostly affected by the shape of the particles ( $\text{CE} \approx E_s$ ) (Willis et al., 2014), an average SP-AMS CE for rBC of 0.35 was estimated and was used for our analysis in the rest of the work.



**Figure 3.1:** a) SP-AMS rBC signal transmission as a function of the wire position during the beam-width probe measurements for Experiment 10. The black circles represent the average signal transmission, for 5 different position of the wire compared to the center of the vaporizer, for 1.5 hours of sampling. The red line represents the fitting of the measurements using a 1-D Gaussian distribution. b) Cumulative 1-D Gaussian probability density function. These fractions represent the particles that impact the vaporizer. For distance equal to the radius of the vaporizer the fraction is equal to the  $E_s$ .

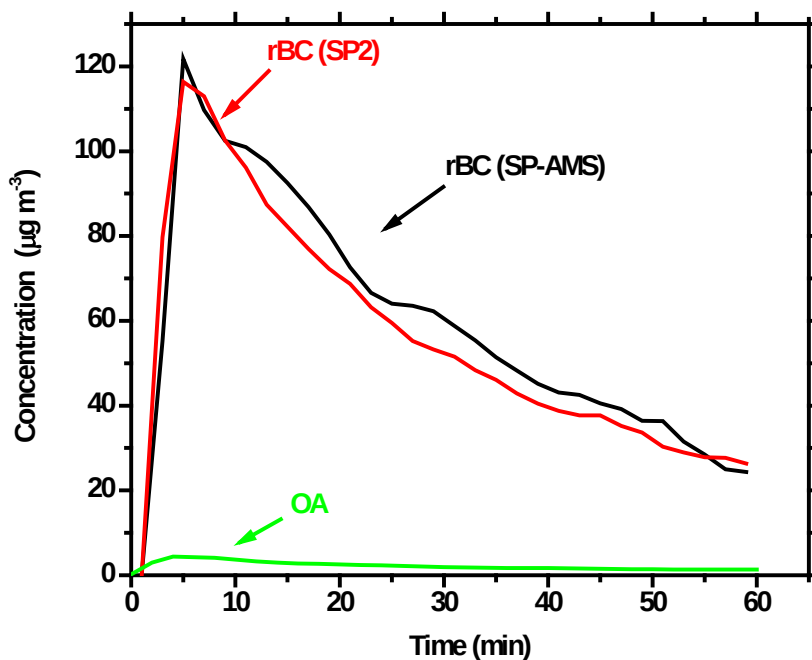
Hennigan et al. (2011) performed laboratory experiments studying emissions from biomass burning. They found a  $CE=1$  for the Quadrupole-AMS (Q-AMS) by comparing measurements of a SMPS and the Q-AMS. Eriksson et al. (2014) studied the organic particulate matter emissions from biomass burning. They estimated a  $CE$  equal to 1 for the HR-ToF-AMS by comparing its measurements with a GC-MS. Both Q-AMS and HR-ToF-AMS use the same focusing system of lens, and tungsten vaporizer as the SP-AMS when it was operated at the laser-off mode to measure the non-refractory components of the particles. Thus, in this study a



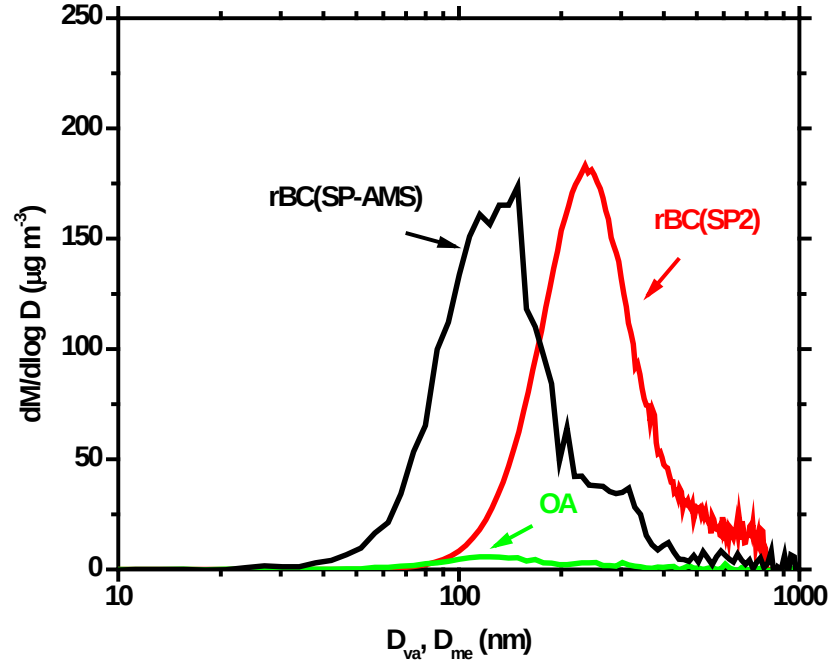
CE=1 is assumed for the OA following the above studies as well as Ortega et al. (2013) and Bruns et al. (2014).

### 3.3.2 Inter-comparison of BC instruments

The measured concentrations during Experiment 1 are shown in Figure 3.2. At time zero the emissions were injected into the chamber. The initial number concentration of the particles inside the chamber was 32,000 particles  $\text{cm}^{-3}$ . According to the SP-AMS measurements the OA/rBC ratio varied from 0.04 to 0.05 during this experiment.



**Figure 3.2:** rBC concentration measurements by the SP-AMS and the SP2 and OA measured by the SP-AMS during Experiment 1. A CE=0.35 is assumed for rBC and CE=1 for the OA.

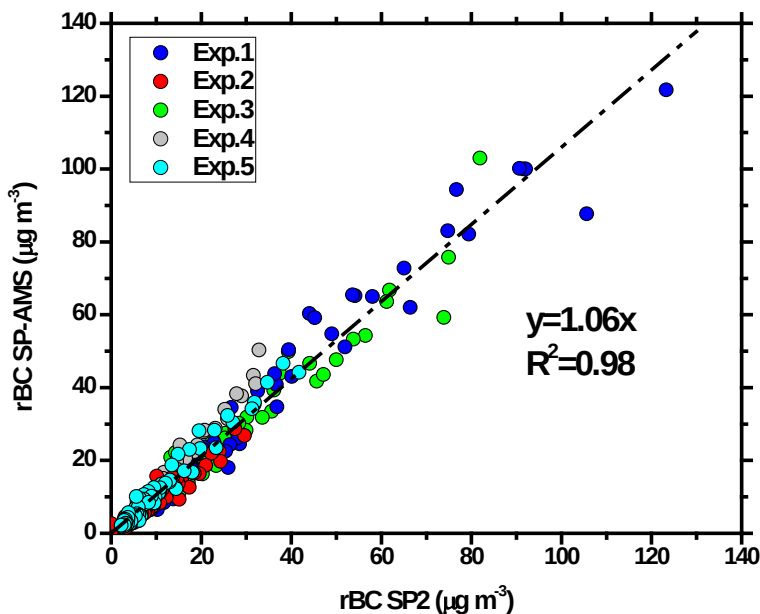


**Figure 3.3:** Average size distributions of the biomass burning particles during the first 30 min of the measurements.

Initially the concentration of the OA was  $4 \mu\text{g m}^{-3}$ , while the rBC concentrations measured by the SP-AMS and the SP2 were  $122 \mu\text{g m}^{-3}$  and  $116 \mu\text{g m}^{-3}$  respectively. Figure 3.3 shows the average mass size distributions measured by the SP2 and the SP-AMS for Experiment 1 from  $t=2$  min to  $t=32$  min. The OA had a mode vacuum aerodynamic diameter ( $D_{va}$ ) equal to 123 nm and the rBC 149 nm. The mode of the mass equivalent diameter ( $D_{me}$ ) for the rBC was at 235 nm. Table A.1.1 shows the average mode diameter for the distributions retrieved from each instrument.

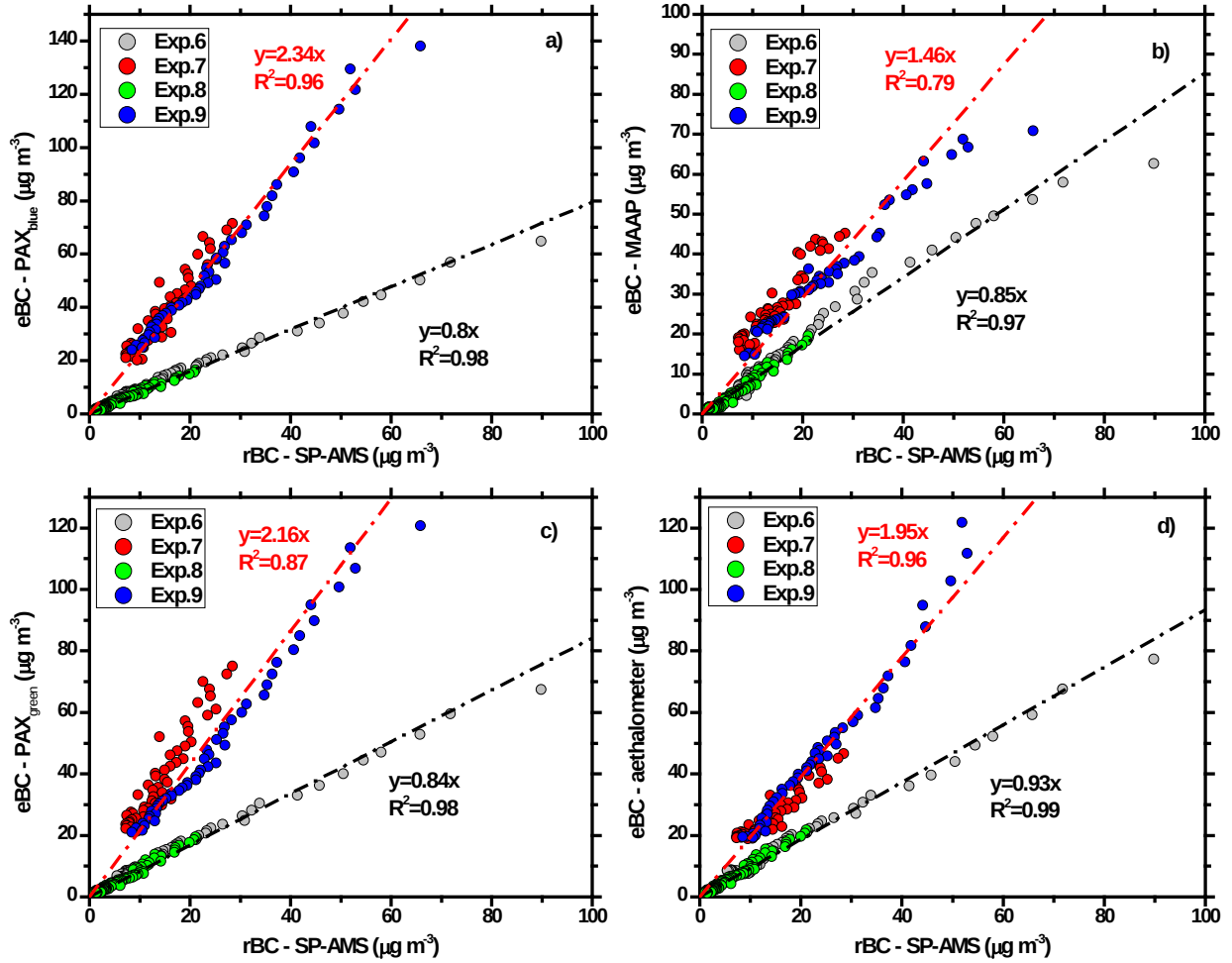
The rBC mass measurements by the SP-AMS and the SP2 for Experiments 1-5 are compared to each other in Figure 3.4. The OA/rBC ranged from 0.02 to 0.33. For individual experiments the SP-AMS rBC measurements ranged from 0.9 to 1.32 of the SP2 values with  $R^2=0.93-0.97$ . On average the rBC measured by the SP-AMS was 6% higher than that of the SP2.

Since a  $CE=E_s$  has been used to correct the rBC measurements of the SP-AMS, the agreement between the two instruments suggests that the rBC measurements of the SP-AMS are mostly affected by the shape of the particles.



**Figure 3.4:** Inter-comparison of the measurements of the rBC by the SP2 and the SP-AMS for Experiments 1 to 5.

The comparisons between the eBC measured by the four optical instruments and the corrected rBC measured by the SP-AMS are shown in Figure 3.5. For low OA/rBC ( $OA/rBC < 0.1$ ) (Experiments 6 and 8) the ratio of the eBC to the rBC ranged from 0.8 to 0.93 depending on the optical instrument used. On the other hand, for the high OA/rBC ( $0.1 < OA/rBC < 0.7$ ) experiments 7 and 9 the ratio of the eBC to the rBC ranged from 1.46 to 2.34. As expected, the measurements of the eBC were closer to the rBC measurements for low OA/rBC. The presence of high OA concentrations in the system can lead to overestimation of the eBC values by a factor of 2 or higher.



**Figure 3.5:** Inter-comparison of the rBC measured by the SP-AMS (corrected for CE=0.35) and the measured eBC from all the optical BC related instruments.

The MAC values were calculated for this system using the  $b_{abs}$  from the optical instrument and the rBC measurements of the SP-AMS (Table 3.3). There is a substantial increase of the MAC values for high OA/rBC compared to values of low OA/rBC. More specifically, the MAC values at high OA/rBC ( $0.1 < \text{OA/rBC} < 0.7$ ) for the PAX<sub>blue</sub> and PAX<sub>green</sub> were 1.9 and 1.6 times higher than the values at low OA/rBC ( $\text{OA/rBC} < 0.1$ ) respectively. Also for high OA/rBC the MAC values of the MAAP and the aethalometer were 0.7 and 1.1 times higher than the values at low OA/rBC. The increase of the OA concentration in the system has a strong effect on

the measurements of the optical instruments, possibly due to the increase of the thickness of the OA coating of the BC core or due to existence of absorbing OA (brown carbon). The new MAC values presented in this study differ from the factory default MAC of the instruments. For high OA/rBC the MAC values were 0.55 to 2.3 times the default MAC values depending on the instrument. For low OA/rBC the MAC values were 0.3 to 0.9 times the default MAC values.

**Table 3.3:** Calculated mass absorption cross-section (MAC) for the two OA/rBC regimes

| Regime                     | MAC ( $\text{m}^2 \text{g}^{-1}$ ) |                      |                       |      |
|----------------------------|------------------------------------|----------------------|-----------------------|------|
|                            | PAX <sub>blue</sub>                | PAX <sub>green</sub> | Aethalometer (880 nm) | MAAP |
| OA/rBC<0.1 (Exp. 6, 8)     | 8.1                                | 6.5                  | 4.4                   | 5.3  |
| 0.1<OA/rBC<0.7 (Exp. 7, 9) | 23.9                               | 16.7                 | 9.1                   | 9.0  |

We also compared the instruments that measure the eBC using the optical properties of the particles, at high and low OA/rBC using the results of Experiments 6-9 (Table 3.4).

**Table 3.4:** Comparison of eBC measurements

| Instrument           |                      | OA/rBC<0.1 (Exp. 6, 8) |                | 0.1<OA/rBC<0.7 (Exp. 7, 9) |                |
|----------------------|----------------------|------------------------|----------------|----------------------------|----------------|
| y                    | x                    | Slope <sup>1</sup>     | R <sup>2</sup> | Slope <sup>1</sup>         | R <sup>2</sup> |
| PAX <sub>blue</sub>  | Aethalometer         | 0.85                   | 0.99           | 1.19                       | 0.93           |
| PAX <sub>green</sub> | Aethalometer         | 0.9                    | 1              | 1.09                       | 0.8            |
| MAAP                 | Aethalometer         | 0.91                   | 0.98           | 0.74                       | 0.69           |
| PAX <sub>blue</sub>  | PAX <sub>green</sub> | 0.95                   | 1              | 1.07                       | 0.97           |
| PAX <sub>blue</sub>  | MAAP                 | 0.92                   | 0.98           | 1.58                       | 0.93           |
| PAX <sub>green</sub> | MAAP                 | 0.98                   | 0.98           | 1.47                       | 0.95           |

<sup>1</sup>Intercept is assumed to be zero

For low OA/rBC (Experiments 6 and 8) the average discrepancies ranged from 5 to 15%, with the aethalometer giving the highest values and the PAX<sub>blue</sub> the lowest measurements of eBC. For high OA/rBC (Experiments 7 and 9) the discrepancies increased varying from 22% to 58%, with the PAX<sub>blue</sub> giving now the highest measurements and the MAAP the lower eBC values. Thus, for low OA/rBC there is better agreement among the optical instruments. The increase of the OA concentration led to significant discrepancies among the eBC measurements of the optical instruments reaching more than 50%.

### **3.4 Comparison with previous studies**

The ratio of MAAP eBC to the rBC for low OA/rBC was 15% lower than the ratio for the glassy carbon spheres measured by Slowik et al. (2007). The ratio of eBC from the MAAP to the rBC for  $0.1 < \text{OA/BC} < 0.7$  that they reported was similar (7% lower) than the ratio that we measured for similar conditions.

The ratio of eBC measurements of the aethalometer to the MAAP for high OA/rBC in this study was also consistent (7% lower) with the ratio for diesel exhaust with OA/BC=0.1-0.4 reported by in Chirico et al. (2010).

Massoli et al. (2015) reported a ratio of the ambient rBC measured by the SP-AMS to the SP2 of 0.55 (range 0.2-1) assuming  $\text{CE}_{\text{rBC}}=1$ . In this study the SP-AMS values, assuming a  $\text{CE}_{\text{rBC}}=1$ , were 37% of the SP2 ones.

### 3.5 Conclusions

The purpose of this study is the comparison of commercial BC instruments that are used widely for atmospheric measurements in relatively well constrained yet complex laboratory environment using biomass burning emissions with  $OA/rBC < 0.7$ .

A CE of 0.35 was estimated for the SP-AMS rBC mass by using the beam-width probe analysis. The corrected SP-AMS rBC measurements were compared with the SP2 measurements. The two instruments agreed within 6% suggesting that the CE of the SP-AMS for the BC measurements was affected mainly by the shape of the particles.

The eBC measurements by the optical instruments were compared with the corrected rBC measurements by the SP-AMS during high and low OA/rBC experiments. For the high OA/rBC experiments the ratio of eBC to rBC was higher (ratios ranging from 1.46 to 2.34) than for the experiments in which OA/rBC was low (ratios ranging from 0.8 to 0.93). The presence of high OA concentrations in the system can lead to an overestimation of the eBC by a factor of 2 or higher.

New MAC values were calculated for the two OA/rBC regimes for all optical instruments. At high OA/rBC ratios the MAC values were higher ( $MAC = 9-23.9 \text{ m}^2 \text{ g}^{-1}$ ) than at low OA/rBC ( $MAC = 4.4-8.1 \text{ m}^2 \text{ g}^{-1}$ ). The OA/rBC ratio has a significant effect in the measurements of the optical instruments, due to the increase of the thickness of the OA coating of the BC core or to existence of absorbing activity of OA (brown carbon).

For the low OA/rBC regime the measurements of eBC of the optical instruments were more consistent (slope ranging from 0.85 to 0.98) than for the high OA/rBC conditions (slope ranging from 0.74 to 1.58). For low OA/rBC the aethalometer gave the highest measurements

and the PAX<sub>blue</sub> the lowest measurements of eBC, while for high OA/rBC the PAX<sub>blue</sub> gave the highest measurements and the MAAP the lowest measurements of eBC.

### 3.6 References

Adachi, K., Chung, S. H., and Buseck, P. R.: Shapes of soot aerosol particles, and implications for their effects on climate, *J. Geophys. Res.*, 115, D15206, 2010.

Arnott, W. P., Moosmüller, H., Rogers, C. F., Jin, T., and Bruch, R.: Photoacoustic spectrometer for measuring light absorption by aerosol: Instrument description, *Atmos. Environ.*, 33, 2845–2852, 1999.

Allen, G. A., Lawrence, J., and Koutrakis, P.: Field validation of a semi-continuous method for aerosol black carbon (aethalometer) and temporal patterns of summertime hourly black carbon measurements in southwestern PA, *Atmos. Environ.* 33, 817–823, 1999.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Berntsen, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, *J. Geophys. Res.*, 118, 5380–5552, 2013.

Bruns, E. A., Krapf, M., Orasche, J., Huang, Y., Zimmermann, R., Drinovec, L., Mocnik, G., El-Haddad, I., Slowik, J. G., Dommen, J., Baltensperger, U. and Prevot, A. S. H: Characterization of primary and secondary wood combustion products generated under different burner loads, *Atmos. Chem. Phys.*, 15, 2825–2841, 2015.



Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative absorption enhancements due to the mixing state of atmospheric black carbon, *Science*, 337, 1078–1081, 2012.

Cappa, C. D., Lack, D. A., Burkholder, J. B., and Ravishankara, A. R.: Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: evidence from laboratory measurements, *Aerosol. Sci. Tech.*, 42, 1022–1032, 2008.

Chakrabarty, R. K., Moosmüller, H., Garro, M. A., Arnott, W. P., Walker, J. W., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from the laboratory combustion of wildland fuels: Particle morphology, and size, *J. Geophys. Res.*, 111, D07204, 2006.

Chan, T. W., Brook, J. R., Smallwood, G. J., and Lu, G.: Time-resolved measurements of black carbon light absorption enhancement in urban and near-urban locations of southern Ontario, Canada, *Atmos. Chem. Phys.*, 11, 10407–10432, 2011.

Chirico, R., DeCarlo, P. F., Heringa, M. F., Tritscher, T., Richter, R., Prevôt, A. S. H., Dommen, J., Weingartner, E., Wehrle, G., Gysel, M., Laborde, and M., Baltensperger, U.: Impact of aftertreatment devices on primary emissions and secondary organic aerosol formation potential from in-use diesel vehicles: results from smog chamber experiments, *Atmos. Chem. Phys.*, 10, 11545–11563, 2010.

DeCarlo, P. F., Kimmel, J. R., Trimborn, A., Northway, M. J., Jayne, J. T., Aiken, A. C., Gonin, M., Fuhrer, K., Horvath, T., Docherty, K. S., Worsnop, D. R., and Jimenez, J. L.: Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer, *Anal. Chem.*, 78, 8281–8289, 2006.

DeCarlo, P. F., Slowik, J. G., Worsnop, D. R., Davidovits, P., and Jimenez, J. L.: Particle morphology, and density characterization by combined mobility and aerodynamic diameter measurements. Part 1: Theory, *Aerosol Sci. Technol.*, 38, 1185–1205, 2004.

Docherty, K. S., Jaoui, M., Corse, E., Jimenez, J. L., Offenberg, J. H., Lewandowski, M., and Kleindienst, T. E.: Collection efficiency of the Aerosol Mass Spectrometer for chamber-generated secondary organic aerosols, *Aerosol Sci. Technol.*, 47, 294–309, 2013.

Eriksson, A. C., Nordin, E. Z., Nystrom, R., Pettersson, E., Swietlicki, E., Bergvall, C., Westerholm, R., Boman, C. and Pagels, J. H.: Particulate PAH emissions from residential biomass combustion: time-resolved analysis with aerosol mass spectrometry, *Environ. Sci. Technol.*, 48, 7143–7150, 2014.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett Jr., J. L., Kreidenweis, S. M. and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, *Atmos. Chem. Phys.*, 11, 7669–7686, 2011.

Hitzenberger, R., Jennings, S. G., Larson, S. M., Dillner, A., Cachier, H., Galambos, Z., Rouc, A., and Spain, T. G.: Intercomparison of measurement methods for black carbon aerosols, *Atmos. Environ.*, 33, 2823–2833, 1999.

Holder, A. L., Hagler, G. S. W., Yelverton, T. L. B., Hays, M. D., On-road black carbon instrument intercomparison and aerosol characteristics by driving environment, *Atmos. Environ.*, 88, 183–191, 2014.

Huffman, J., Jayne, J. T., Drewnick, F., Aiken, A. C., Onasch, T. B., Worsnop, D. R., Jimenez, J., Design, modeling, optimization, and experimental tests of a particle beam width probe for the aerodyne aerosol mass spectrometer, *Aerosol Sci. Tech.*, 39, 1143–1163, 2005.

Huntzicker, J. J., Johnson, R. L., Shah, J. J., and Cary, R. A.: Analysis of organic and elemental carbon in ambient aerosols by a thermal-optical method, in: *Particulate Carbon: Atmospheric Life Cycle*, edited by: Wolff, G. T. and Klimisch, R. L., Plenum Press, New York, USA, 79–85, 1982.

Jacobson, M. Z.: Strong Radiative Heating due to the mixing state of black carbon in atmospheric aerosols, *Nature*, 409, 695– 697, 2001.

Jeong, C.-H., Hopke, P. K., Kim, E., and Lee, D.-W.: The comparison between thermal-optical transmittance elemental carbon, and Aethalometer black carbon measured at multiple monitoring sites, *Atmos. Environ.*, 38, 5193–5204, 2004.

Karanasiou, A., Minguillón, M. C., Viana, M. , Alastuey, A., Putaud, J.-P., Maenhaut, W., Panteliadis, P., Mocnik, G., Favez, O., and T. A. J. Kuhlbusch.: Thermal-optical analysis for the measurement of elemental carbon (EC) and organic carbon (OC) in ambient air a literature review, *Atmos. Meas. Tech. Discuss.*, 8, 9649–9712, 2015.

Kirchstetter, T. W., and Novakov, T.: Controlled generation of black carbon particles from a diffusion flame and applications in evaluating black carbon measurement methods, *Atmos. Environ.*, 41, 1874–1888, 2007.

Lavanchy, V. M. H., Gaggeler, H. W., Nyeki, S., and Baltensperger, U.: Elemental carbon (EC), and black carbon (BC) measurements with a thermal method and an aethalometer at the high-alpine research station Jungfraujoch, *Atmos. Environ.*, 33, 2759–2769, 1999.

Lack, D. A., Justin M. Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, A. N., and Schwarz, J. P.: Brown carbon, and internal mixing in biomass burning particles, *PNAS*, 109, 14802-14807, 2012.

Lack, D. A., Cappa, C. D., Covert, D. S., Baynard, T., Massoli, P., Sierau, B., Bates, T. S., Quinn, P. K., Lovejoy, E. R., and Ravishankara, A. R.: Bias in filter-based aerosol light absorption measurements due to organic aerosol loading: Evidence from ambient measurements, *Aerosol. Sci. Tech.*, 42, 1033–1041, 2008.

Lack, D. A., Lovejoy, E. R., Baynard, T., Pettersson, A., and Ravishankara, A. R.: Aerosol Absorption Measurement using Photoacoustic Spectroscopy: Sensitivity, Calibration, and Uncertainty Developments *Aerosol. Sci. Tech.*, 4, 697–708, 2006.

Massoli, P., Onasch, T. B., Cappa, C. D., Nuamaan, I., Hakala, J., Hayden, K., Li, S.-M., Sueper, D. T., Bates, T. S., Quinn, P. K., Jayne, J. T., and Worsnop, D. R.: Characterization of black carbon-containing particles from soot particle aerosol mass spectrometer measurements on the R/V Atlantis during CalNex 2010, *J. Geophys. Res.*, 120, 2575–2593, 2015.

Matthew, B. M., Middlebrook, A. M., and Onasch, T. B.: Collection efficiencies in an Aerodyne Aerosol Mass Spectrometer as a function of particle phase for laboratory generated aerosols, *Aerosol Sci. Technol.*, 42, 884–898, 2008.

Medalia, A. I., and Heckman, F. A.: Morphology of aggregates—II. Size, and shape factors of carbon black aggregates from electron microscopy, *Carbon*, 7, 569–582, 1969.

Melton, L. A.: Soot diagnostics based on laser heating, *Appl. Opt.*, 23, 2201–2208, 1984.

Middlebrook, A. M., Bahreini, R., Jimenez, J. L., and Canagaratna, M. R.: Evaluation of composition-dependent collection efficiencies for the Aerodyne aerosol mass spectrometer using field data, *Aerosol Sci. Technol.*, 46, 258–271, 2012.

Mullins, J., and Williams, A.: The optical properties of soot: a comparison between experimental and theoretical values, *Fuel*, 66, 277–280, 1987.

Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., and Worsnop, D. R.: Soot particle aerosol mass spectrometer: Development, validation, and initial application, *Aerosol Sci. Technol.*, 46, 804–817, 2012.

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A. and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass burning smoke in a flow reactor during FLAME-3, *Atmos. Chem. Phys.*, 13, 11551–11571, 2013.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, *Journal of Nanoparticle Research*, 6, 267–272, 2004.

Petzold, A., Schloesser, H., Sheridan, P., Arnott, W., Ogren, J., and Virkkula, A.: Evaluation of multiangle absorption photometry for measuring aerosol light absorption, *Aerosol Sci. Technol.*, 39, 40–51, 2005.

Petzold, A., and Schönlinner, M.: Multi-angle absorption photometry - a new method for the measurement of aerosol light absorption and atmospheric black carbon, *J. Aerosol Sci.*, 35, 421–441, 2004.

Petzold, A., Kramer, H., and Schönlinner, M.: Continuous measurement of atmospheric black carbon using a multi-angle absorption photometer, *Environ. Sci. Poll. Res.*, 4, 78–82, 2002.

Petzold, A., Ogren, J. A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., and Zhang, X.-Y.: Recommendations for the interpretation of "black carbon" measurements, *Atmos. Chem. Phys.*, 13, 8365–8379, 2013.

Ram, K., Sarin, M. M., and Tripathi, S. N.: Inter-comparison of thermal, and optical methods for determination of atmospheric black carbon and attenuation coefficient from an urban location in northern India, *Atmos. Res.*, 97, 335–342, 2010.

Ramanathan, V., and Carmichael, G.: Global and regional climate changes due to back carbon, *Nat. Geosci.*, 1, 221–227, 2008.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Prest, A. A., Manvendra, K. D., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, *Nature Geoscience*, 7, 647–650, 2014.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Darbeheshti, M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Loewenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, *J. Geophys. Res.*, 111, 207, 2006.

Seinfeld, J. H.: Black carbon, and brown clouds, *Nature Geoscience*, 1, 15, 2008.

Slowik, J. G., Cross E. S., Han, J-H, Davidovits, P., Onasch, T. B., Jayne, J.T., Williams L. R., Canagaratna, M. R., Worsnop D. R., Chakrabarty R. K., Moosmüller, H., Arnott, W. P., Schwarz, J. P., Gao, R-S., Fahey, D. W., Kok, G. L., and Petzold, A.: An inter-comparison of instruments measuring black carbon content of soot particles, *Aerosol Sci. Technol.*, 41, 295–314, 2007.

Snelling, D. R., Smallwood, G. J., Liu, F., Gülder, Ö. L., and Bachalo, W. D.: A calibration-independent laser-induced incandescence technique for soot measurement by detecting absolute light intensity, *Appl. Opt.*, 44, 6773–6785, 2005.

Stephens, M., Turner, N., and Sandberg, J.: Particle identification by laser-induced incandescence in a solid-state laser cavity, *Appl. Opt.*, 42, 3726–3736, 2003.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Baumgardner, D. G., Kok, G. L., Chung, S., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Lowenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, *J. Geophys. Res.*, 111, D16207, 2006.

Tasoglou, A., Saliba, G., Subramanian, R., and Pandis, S. N.: An investigation of the chemical aging on the absorption of biomass burning carbonaceous aerosol, to be submitted, 2016.

Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers, *J. Aerosol. Sci.*, 34, 1445–1463, 2003.

Weingartner, E., Burtscher, H., and Baltensperger, U.: Hygroscopic properties of carbon and diesel soot particles, *Atmos. Environ.*, 31, 2311–2327, 1997.

Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D.: Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, *Atmos. Meas. Tech.*, 7, 4507–4516, 2014.

Wu, J.-S., Krishnan, S. S., and Faeth, G. M.: Refractive indices at visible wavelengths of soot emitted from buoyant turbulent diffusion flames, *J. Heat Trans.*, 119, 230–237, 1997.

## **Chapter 4**

### **Absorption of chemically aged biomass burning carbonaceous aerosol**



## **Abstract**

Smog chamber experiments were conducted to study the changes of the physical properties and chemical composition of biomass burning particles as they evolve in the atmosphere. A Soot Particle Aerosol Mass Spectrometer (SP-AMS) and a Single Particle Soot Photometer (SP2) were used for the chemical characterization of the particles. An Aethalometer as well as a green and a blue photoacoustic extinctionmeter (PAX) were used for the study of the aerosol optical properties. As the biomass burning smoke aged, exposed to UV light, ozone, or OH radicals, organic material condensed on the preexisting particles. This coating led to an increase of the absorption of the black carbon-containing particles by as much as a factor of two. The absorption enhancement of biomass burning particles due to their coating with aromatic secondary organic aerosol (SOA) was also studied. The resulting absorption enhancement was determined mainly by the changes in the SOA mass concentration and not the changes of its oxidation state. The enhancement of the absorption of the aging biomass burning particles was consistent with the predictions of a core-shell Mie theory model assuming spherical particles and non-absorbing coating.

## 4.1 Introduction

Primary organic aerosol (POA) is directly emitted into the atmosphere from a range of sources including diesel and gasoline vehicle exhaust, biomass burning, meat cooking, etc. On a global scale biomass burning is responsible for almost 90% of primary OA emissions (Bond et al., 2004). Biomass burning particles consist of black carbon (BC), organic compounds, and inorganic salts.

BC strongly absorbs visible light (Bond et al., 2006), is refractory with vaporization temperature near 4000 K (Schwarz et al., 2006), has an aggregate morphology (Medalia et al., 1969), and is insoluble in water and common organic solvents (Fung, 1990). Its refractive index is constant across the visible spectrum (Marley et al., 2001). All sources that emit BC also emit primary organic aerosol (POA), as well as vapors that can be precursors of secondary organic aerosol (SOA) in the atmosphere. Residential coal and biomass fuel combustion dominate the global BC emissions (60–80%), while on-road and non-road diesel engines are leading emitters (about 70%) in Europe, North America, and Latin America (Bond et al., 2013).

The composition of biomass burning particles depends on the fuel type, moisture content, and combustion conditions. Oxygen-rich flaming combustion generally releases more BC and heat, while lower-temperature smoldering fires emit more total particulate matter and CO (Lobert et al., 1991). The emitted organic particulate matter and surrounding vapors can undergo subsequent reactions in the gas and particulate phases leading to changes in the organic compound volatility and thus its phase partitioning. This series of processes is called chemical aging and can be a significant source of SOA in the atmosphere (Donahue et al., 2012). As smoke ages, organic material condenses or evaporates from the particle phase, but there is no additional BC production.

The presence of a purely scattering shell around an absorbing core can increase its absorption efficiency by focusing more photons onto the core (Fuller et al., 1999). For an internal mixture of BC with OA and inorganic salts such as sulfate the absorption of the BC core is enhanced due to this lensing effect (Jacobson, 2001; Lack and Cappa, 2010). Lensing has been shown theoretically to increase the absorption of the BC core up to a factor of two for atmospherically relevant core and shell sizes (Jacobson, 2001; Schnaiter et al., 2005; Bond et al., 2006; Saliba et al., 2016). Understanding the photochemical evolution of biomass burning OA (bbOA) and the corresponding volatile organic compound (VOC) emissions which can undergo atmospheric aging is crucial in the effort to obtain a complete picture of the role of biomass burning in the atmosphere including its effect on climate.

A number of previous studies have examined the chemical aging of bbOA. Grieshop et al. (2009) exposed biomass burning emissions from three different sources to UV-light. The experiments were performed under high  $\text{NO}_x$  conditions. They found that the emissions from burning laurel oak under smoldering and flaming conditions had an O:C of 0.25 and 0.36 respectively. The photochemical aging of these emissions resulted in a 15-20% increase of the OA, while the O:C increased to 0.56 and 0.42 respectively. The fresh yellow pine emissions under flaming conditions with embers had an O:C of 0.13 and 0.2 for smoldering conditions. The photochemical aging resulted in a 110-170% increase of the OA/BC, while the O:C increased to 0.38 and 0.5 respectively. Hennigan et al. (2011) performed chemical aging experiments of emissions coming from the combustion of 12 types of wood fuel. They initiated chemical aging using UV lights, sunlight or the combination of both. In other experiments they produced hydroxyl (OH) radicals under high  $\text{NO}_x$  conditions by the photolysis of nitrous acid (HONO). In all the experiments in which ponderosa pine was used as fuel the chemical aging of the emissions

resulted in a 10% decrease of the OA/BC. In the lodgepole pine burning experiments exposure to UV led to a 130% increase of the OA/BC. When the chemical aging was initiated by the photolysis of HONO the OA/BC increased 40%. Moreover for turkey oak emissions the OA/BC increased 80% in the presence of either natural or and UV lights. Ortega et al. (2013) used a potential aerosol mass (PAM) flow reactor to study the chemical aging of different fuel types. They found that the OA change during the chemical aging varies with the fuel type and the OH exposure. As exposure to OH radicals increased the OA increased until it reached a maximum. Aging of smoke from most fuels resulted in a net OA increase. Negligible increase or net decrease was observed for ponderosa and lodgepole pine. During the chemical aging of the ponderosa pine emissions the OA remains almost stable (3% increase) or decreased by as much as 38%. For the lodgepole pine experiments the OA decreased 10-14%, while for the turkey oak the OA increased up to 80%. These results indicate that the photochemical aging of the smoke of fuels with higher emissions resulted in a lower relative OA enhancement. Tiitta et al. (2016) performed aging experiments of biomass burning emissions under dark conditions (ozone injection), photooxidation, or a combination of both. They used three different kinds of wood (birch, beech and spruce) as fuel. For the experiment with birch logs the ratio OA/BC was 0.2, the O:C was 0.35, and the H:C was 1.5. The exposure of the emissions to ozone led to a 77% OA mass increase. The O:C increased to 0.75 and the H:C increased to 1.29. The above elemental ratios were calculated using the Canagaratna et al. (2015) method.

A number of studies have focused on the absorption of BC and the absorption enhancement ( $E_{Abs}$ ) after these particles are coated with OA. Lack et al. (2012) investigated the optical properties of particles produced by a large ponderosa pine forest smoldering fire. They measured an average background  $E_{Abs}=1.3$  at wavelength of 532 nm, while at  $\lambda=404$  nm it

ranged from 1.3 up to 1.5. The absorption Angström exponent (AAE) was 1.1-1.4. During two biomass burning events, the average  $E_{Abs}$  at  $\lambda=532$  nm increased to 1.4-1.5, while at 404 nm it increased to 2.1-2.5. The AAE during these two periods was 2.3. The POA was very weakly absorbing at 532 nm, but very absorbing at 404 nm. The difference in the  $E_{Abs}$  at different wavelengths and the high values of the AAE suggested the existence of internally or externally mixed absorbing POA. Using Mie theory they estimated that 83% of the absorbing POA was externally mixed. On the contrary, Cappa al. (2012) reported that during the CalNex study and the Carbonaceous Aerosol and Radiative Effects Study (CARES) the photochemical aging of the OA did not cause a substantial absorption enhancement. They measured in both campaigns on average an  $E_{Abs}$  at 532 nm equal to 1.06, and at 404 nm equal to 1.13. Their calculated  $E_{Abs}$  values using Mie theory were significantly higher than their measured values.

In this study we want to close the scientific gap between the two sets of studies that have explored the chemical aging of the biomass burning emissions and the ones that have focused on the absorption enhancement of the BC particles coated with aged OA. More specifically, we investigate how the changes of the properties of the bbOA during chemical aging affect the absorption enhancement of the BC particles.

## 4.2 Experimental methods

Experiments were carried out in the smog chamber of Carnegie Mellon University at the Center for Atmospheric Particle Studies (CAPS). The smog chamber is a 12 m<sup>3</sup> Teflon reactor (Welch Fluorocarbons) suspended inside of a temperature-controlled room. The walls of the smog chamber room are lined with UV lights (General Electric model 10526 black). Prior to an experiment, the chamber was flushed with purified air for 12-48 h. Air was purified by passing

through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity to <10%. All the experiments were carried out at a constant temperature of  $20\pm 2^{\circ}\text{C}$  and at  $\text{RH}<10\%$  unless mentioned otherwise.

Two different kinds of wood were used as fuels: longleaf pine wood and white birch bark. An environmentally efficient cook stove (G3 Rocketstove, Envirofit) was used for the burning. The emissions were injected in the smog chamber using two Dekati diluters (DI-1000) in a parallel configuration. The emissions were injected during the flaming phase of the combustion for 5 minutes resulting in approximately  $10,000 \text{ particle cm}^{-3}$  in the smog chamber.

Ozone or OH radicals were introduced in the system after the injection of the biomass burning emissions. Ozone was added to the chamber using an electrical discharge generator (AZCO, model HTU-500ACPS). For the production of OH radicals, HONO or  $\text{H}_2\text{O}_2$  (Sigma-Aldrich, 50-50% solution) photolysis was used. A fresh solution of HONO was produced and used in each experiment by mixing a  $4.9 \text{ g L}^{-1}$  sulfuric acid solution with a  $6.9 \text{ g L}^{-1}$  sodium nitrite solution with a volumetric ratio of 2:1. HONO or  $\text{H}_2\text{O}_2$  were injected into the chamber using a bubbler. After the injection, the UV light was turned on to initiate the production of OH radicals. We tested the injection method by measuring the concentration of the OH radicals using 2-butanol as a tracer and a GC/FID (Chromatotec airmoBTX). The estimated concentration of OH radicals was approximately  $10^7 \text{ molecules cm}^{-3}$  for HONO photolysis and  $10^6 \text{ molecules cm}^{-3}$  for  $\text{H}_2\text{O}_2$  photolysis.

A Scanning Mobility Particle Sizer (SMPS, TSI classifier model 3080, CPC model 3772 or 3010) was used for the measurement of the number and the volume distributions of aerosols. The mass concentration and the chemical composition of the particles were monitored using a Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research, Inc.). For the SP-AMS

data analysis SQUIRREL 1.54B and PIKA 1.13B was used. In our analysis we used the fragmentation table suggested by Aiken et al. (2008). The SP-AMS was operated in two modes: the V mode with the tungsten vaporizer on, and the V mode with the tungsten vaporizer on and the laser vaporizer on. The measurement time for each mode was 1 min. The non-refractory components of the particles were measured at the laser off mode. The O:C and H:C ratios of the OA were calculated using the laser off data without including the organonitrate fragments in the analysis (Farmer et al., 2010). For the analysis we assumed a collection efficiency equal to unity following Hennigan et al. (2011), Ortega et al. (2013), Eriksson et al. (2014), and Bruns et al. (2014).

The refractory BC (rBC) concentration was measured by the SP-AMS when both the tungsten and the laser vaporizer were on. The SP-AMS was calibrated according to the recommendations of Onasch et al. (2012), using Regal black (REGAL 400R pigment black Cabot Corp.), resulting in a rBC relative ionization efficiency  $RIE_{rBC}=0.2$ . In a separate subset of experiments rBC concentrations were also measured using a Single Particle Soot Photometer (SP2, Droplet Measuring Techniques). The SP2 measures refractory rBC concentrations by vaporizing BC particles using a 1064 nm laser (Stephens et al., 2003; Schwarz et al., 2006). The vaporizing signal of the SP2 was calibrated for the rBC mass using fullerene soot (Gysel et al., 2011). The data were analyzed using the Probe Analysis Package for Igor (PAPI). When sampling in high concentrations ( $>10,000$  particles  $\text{cm}^{-3}$ ) particle coincidence can be a major measurement artifact. The data were corrected for coincidence using the calculation method described in Holder et al. (2014). The mass was increased by 1 to 15%. The comparison showed a very good correlation between the SP2 and the SP-AMS rBC mass concentrations ( $R^2=0.98$ ), with the SP-AMS measuring 37% lower BC than the SP2. The results of this comparison have

been discussed in Chapter 3. In the current study we used this scaling factor to correct the SP-AMS BC measurements.

The concentrations of the VOCs were measured using a Proton Transfer Reaction Mass Spectrometer (PTR-MS, Ionicon Analytic GmbH). A calibration gas with known concentrations of different VOCs including toluene, o-xylene, and benzene was used. The concentration of O<sub>3</sub> was measured using a continuous O<sub>3</sub> analyzer (Dasibi 1008-PC) and of nitrogen oxides using a Teledyne chemiluminescent NO/NO<sub>2</sub>/NO<sub>x</sub> analyzer Model 200A. Also, a carbon dioxide (CO<sub>2</sub>) gas analyzer (LI-820, LI-Cor Biosciences) and a carbon monoxide (CO) gas analyzer (model 300A, API-Teledyne) were used. Gas-phase instruments were calibrated before each experiment.

A suite of instruments was used to study the optical properties of the BC particles. A set of two photoacoustic extinctionimeters (Arnott et al., 1999) (PAXs, Droplet Measurement Techniques), using a green (532 nm) and a blue (405 nm) laser respectively, were used to measure the absorption ( $b_{abs}$ ) and the scattering ( $b_{scat}$ ) coefficients. The advantage of these instruments compared to other optical instruments is that no filter collection is required thus there are no filter-related artifacts. Fullere soot and PSL spheres were used to calibrate the absorption and the scattering signals respectively. An activated carbon denuder was in front of the PAXs to remove NO<sub>2</sub>.

A seven wavelength Aethalometer (Magee Scientific) was also used to measure the  $b_{abs}$  at 370, 470, 520, 590, 660, 880 and 950 nm and to calculate the absorption Angström exponent (AAE) which describes the wavelength dependence of the  $b_{abs}$ . For the calculation of the  $b_{abs}$  from the Aethalometer measurements we used the equation

$$b_{abs}(\lambda) = MAC \times c_{BC} \quad (1)$$



where  $MAC = 14625/\lambda$  ( $m^2 g^{-1}$ ) is the manufacturer's specified mass absorption cross-section, and  $c_{BC}$  is the BC concentration reported by the instrument. The Aethalometer measurements were corrected for filter artifacts using the equation of Saleh et al. (2014):

$$b_{abs,cor}(\lambda) = \frac{b_{abs,raw}(\lambda)}{2.14 \times (0.55 \times T(\lambda) + 0.42)} \quad (2)$$

where  $b_{abs,cor}$  is absorption coefficient corrected from filter artifacts,  $b_{abs,raw}$  is the raw measurement of the absorption coefficient by the Aethalometer, and  $T(\lambda)$  is the instrument transmission defined as  $T(\lambda) = \exp[-A(\lambda)/100]$  with  $A$  being the attenuation at a wavelength  $\lambda$ . Eq. 2 is used to correct the artifact of the absorption enhancement due to multiple scattering in the collection filter using a multiple scattering correction of 2.14 as proposed by Weingartner et al. (2003). In addition Eq. 2 corrects for the decrease of the Aethalometer response as the particle loading increases due to scattering of aerosols embedded in the filter or due to some particles being shadowed by others (scattering correction) (Kirchstetter and Novakov, 2007). Finally, the light absorbing particles accumulating in the filter reduce the optical path. To correct for this artifact we scaled the Aethalometer measurements according to the PAXs' ones. This correction was made without altering the wavelength dependence of the data.

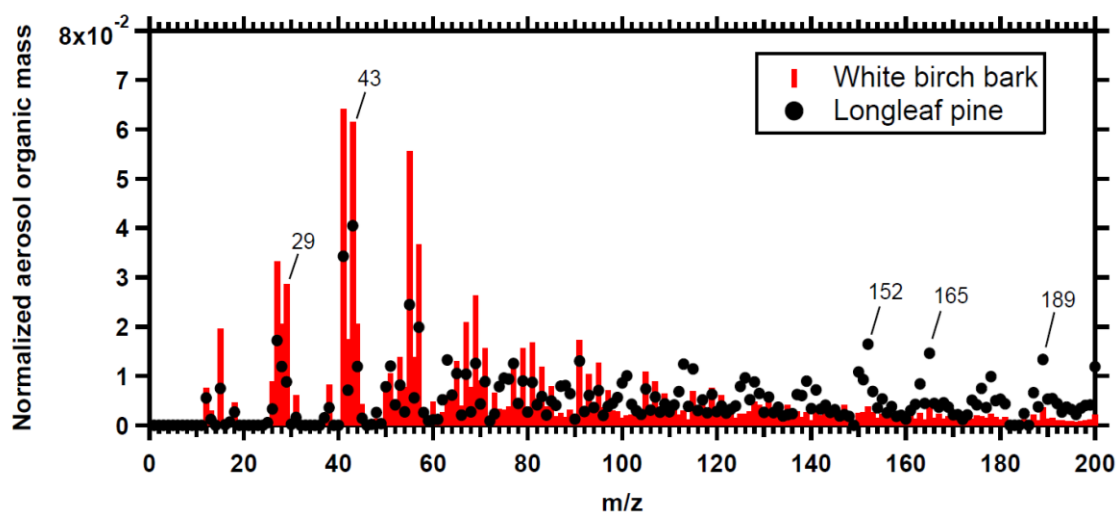
## 4.3 Results and discussion

### 4.3.1 Fresh biomass burning emissions

We conducted 13 biomass burning experiments, five with longleaf pine wood and eight with white birch bark (Table 4.1). The modified combustion efficiency (MCE) (Ward and Radke, 1993), is defined as  $\Delta CO_2 / (\Delta CO_2 + \Delta CO)$ , where  $\Delta CO_2$  and  $\Delta CO$  are the background corrected  $CO_2$  and  $CO$  (Table 4.1).

**Table 4.1:** Composition of the fresh biomass burning emissions

| Exp. | Fuel             | OA<br>( $\mu\text{g m}^{-3}$ ) | BC<br>( $\mu\text{g m}^{-3}$ ) | OA/BC | $\Delta\text{CO}$<br>(ppm) | $\Delta\text{CO}_2$<br>(ppm) | MCE  |
|------|------------------|--------------------------------|--------------------------------|-------|----------------------------|------------------------------|------|
| 1    | Longleaf pine    | 3.9                            | 95.1                           | 0.04  | 2.81                       | 22.19                        | 0.89 |
| 2    | Longleaf pine    | 4                              | 81.7                           | 0.05  | 4.43                       | 44.43                        | 0.91 |
| 3    | Longleaf pine    | 13.2                           | 169                            | 0.08  | 5.20                       | 52.37                        | 0.91 |
| 4    | Longleaf pine    | 2.3                            | 77.3                           | 0.03  | 0.06                       | -                            | -    |
| 5    | Longleaf pine    | 5.5                            | 26.5                           | 0.21  | 0.43                       | 3.43                         | 0.89 |
| 6    | White birch bark | 5                              | 25.9                           | 0.19  | 0.57                       | 35.52                        | 0.98 |
| 7    | White birch bark | 4.1                            | 26.4                           | 0.16  | 0.19                       | 12.70                        | 0.99 |
| 8    | White birch bark | 15.5                           | 36.7                           | 0.42  | 0.41                       | 18.55                        | 0.98 |
| 9    | White birch bark | 6.6                            | 51.7                           | 0.13  | 0.07                       | -                            | -    |
| 10   | White birch bark | 1.7                            | 48.0                           | 0.04  | 0.04                       | 2.25                         | 0.98 |
| 11   | White birch bark | 1.5                            | 50                             | 0.03  | 0.03                       | 1.86                         | 0.98 |
| 12   | White birch bark | 4.2                            | 79.4                           | 0.05  | 0.05                       | 3.43                         | 0.98 |
| 13   | White birch bark | 4.3                            | 76.5                           | 0.06  | 0.09                       | 5.28                         | 0.98 |

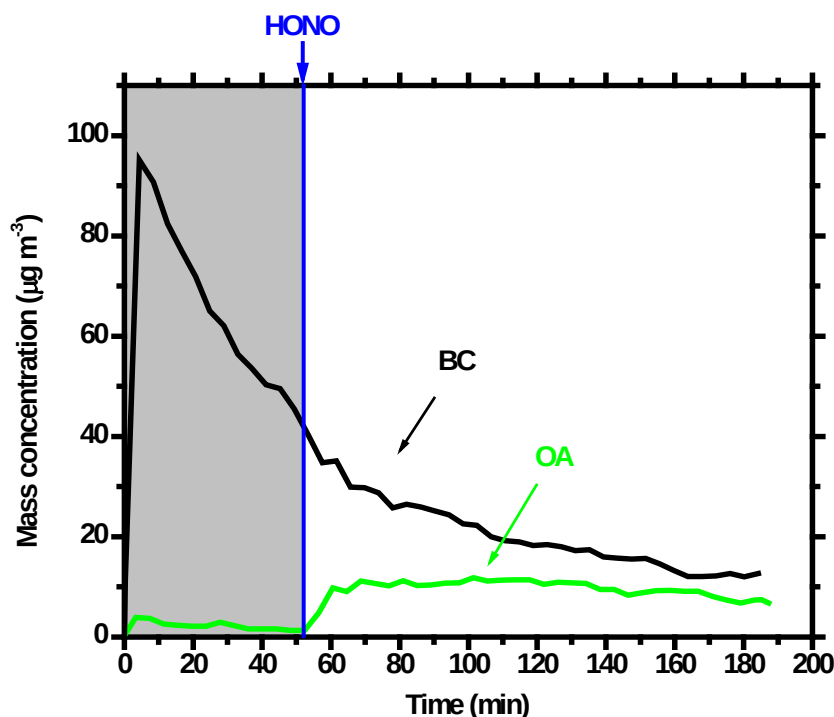


**Figure 4.1:** The organic AMS spectra of the fresh emissions from the burning of white birch bark (red) and longleaf pine (black).

For the pine wood experiments the MCE ranged from 0.89 to 0.91, while for the white birch bark the MCE was much higher ranging from 0.98 to 0.99. For flaming conditions the MCE is  $\sim 0.99$  (Chen et al., 2007; Yokelson et al., 1996), while for smoldering conditions the MCE varies from 0.65 to 0.85 (Akagi et al., 2011). In both sets of experiments the emissions were injected in the chamber during the flaming phase. The MCE difference between the two sets indicates that the burning of the pine wood was less complete compared to the white birch bark.

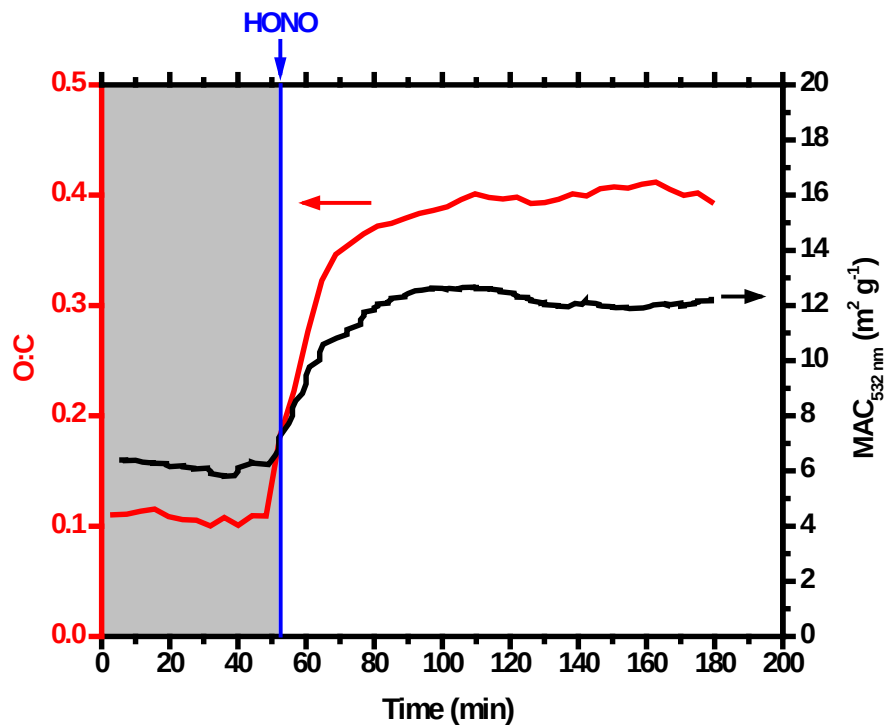
The average SP-AMS spectra of the fresh bbOA (30 minutes after the injection of the emissions in the chamber) of the two different types of fuels are shown in Figure 4.1. The mass spectrum of the fresh pine wood emission had peaks at the  $m/z$  values 152, 165, 189. These peaks are usually attributed to polycyclic aromatic hydrocarbons (PAHs) (Gross et al., 2000; Silva and Prather, 2000). The O:C ratio for the fresh pine emissions was  $0.15 \pm 0.05$  while for the white birch bark it was  $0.2 \pm 0.11$ .

### 4.3.2 Chemical aging of fresh bbOA



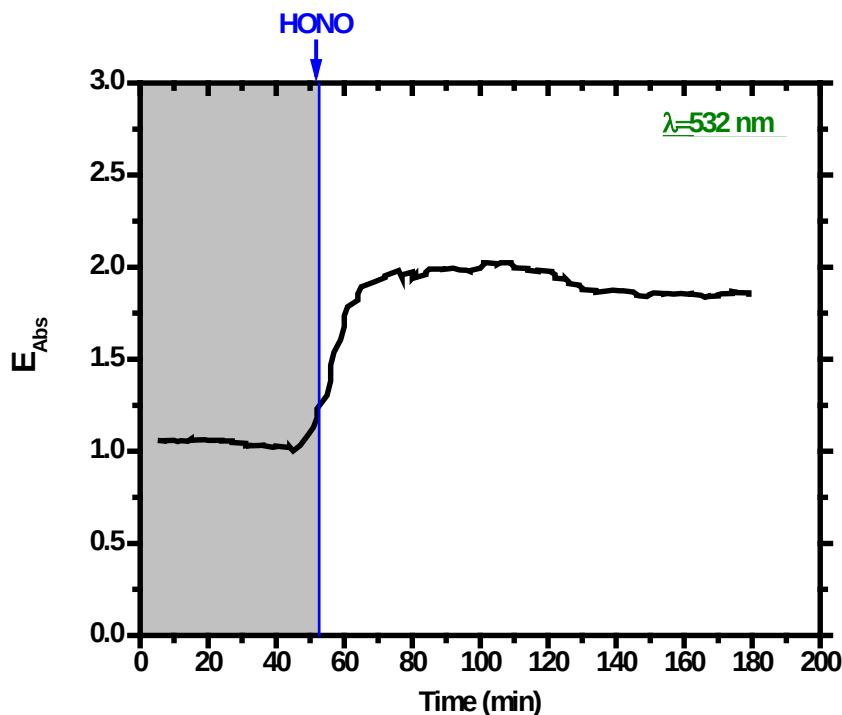
**Figure 4.2:** The measured organic aerosol and black carbon mass concentration in the chamber as a function of time for Experiment 1. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on.

In the first set of experiments we investigated the chemical aging of the emissions produced by the burning of pine wood and white birch bark. The results of a typical experiment (Experiment 1) are presented in Figure 4.2. The fresh emissions from the pine wood burning had an OA/BC ratio of 0.04. The concentrations of the other species were negligible (<5%). Almost one hour later we introduced OH radicals in the chamber by photolysing HONO. The reactions resulted in an immediate production of SOA and the OA/BC ratio increased to 0.38 after 70 min.



**Figure 4.3:** The red line represents the oxygen to carbon ratio of the organic aerosol as a function of time for Experiment 1. The black line represents the absorption cross section at 532 nm for the same experiment. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on.

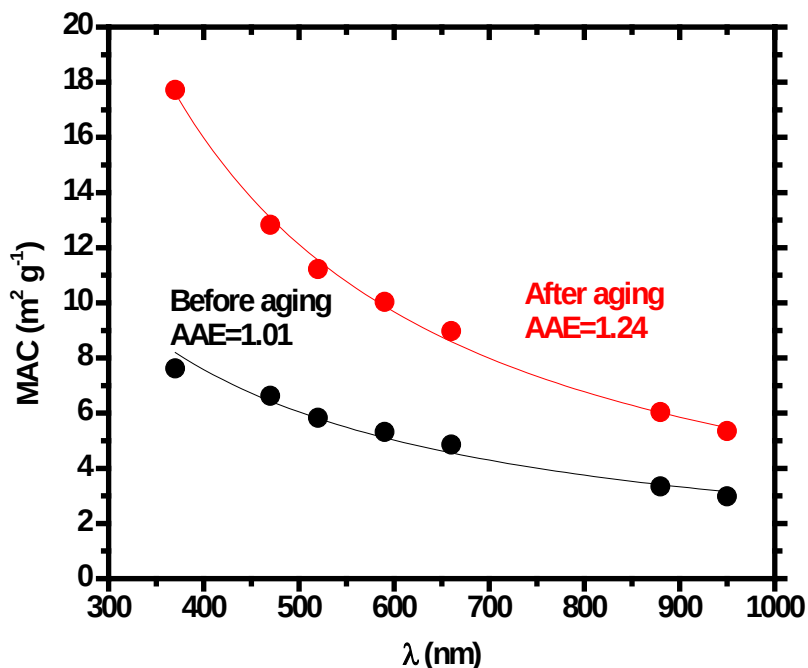
The O:C ratio of the organic aerosol and the mass absorption cross section at 532 nm for Experiment 1 are shown in Figure 4.3. The O:C ratio of the fresh organic aerosol was 0.13. The OA concentration and the O:C ratio changes suggest that the organic aerosol underwent rapid chemical aging. The mass absorption cross section at 532 nm ( $MAC_{532}$ ) is shown in Figure 4.3. Initially the  $MAC_{532}$  was equal to  $6.3 \text{ m}^2 \text{ g}^{-1}$ . At  $t=140 \text{ min}$  after some chemical aging of the bbOA the  $MAC_{532}$  increased to  $12.1 \text{ m}^2 \text{ g}^{-1}$ . We define the absorption enhancement ( $E_{Abs}$ ) as the ratio of the  $MAC_{532}$  after the aging over the  $MAC_{532}$  before the aging. After the chemical aging of the bbOA the absorption approximately doubled (Figure 4.4).



**Figure 4.4:** The absorption enhancement of the black carbon at 532 nm as a function of time for Experiment 1. The shaded region indicates the period during which the chamber was dark. Also shown, the time when HONO was injected in the chamber and the UV light was turned on.

The AAE describes the wavelength dependence of absorption. Typically for “pure” BC in the atmosphere the AAE is assumed to be 1 (Bond and Bergstrom, 2006). The MAC values are calculated using the aethalometer data and corrected for filter artifacts using the PAXs measurements assuming that the artifacts are the same for all the wavelengths. The calculated AAE measurement was not affected by this correction. For the fresh biomass burning aerosol, consisting mainly of BC in this experiment, the AAE was 1.01 while after the chemical aging it increased to 1.24 (Figure 4.5). This increase in the absorption could be due to the presence of absorbing OA (often called brown carbon, BrC) in our system. However, according to Lack and

Cappa, (2010) the increase in the absorption can be definitely attributed to the presence of brown carbon only if the AAE is higher than 1.6, something that was not observed in this experiment.



**Figure 4.5:** The mass absorption cross-section (MAC) values as a function of the wavelength for the fresh and aged bbOA emissions. Also shown, the absorption Angström exponent (AAE) for the two periods.

In Experiment 4, excess ozone was introduced into the chamber after the injection of the fresh bbOA emissions. The ozone concentration reached approximately 2 ppm. The OA/BC ratio increased from 0.04 to 0.06 and the O:C from 0.25 to 0.5. The chemical aging resulted in only a 2% increase of the absorption of the BC. In Experiment 2 the injection of ozone was followed by the injection of 2,3-dimethyl-2-butene (tetramethyl ethylene, TME) (OH dark formation). Using a TME flux of  $10^9 \text{ molecules cm}^{-3} \text{ s}^{-1}$  we produced, through the reaction of ozone with TME  $4\text{--}8 \times 10^6 \text{ molecules cm}^{-3}$  (Lambe et al., 2007). For the fresh emissions the OA/BC ratio was equal to

0.05 and the O:C was 0.13. After the OH dark formation the OA/BC increased to 0.84 and the O:C was 0.37. The absorption increased 25%.

In Experiments 3 and 5 the chemical aging was initiated by the photolysis of HOOH (OH+UV light under low NO<sub>x</sub>). In Experiment 3 the OA/BC ratio was low both before and after the chemical aging, 0.04 and 0.09 respectively. The light absorption increased by 6%. In Experiment 5 the OA/BC ratio before the chemical aging was 0.16. The reaction of the OA with OH radicals in the presence of UV light increased the OA resulting in an OA/BC=0.19. The O:C increased from 0.12 to 0.22. The chemical aging increased the light absorption of the BC by 10% in this case.

In the Experiments 6 to 10, in which white birch bark was used as a fuel, the aging did not affect the OA mass and the absorption as much as in the pine wood experiments (Table 4.2). The  $E_{Abs}$  ranged from 1 to 1.05. The AAE suggests no presence of BrC. The highest  $E_{Abs}$  was measured during the aging of the soot with OH radicals at high NO<sub>x</sub> conditions (Experiments 10).

The above results suggest that the emissions from the pine wood burning had higher concentrations of gas-phase organic compounds. This is consistent with the production of higher mass of organic aerosol during the chemical aging step. In separate experiments we compared the VOC levels in the emissions of the two fuels, using a PTR-MS. The results confirmed that the pine wood emissions had higher concentrations than the white birch bark emissions. The biggest differences were found at PTRMS  $m/z$  values 45, 57, 59, 79, 93, 107 (Figure A.2.1). The  $m/z$  45 is associated with acetaldehyde,  $m/z$  57 with acrolein, alkenes and Methyl tert-butyl ether (MTBE),  $m/z$  59 with acetone, propanal and 2,3 butanedione,  $m/z$  79 with benzene and ethylbenzene,  $m/z$  93 with toluene, and  $m/z$  107 with xylenes and ethylbenzene (Karl et al., 2007).



**Table 4.2:** Conditions before and after the chemical aging of the organic aerosol

| Exp. | Before aging                  |       |      |                                                         | Aging agent                              | After aging                   |       |      |                                                         | E <sub>Abs</sub> |
|------|-------------------------------|-------|------|---------------------------------------------------------|------------------------------------------|-------------------------------|-------|------|---------------------------------------------------------|------------------|
|      | Mass<br>(μg m <sup>-3</sup> ) |       | O:C  | MAC <sub>532</sub><br>(m <sup>2</sup> g <sup>-1</sup> ) |                                          | Mass<br>(μg m <sup>-3</sup> ) |       | O:C  | MAC <sub>532</sub><br>(m <sup>2</sup> g <sup>-1</sup> ) |                  |
|      | OA                            | BC    |      |                                                         |                                          | OA                            | BC    |      |                                                         |                  |
| 1    | 1.33                          | 40.3  | 0.13 | 6.3                                                     | OH + UV light<br>(high NO <sub>x</sub> ) | 11.2                          | 29.8  | 0.37 | 12.1                                                    | 1.9              |
| 2    | 1.80                          | 41.4  | 0.13 | 6.5                                                     | OH<br>(dark formation)                   | 6.6                           | 7.9   | 0.37 | 8.1                                                     | 1.25             |
| 3    | 5.1                           | 127.5 | 0.14 | 8.6                                                     | OH + UV light<br>(Low NO <sub>x</sub> )  | 9.8                           | 107.8 | 0.41 | 9.1                                                     | 1.06             |
| 4    | 0.9                           | 23.9  | 0.25 | 6.5                                                     | Ozone                                    | 1.2                           | 19.8  | 0.5  | 6.6                                                     | 1.02             |
| 5    | 3.1                           | 19.6  | 0.12 | 14.9                                                    | OH + UV light<br>(Low NO <sub>x</sub> )  | 3.3                           | 17.9  | 0.22 | 16.4                                                    | 1.1              |
| 6    | 1.5                           | 10.9  | 0.15 | 10.5                                                    | OH + UV light<br>(high NO <sub>x</sub> ) | 2.2                           | 8.8   | 0.24 | 10.8                                                    | 1.05             |
| 7    | 0.84                          | 6.1   | 0.11 | 10.4                                                    | OH + UV light<br>(Low NO <sub>x</sub> )  | 0.9                           | 5.6   | 0.2  | 10.8                                                    | 1.03             |
| 8    | 3.9                           | 13.3  | 0.19 | 10.5                                                    | OH<br>(dark formation)                   | 3.7                           | 6.6   | 0.3  | 10.7                                                    | 1.02             |
| 9    | 4                             | 34.9  | 0.12 | 6.9                                                     | OH + UV light<br>(high NO <sub>x</sub> ) | 4.7                           | 30.0  | 0.28 | 6.9                                                     | 1.0              |
| 10   | 1.2                           | 36.1  | 0.09 | 6.6                                                     | OH + UV light<br>(high NO <sub>x</sub> ) | 1.7                           | 33.8  | 0.27 | 6.9                                                     | 1.05             |

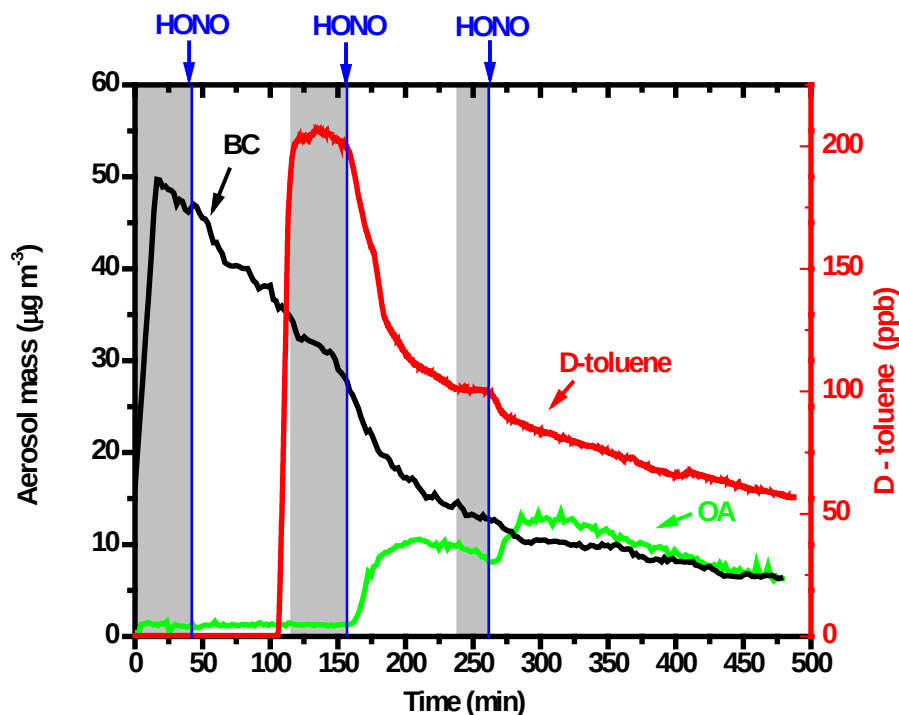
### 4.3.3 Coating of biomass burning particles with aromatic SOA

#### 4.3.3.1 Coating with D-Toluene SOA

In another set of experiments (Table 4.3) the biomass burning particles were used as seeds for the condensation of aromatic SOA. The emissions of white birch bark combustion were used for these experiments because of their low SOA formation potential, as discussed in the previous section. Initially, OH radicals were produced forcing the bbOA to chemical age.

**Table 4.3:** Measurements during the chemical aging of the bbOA (first period), formation of the aromatic SOA (second period), and chemical aging of the SOA (third period)

| Exp. | Aging agent                            | First period                     |      |       |      |                  | Second period                    |      |       |      |                  | Third period                     |      |       |      |                  |
|------|----------------------------------------|----------------------------------|------|-------|------|------------------|----------------------------------|------|-------|------|------------------|----------------------------------|------|-------|------|------------------|
|      |                                        | Mass<br>( $\mu\text{g m}^{-3}$ ) |      | OA/BC | O:C  | $E_{\text{Abs}}$ | Mass<br>( $\mu\text{g m}^{-3}$ ) |      | OA/BC | O:C  | $E_{\text{Abs}}$ | Mass<br>( $\mu\text{g m}^{-3}$ ) |      | OA/BC | O:C  | $E_{\text{Abs}}$ |
|      |                                        | OA                               | BC   |       |      |                  | OA                               | BC   |       |      |                  | OA                               | BC   |       |      |                  |
| 11   | OH + UV light<br>(High $\text{NO}_x$ ) | 1.3                              | 44.9 | 0.03  | 0.32 | 1.02             | 10.6                             | 16.0 | 0.66  | 0.53 | 1.72             | 12.9                             | 10.3 | 1.26  | 0.54 | 2.0              |
| 12   | OH + UV light<br>(High $\text{NO}_x$ ) | 4.2                              | 73.8 | 0.06  | 0.45 | 1.02             | 27.1                             | 57.0 | 0.48  | 0.51 | 1.19             | 32.9                             | 48.5 | 0.68  | 0.51 | 1.23             |
| 13   | OH + UV light<br>(High $\text{NO}_x$ ) | 4.5                              | 56.4 | 0.08  | 0.5  | 1.02             | 76.9                             | 26.4 | 2.92  | 0.43 | 1.54             | 90.1                             | 16.5 | 5.47  | 0.45 | 1.85             |



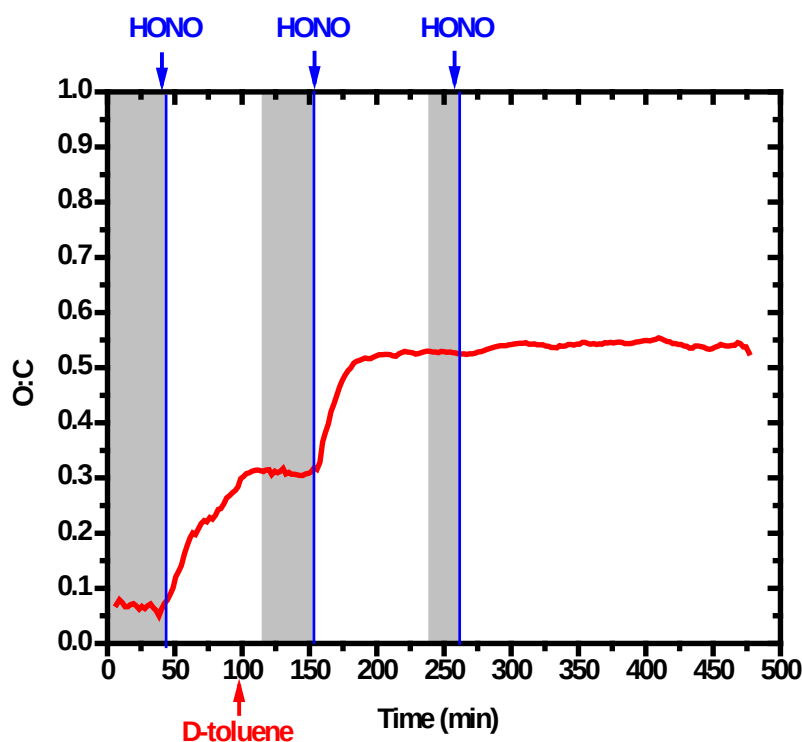
**Figure 4.6:** Measured organic aerosol and black carbon, and D-toluene concentrations during Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when HONO was injected in the chamber and the UV light was turned on.

Deuterated toluene was used as an anthropogenic SOA precursor in order to facilitate the quantification of the produced aromatic SOA using the corresponding AMS mass spectra. For the high resolution data analysis of the SP-AMS measurements (PIKA analysis), a number of new HR ions were added to the fragmentation table to account for the fragments of the D-toluene SOA. Details of this method can be found in Hidlebrandt et al. (2011).

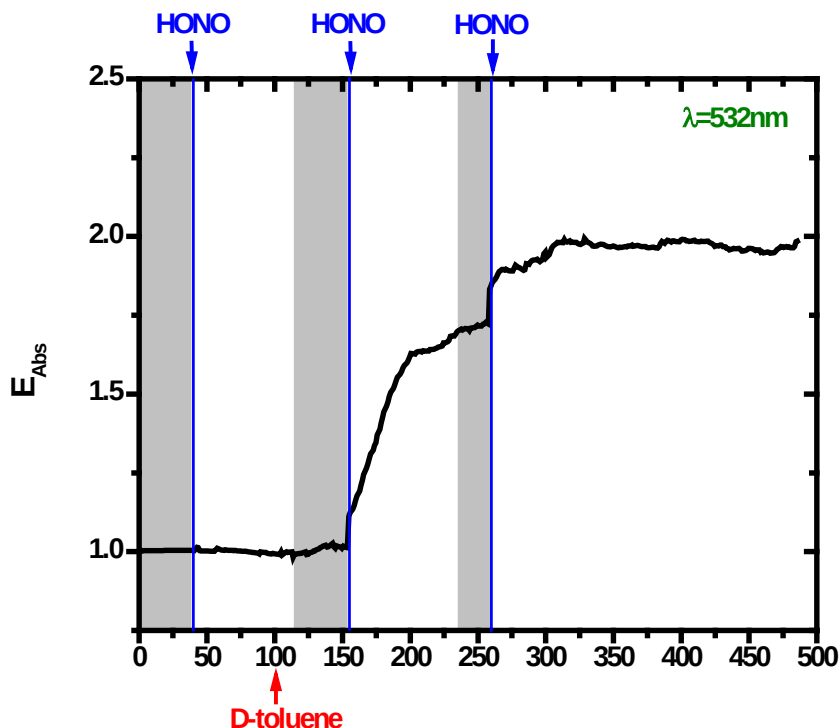
The timeseries of BC, OA and D-toluene for a typical experiment (Experiment 11) are shown in Figure 4.6. After the injection of the emissions,  $50 \mu\text{g m}^{-3}$  of BC and  $1.5 \mu\text{g m}^{-3}$  of OA were measured. The experiments can be separated in three periods. In the first period, the production of OH radicals via the photolysis of HONO caused a small increase of the OA

concentration, OA/BC=0.03. During the second period, 200 ppb of D-toluene were injected in the chamber and after the further introduction of OH radicals, toluene SOA was produced increasing the OA/BC to 0.66. No nucleation occurred during the production of toluene SOA (Figure A.2.2). In the third period, the additional production of OH radicals caused further increase of the organic aerosol resulting in OA/BC= 1.26.

The timeseries of the O:C ratio of the OA is shown in Figure 4.7. In the first period the O:C increased from 0.07 to 0.32. In the second period the O:C increased to 0.53 while in the third period it remained stable.



**Figure 4.7:** The oxygen over carbon ratio of the organic aerosol as a function of time for Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when D-toluene and HONO were injected in the chamber and the UV light was turned on.



**Figure 4.8:** The absorption enhancement of the black carbon as a function of time for Experiment 11. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when D-toluene and HONO were injected in the chamber and the UV light was turned on.

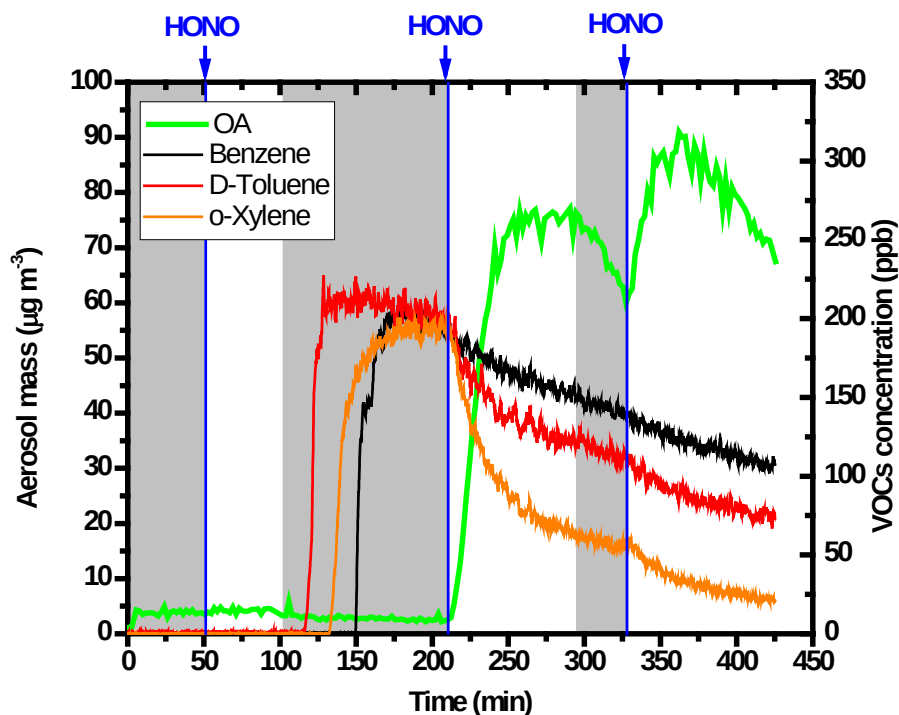
The chemical aging of the bbOA caused no change in the  $E_{Abs}$  (Figure 4.7), but the toluene SOA formation led to a 72% increase of the absorption. The further chemical aging caused the absorption to double (Figure 4.8).

Experiment 12 was similar to Experiment 11. The chemical aging of the bbOA resulted in OA/BC=0.06 while the O:C increased from 0.32 to 0.45. The  $E_{Abs}$  was equal to 1.02. During the second period the OA/BC increased to 0.48 and the O:C increased to 0.51. The  $E_{Abs}$  increased 19%. In the third period the OA/BC increased to 0.68, the O:C remained stable, while the  $E_{Abs}$  increased to 1.23.

In summary, in these high  $\text{NO}_x$  experiments the coating of the particle with D-toluene SOA increased the absorption of the BC core as much as a factor of 2, while the changes of the oxidation state of the organic shell did not affect the absorption.

#### 4.3.3.2 Coating with a mixture of aromatic SOA

In Experiment 13, HONO photolysis was used for the production of OH radicals and aromatic SOA by the simultaneous oxidation of 200 ppb D-toluene, 200 ppb o-xylene, and 200 ppb benzene.



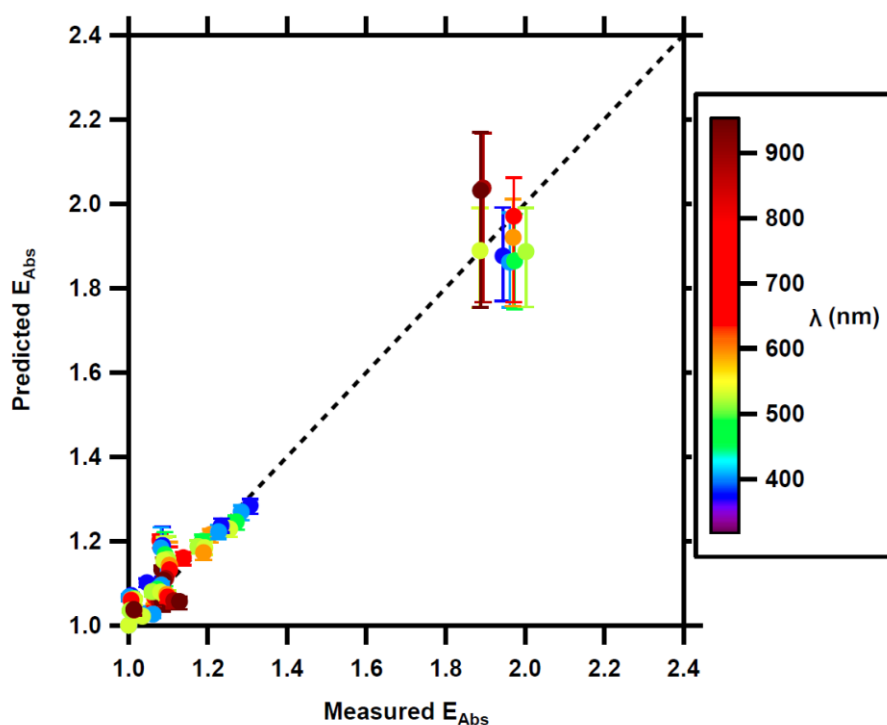
**Figure 4.9:** The timeseries of the measured organic aerosol and the aromatic VOCs concentration in the chamber for Experiment 15. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when HONO was injected in the chamber and the UV light was turned on.

The concentration timeseries of the aromatic compounds along with the mass of the organic aerosol are shown in Figure 4.9. The formation of the aromatic SOA (second period) led to the decrease of the O:C ratio from 0.5 to 0.43 (Figure A.2.3), while the OA/BC ratio increased from 0.08 to 2.92 and the  $E_{abs}$  increased from 1.02 to 1.54 (Figure A.2.4). Between the second and the third period the O:C was almost constant while the further increase of the organics (the OA/BC ratio increased from 2.92 to 5.48) caused the absorption enhancement to increase from 1.54 to 1.85. The increase of the OA mass during the coating of the biomass burning emissions with the mixture of anthropogenic SOA, resulted in an increase of absorption, while the O:C decreased and later remained stable.

#### 4.3.4 Theoretical analysis

Mie theory describes the extinction of light by spherical particles due to an incoming planar electromagnetic wave. A Mie theory model, based in the work of Bohren and Huffman (1983), was used to calculate the theoretical  $E_{Abs}$ . For the calculations we used a refractive index of BC  $n_{BC}=1.85+0.71i$  (Bond and Bergstrom, 2006). A minimum and a maximum value were also used for sensitivity testing  $n_{BC}=1.55+0.5i$ ,  $n_{BC}=2+1.0i$  (Bond and Bergstrom, 2006). For the organic aerosol created by the aging of the BBOA we assumed a refractive index of  $n_{OA}=1.55+0i$  (Bond and Bergstrom, 2006). We also assumed the following densities:  $\rho_{BC}=1.8 \mu\text{g m}^{-3}$  (Mullins and Williams, 1987; Wu et al. 1997; Park et al. 2004) and  $\rho_{OA}=1.4 \mu\text{g m}^{-3}$  (Kostenidou et al., 2007). The inputs of the model were the measured vacuum aerodynamic size distributions for the fresh and aged emissions.

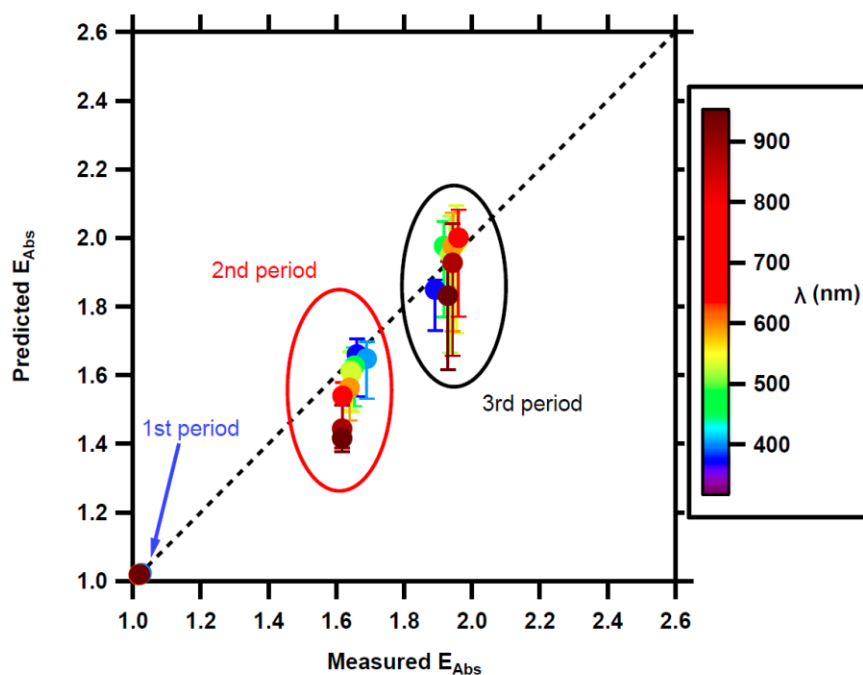
Measured and predicted values of the  $E_{Abs}$  are compared for Experiments 1 to 10 in Figure 4.10. The core-shell model reproduces well the observations in all experiments.



**Figure 4.10:** The comparison between the measured  $E_{Abs}$  and the  $E_{Abs}$  predicted by Mie theory for Experiments 1 to 10.

For the experiments 11-13 Mie theory was used to predict the changes of the  $E_{Abs}$  during the three periods of each experiment (chemical aging of bbOA, formation of aromatic SOA, chemical aging of the SOA). In Figure 4.11 we present the comparison of the measured and predicted absorption for Experiment 11. The results of the analysis for the Experiments 12 and 13 are shown in Figures A.2.5 and A.2.6. The measurements in all three periods are consistent with the Mie predictions.





**Figure 4.11:** The comparison between the measured  $E_{Abs}$  and the  $E_{Abs}$  predicted by Mie theory for Experiment 11, for all three periods of the experiment.

## 4.4 Conclusions

The changes that occur in the absorption of light by biomass burning particles as they age in the atmosphere were investigated in a series of smog chamber experiments.

In the first part of the study the emissions from the burning of longleaf pine wood and white birch bark were aged. The chemical aging resulted in the increase of the mass concentration and the O:C of the organic aerosol. At the same time the aerosol absorption was enhanced. For the pine wood experiments the absorption increased by as much as a factor of 1.9. For the white birch bark experiments the  $E_{Abs}$  was less than 1.05. For both types of experiments the  $E_{Abs}$  was higher after the chemical aging of the emissions with OH radicals. The calculated AAE from the aethalometer suggests that there was no brown carbon in both systems.

In the second part of the study we coated the white birch bark emissions with aromatic SOA. These experiments suggested that the absorption activity of the BC core was mainly affected by the changes of the organic aerosol mass and not by the changes of the chemical composition of the organic shell.

To confirm the core-shell morphology of the aging particles and the particles of the aromatic SOA-soot system we used Mie theory assuming spherical particles, core-shell morphology, and a non-absorbing coating. The measurements were consistent with the corresponding Mie predictions.

## 4.5 References

Aiken, A. C. , DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U., and Jimenez, J. L.: O/C, and OM/OC ratios of primary, secondary, and ambient organic aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, 2008.

Akagi, S. K., Yokelson, R. J., Wiedinmyer, C., Alvarado, M. J., Reid, J. S., Karl, T., Crounse, J. D., and Wennberg, P. O.: Emission factors for open and domestic biomass burning for use in atmospheric models, *Atmos. Chem. Phys.*, 11, 4039-4072, 2011.

Arnott, W. P., Moosmüller, H., Rogers, C. F., Jin, T., and Bruch, R.: Photoacoustic spectrometer for measuring light absorption by aerosol: Instrument description, *Atmos. Environ.*, 33, 2845–2852, 1999.

Bohren, C. F., and Huffman, D. R.: Absorption and Scattering of Light by Small Particles, Res. Support. by Univ. Arizona Inst. Occup. Environ. Heal. New York Wiley Interscience, 541 p1, xiv, 530 p., 1983.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., and Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion, J. Geophys. Res., 109, D14203, 2004.

Bond, T. C., and Bergstrom, R. W.: Light absorption by carbonaceous particles: An investigative review, Aerosol Sci. Tech., 40, 27–67, 2006.

Bond, T. C., Doherty, S. J., Fahey, D. W., Forster, P. M., Bernsten, T., DeAngelo, B. J., Flanner, M. G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P. K., Sarofim, M. C., Schultz, M. G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S. K., Hopke, P. K., Jacobson, M. Z., Kaiser, J. W., Klimont, Z., Lohmann, U., Schwarz, J. P., Shindell, D., Storelvmo, T., Warren, S. G., and Zender, C. S.: Bounding the role of black carbon in the climate system: A scientific assessment, J. Geophys. Res, 118, 5380–5552, 2013.

Bruns, E. A., Krapf, M., Orasche, J., Huang, Y., Zimmermann, R., Drinovec, L., Mocnik, G., El-Haddad, I., Slowik, J. G., Dommen, J., Baltensperger, U., and Prevot, A. S. H: Characterization of primary and secondary wood combustion products generated under different burner loads, Atmos. Chem. Phys., 15:2825–2841, 2015.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R et al: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, Atmos. Chem. Phys., 15, 253-272, 2015.

Cappa, C. D., Onasch, T. B., Massoli, P., Worsnop, D. R., Bates, T. S., Cross, E. S., Davidovits, P., Hakala, J., Hayden, K. L., Jobson, B. T., Kolesar, K. R., Lack, D. A., Lerner, B. M., Li, S.-M., Mellon, D., Nuaaman, I., Olfert, J. S., Petäjä, T., Quinn, P. K., Song, C., Subramanian, R., Williams, E. J., and Zaveri, R. A.: Radiative absorption enhancements due to the mixing state of atmospheric black carbon, *Science*, 337, 1078–1081, 2012.

Chen, L.-W. A., Moosmuller, H., Arnott, W. P., Chow, J. C., Watson, J. G., Susott, R. A., Babbitt, R. E., Wold, C. E., Lincoln, E. N., and Hao, W. M.: Emissions from laboratory combustion of wildland fuels: emission factors, and source profiles, *Env. Sci. Tech.*, 41, 4317–4325, 2007.

Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K. H., Möhler, O., Leisner, T., Müller, L., Reinnig, M. C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Urs Baltensperger, U: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, *PNAS*, 109, 13503–13508, 2012.

Eriksson, A. C., Nordin, E. Z., Nystrom, R., Pettersson, E., Swietlicki, E., Bergvall, C., Westerholm, R., Boman, C., and Pagels, J. H.: Particulate PAH emissions from residential biomass combustion: time-resolved analysis with aerosol mass spectrometry, *Environ. Sci. Technol.*, 48, 7143–7150, 2014.

Farmer, D. K., Matsunaga, A., Docherty, K. S., Surratt, J. D., Seinfeld, J. H., Ziemann, P. J., and Jimenez, J. L.: Response of an aerosol mass spectrometer to organonitrates and organosulfates, and implications for atmospheric chemistry, *P. Natl. Acad. Sci. USA*, 107, 6670–6675, 2010.

Fuller, K. A., Malm, W. C., and Kreidenweis, S. M.: Effects of mixing on extinction by carbonaceous particles, *J. Geophys. Res.*, 104, 15941–15954, 1999.

Fung, K.: Particulate carbon speciation by MnO<sub>2</sub> oxidation, *Aerosol Sci. Tech.*, 12, 122–127, 1990.

Grieshop, A. P., Logue, J. M., Donahue, N. M, and Robinson, A. L.: Laboratory investigation of photochemical oxidation of organic aerosol from wood fires 1: measurement, and simulation of organic aerosol evolution, *Atmos. Chem. Phys.*, 9, 1263–1277, 2009.

Gross, D. S., Galli, M. E., Silva, P. J., Wood, S. H., Liu, D. Y., and Prather K. A.: Single particle characterization of automobile and diesel truck emissions in the Caldecott Tunnel, *Aerosol Sci. Technol.*, 32, 152–163, 2000.

Gysel, M., Laborde, M., Olfert, J. S., Subramanian, R., and Gröhn, A. J.: Effective density of Aquadag and fullerene soot black carbon reference materials used for SP2 calibration, *Atmos. Meas. Tech.*, 4, 2851–2858, 2011.

Hennigan, C. J., Miracolo, M. A., Engelhart, G. J., May, A. A., Presto, A. A., Lee, T., Sullivan, A. P., McMeeking, G. R., Coe, H., Wold, C. E., Hao, W. M., Gilman, J. B., Kuster, W. C., de Gouw, J., Schichtel, B. A., Collett Jr., J. L., Kreidenweis, S. M., and Robinson, A. L.: Chemical and physical transformations of organic aerosol from the photo-oxidation of open biomass burning emissions in an environmental chamber, *Atmos. Chem. Phys.*, 11, 7669–7686, 2011.

Hildebrandt, L., Henry, K. M., Kroll, J. H., Worsnop, D. R., Pandis, S. N., and Donahue, N. M.: Evaluating the mixing of organic aerosol components using High-Resolution Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 45, 6329–6335, 2011.

Holder, A. L., Hagler, G. S. W., Yelverton, T. L. B., and Hays, M. D.: On-road black carbon instrument intercomparison and aerosol characteristics by driving environment, *Atmos. Environ.*, 88, 183–191, 2014.

Jacobson, M. Z.: Strong radiative heating due to the mixing state of black carbon in atmospheric aerosols, *Nature*, 409, 695– 697, 2001.

Karl, T. G., Christian, T. J., Yokelson, R. J., Artaxo, P., Hao, W. M., and Guenther, A.: The Tropical Forest and Fire Emissions Experiment: method evaluation of volatile organic compound emissions measured by PTR-MS, FTIR,, and GC from tropical biomass burning, *Atmos. Chem. Phys.*, 7, 5883–5897, 2007.

Kirchstetter, T. W., and Novakov, T.: Controlled generation of black carbon particles from a diffusion flame and applications in evaluating black carbon measurement methods, *Atmos. Environ.*, 41, 1874–1888, 2007.

Kostenidou, E., Pathak, R. K., and Pandis, S. N.: An algorithm for the calculation of secondary organic aerosol density combining AMS and SMPS data, *Aerosol Sci. Tech.*, 41, 1002-1010, 2007.

Lack, D. A., and Cappa, C. D.: Impact of brown, and clear carbon on light absorption enhancement, single scatter albedo, and absorption wavelength dependence of black carbon, *Atmos. Chem. Phys.*, 10, 4207-4220, 2010.

Lack, D. A., Justin M. Langridge, J. M., Bahreini, R., Cappa, C. D., Middlebrook, and A. N., Schwarz, J. P.: Brown carbon and internal mixing in biomass burning particles, *PNAS*, 109, 14802-14807, 2012.

Lambe, A. T., Zhang, J., Sage, A. M., and Donahue, N. M.: Controlled OH radical production via ozone-alkene reactions for use in aerosol aging studies, *Environ. Sci. Technol.*, 41, 2357-2363, 2007.

Lobert, J. M., Scharffe, D. H., Hao, W. M., Kuhlbusch, T. A., Seuwen, R., Warneck, P., and Crutzen, P. J.: Experimental evaluation of biomass burning emissions: Nitrogen and carbon containing compounds, in *Global Biomass Burning, Atmospheric, climatic,, and Biospheric Implications*, edited by J. S. Levine, Massachusetts Institute of Technology, The MIT Press, Cambridge, Massachusetts, 1991.

Marley, N. A., Gaffney, J. S., Baird, J. C., Blazer, C. A., Drayton, P. J., and Frederick, J. E.: An empirical method for the determination of the complex refractive index of size-fractionated atmospheric aerosols for radiative transfer calculations, *Aerosol Sci. Tech.*, 34, 535–549, 2001.

Medalia, A. I., and Heckman, F. A.: Morphology of aggregates—II. Size and shape factors of carbon black aggregates from electron microscopy, *Carbon*, 7, 569–582, 1969.

Mullins, J., and Williams, A.: The optical properties of soot: a comparison between experimental, and theoretical values, *Fuel*, 66, 277–280, 1987.

Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., and Worsnop, D. R.: Soot particle aerosol mass spectrometer: Development, validation, and initial application, *Aerosol Sci. Technol.*, 46, 804–817, 2012.

Ortega, A. M., Day, D. A., Cubison, M. J., Brune, W. H., Bon, D., de Gouw, J. A., and Jimenez, J. L.: Secondary organic aerosol formation and primary organic aerosol oxidation from biomass burning smoke in a flow reactor during FLAME-3, *Atmos. Chem. Phys.*, 13, 11551–11571, 2013.

Park, K., Kittelson, D. B., Zachariah, M. R., and McMurry, P. H.: Measurement of inherent material density of nanoparticle agglomerates, *Journal of Nanoparticle Research*, 6, 267–272, 2004.

Saliba, G., Subramanian, R., Saleh, R., Ahern, A., Lipsky, E., Tasoglou, A., Sullivan, R., Bhandari, J., Mazzoleni, C., and Robinson, A. L.: Optical properties of black carbon in cook stove emissions coated with secondary organic aerosols: Measurements and modeling, *Aerosol Sci. Technol.*, submitted.

Saleh, R., Robinson, E. S., Tkacik, D. S., Ahern, A. T., Liu, S., Aiken, A. C., Sullivan, R. C., Prest, A. A., Manvendra, K. D., Yokelson, R. J., Donahue, N. M., and Robinson, A. L.: Brownness of organics in aerosols from biomass burning linked to their black carbon content, *Nature Geoscience*, 7, 647–650, 2014.

Schnaiter, M., Linke, C., Möhler, O., Naumann, K.-H., Saathoff, H., Wagner, R., and Schurath, U.: Absorption amplification of black carbon internally mixed with secondary organic aerosol, 110, D19204, 2005.

Schwarz, J. P., Gao, R. S., Fahey, D. W., Thomson, D. S., Watts, L. A., Wilson, J. C., Reeves, J. M., Darbeheshti, M., Baumgardner, D. G., Kok, G. L., Chung, S. H., Schulz, M., Hendricks, J., Lauer, A., Kärcher, B., Slowik, J. G., Rosenlof, K. H., Thompson, T. L., Langford, A. O., Loewenstein, M., and Aikin, K. C.: Single-particle measurements of midlatitude black carbon and light-scattering aerosols from the boundary layer to the lower stratosphere, *J. Geophys. Res.*, 111, 207, 2006.

Silva, P. J., and Prather K. A., Interpretation of mass spectra from organic compounds in aerosol time-of-flight mass spectrometry, *Anal. Chem.*, 72, 3553–3562, 2000.

Stephens, M., Turner, N., and Sandberg, J.: Particle identification by laser-induced incandescence in a solid-state laser cavity, *Appl. Opt.*, 42, 3726–3736, 2003.

Tasoglou A., Kostenidou E., Subramanian, R., and Pandis S. N.: An inter-comparison of black carbon related instruments: a smog chamber study of biomass burning aerosol, in preparation.

Ward, D. E., and Radke, L. F.: Emission measurements from vegetation fires: A comparative evaluation of methods and results, in: *Fire in the Environment: The Ecological, Atmospheric, and Climatic Importance of Vegetation Fires*, edited by: Crutzen, P. J., and Goldammer, J. G., John Wiley, New York, 53–76, 1993.



Weingartner, E., Saathoff, H., Schnaiter, M., Streit, N., Bitnar, B., and Baltensperger, U.: Absorption of light by soot particles: determination of the absorption coefficient by means of aethalometers, *J. Aerosol. Sci.*, 34, 1445–1463, 2003.

Wu, J.-S., Krishnan, S. S., and Faeth, G. M.: Refractive indices at visible wavelengths of soot emitted from buoyant turbulent diffusion flames, *J. Heat Trans.* 119, 230–237, 1997.

Yokelson, R. J., Griffith, D., and Ward, D.: Open-path Fourier transform infrared studies of large-scale laboratory biomass fires, *J. Geophys. Res.*, 101, 21067–21080, 1996.

## **Chapter 5**

**The chemical composition and CCN activity of fresh  
and chemically aged cooking organic aerosol**

## **Abstract**

Cooking organic aerosol (COA) is a significant fraction of the total fine aerosol in urban areas around the world. COA chemical aging experiments using aerosol produced by grilled hamburgers took place in a smog chamber in the presence of UV light or in excess of ozone. Positive matrix factorization was used to characterize the changes in the chemical composition of the COA during the chemical aging. The chemical aging processes caused an increase of the organic aerosol mass and its oxidation state. The fresh COA particles have a low CCN activity but their hygroscopicity increased significantly as they aged.

## **5.1 Introduction**

Atmospheric aerosol serve as cloud condensation nuclei (CCN), on which cloud droplets particles can be formed (Rosenfeld et al., 2008; Clement et al., 2009). When the concentration of aerosols increases, clouds tend to have more but smaller droplets, reflecting more solar radiation (Twomey, 1977), and having a potentially significant effect on climate. Aerosol-cloud interactions also influence the spatio-temporal distribution of precipitation (Rosenfeld et al., 2008; IPCC 2013).

The ability of an aerosol particle to act as CCN depends on both its size and composition (Kohler, 1936; Seinfeld and Pandis, 2006). Atmospheric aerosols have mixed chemical composition, with a variety of species often present in a single particle. Organic compounds can represent 10-70% of the fine aerosol mass (Wolff et al., 1991; Sloane et al., 1991; Chow et al., 1994; Murphy et al., 1998; Carrico et al., 2003; Malm et al., 2004; Heald et al., 2006). The processes by which the inorganic components of atmospheric particles activate and become cloud droplets are well understood (Kohler, 1936; Pruppacher and Klett, 1980). The role of the

organics remains uncertain because the atmospheric organic aerosol fraction consists of thousands of compounds with different physicochemical properties (Saxena et al., 1995; Cruz and Pandis, 2000).

There have been several previous studies that have investigated the CCN activities of organic aerosol (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Raymond and Pandis, 2002; Huff-Hartz et al., 2006; Lambe et al., 2011; Engelhart et al., 2011; Asa-Awuku et al., 2009; Varutbangkul et al., 1991) and explore the effect of the solubility of the organic aerosol components on the particle CCN activity (Cruz and Pandis, 1997, 2000; Hansson et al., 1998; Abbatt et al., 2005; Henning et al., 2005; Svenningsson et al., 2006; King et al., 2010). Riipinen et al. (2015) suggested that organic compounds with solubility in the 0.1-100 g L<sup>-1</sup> range affect mostly the CCN activity of the particle..

Fine particulate matter emitted during meat cooking contributes a significant fraction of the total fine aerosol concentration in urban areas (Schauer et al., 1996; Schauer and Cass, 2000; Rogge et al., 1991; Zheng et al., 2006; Wang et al., 2009). Cooking emissions are an important source for alkenoic acids, especially for oleic and palmitoleic acids (Rogge et al., 1991; Schauer et al., 1999, 2002). There have been no studies, to the best of our knowledge, examining the hygroscopic properties of these particles.

In this study, we grilled beef burgers to produce COA. After the characterization of the fresh COA they were exposed to UV or ozone and were allowed to chemically age. The composition of the fresh and aged COA was characterized by aerosol mass spectrometry. The CCN activity of the fresh and aged emissions was also quantified.

## 5.2 Experimental Methods

The experiments were carried out in a smog chamber in the Air Quality Laboratory of Carnegie Mellon University. The smog chamber is a 12 m<sup>3</sup> Teflon reactor inside a temperature controlled room. The walls of the smog chamber room are lined with UV lights (General Electric model 10526 black). Prior to an experiment, the chamber was flushed with purified air for 12-48 h. Air was passed through HEPA and carbon filters to remove particles and gas-phase organics respectively and silica gel to reduce relative humidity. All the experiments were carried out at a constant temperature of 20±2°C and at RH<10%.

Beef burgers (fat 25%) were cooked on a grill using charcoal. The cooking emissions were injected into the smog chamber using two ejector diluters in parallel (Dekati, Finland). After the injection there were around 3x10<sup>4</sup> to 10<sup>5</sup> particles cm<sup>-3</sup> in the smog chamber. After 1 to 4 hr, the chemical aging of COA was initiated by turning on the UV lights or by injecting ozone. The required ozone was generated by an electrical discharge generator (AZCO, model HTU-500ACPS). The ozone concentration was monitored using a continuous ozone analyzer (Dasibi 1008-PC).

The CCN concentration was measured with a continuous-flow stream-wise thermal gradient CCN counter (CCNC-100, DMT). The CCN counter operates on the principle that diffusion of heat in air is slower than diffusion of water vapor (Roberts and Nenes, 2005). An optical particle counter (OPC) is used to count the formed droplets in the CCNC. The CCNC was used downstream of a differential mobility analyzer (DMA, TSI classifier model 3080) and in parallel with a condensation particle counter (CPC, TSI model 3772). The CCNC was calibrated with ammonium sulfate following the procedure of Rose et al. (2008) and Engelhart et al. (2008). During the experiments, the total airflow to DMA was set at 0.8 L min<sup>-1</sup>. The CCNC total airflow

was  $0.5 \text{ L min}^{-1}$ , and the CPC sample flow was controlled  $0.3 \text{ L min}^{-1}$ . The sheath flow of the DMA was set at  $4 \text{ L min}^{-1}$ . For the CCNC, water supersaturations of 0.2% and 0.4% were used. The sampling period was 12 minutes for each supersaturation. The sample and sheath flow rates of the CCNC were  $0.045$  and  $0.45 \text{ L min}^{-1}$  respectively. For each supersaturation the activation diameter is the diameter at which 50% of the particles are activated given the symmetry of the close to monodisperse aerosol distribution leaving the DMA.

A Soot Particle Aerosol Mass Spectrometer (SP-AMS, Aerodyne Research, Inc.) was used to monitor the mass concentration and the chemical composition of the particles. The SP-AMS was operated in two modes: the V mode with the tungsten vaporizer on and the V mode with both the tungsten and the laser vaporizer on. The measuring time for each mode was 1 min. The non-refractory components of the particles were measured at the laser off mode. The rBC (refractory black carbon) concentration was measured by the SP-AMS when both the tungsten and the laser vaporizer were on. The rBC relative ionization efficiency ( $\text{RIE}_{\text{rBC}}$ ) of the SP-AMS was calculated according to the recommendations of Onasch et al. (2012), using Regal black (REGAL 400R pigment black Cabot Corp.) resulting in  $\text{RIE}_{\text{rBC}}=0.2$ . For the SP-AMS data analysis SQUIRREL 1.57G and PIKA 1.16H were used. The elemental ratios O:C and H:C of the OA were calculated using the laser off data. In the analysis we used the algorithms suggested by both Aiken et al. (2008) and Canagaratna et al. (2015).

Filter samples were collected and prepared for thermal optical analysis for selected experiments. Pallflex Tissuquartz 2500QAT-UP membrane filters in a 25 mm stainless steel in-line filter holder (Pall Corporation) were used. The sampling flow rate was controlled by a mass flow controller at  $20 \text{ L min}^{-1}$ , and the sampling time ranged from 10 to 25 minutes in order to collect enough mass on the filter. The sample was analyzed by an OC-EC Aerosol Analyzer

(Sunset Laboratory Inc.) using the EUSAAR 2 protocol, which is described in detail by Cavalli et al. (2010).

### 5.3 Results and discussion

Five experiments were conducted to chemically characterize the fresh and aged emissions from grilling burgers (Table 5.1). At time zero cooking emissions were injected in the chamber.

**Table 5.1:** Composition of the fresh and aged cooking emissions

| Exp. | Fresh                          |                                 |                  |                  | Aging method | Aged                           |                                 |                  |                  |
|------|--------------------------------|---------------------------------|------------------|------------------|--------------|--------------------------------|---------------------------------|------------------|------------------|
|      | OA<br>( $\mu\text{g m}^{-3}$ ) | rBC<br>( $\mu\text{g m}^{-3}$ ) | O:C <sup>1</sup> | H:C <sup>1</sup> |              | OA<br>( $\mu\text{g m}^{-3}$ ) | rBC<br>( $\mu\text{g m}^{-3}$ ) | O:C <sup>1</sup> | H:C <sup>1</sup> |
| 1    | 273                            | 13.9                            | 0.1(0.13)        | 1.76(1.89)       | UV           | 251                            | 10.9                            | 0.15(0.2)        | 1.74(1.88)       |
| 2    | 310                            | 3.5                             | 0.09(0.12)       | 1.86(2.01)       | UV           | 277                            | 3.1                             | 0.14(0.18)       | 1.82(1.97)       |
| 3    | 163                            | 4.4                             | 0.08(0.11)       | 1.86(2)          | Ozone        | 145                            | 3.4                             | 0.13(0.16)       | 1.84(1.99)       |
| 4    | 263                            | 5.2                             | 0.10(0.13)       | 1.83(1.97)       | Ozone        | 160                            | 2.6                             | 0.15(0.19)       | 1.79(1.94)       |
| 5    | 261                            | 14.5                            | 0.13(0.17)       | 1.78(1.92)       | Ozone        | 119                            | 6.2                             | 0.17(0.22)       | 1.76(1.92)       |

<sup>1</sup> The values for the elemental ratios were calculated using the Aiken et al. (2008) algorithm while the values in the parenthesis were calculated using the Canagaratna et al. (2015) algorithm.

The fresh emissions had high concentration in OA, while the rBC concentration was <6% of the OA. The levels of the other chemical components of the particles were negligible (<0.5%). In Experiment 1 and 2 the cooking emissions were exposed to UV light 1 hr after the injection of the emissions. In Experiment 3 the emissions were exposed to 180 ppb of ozone 1 hr after the

beginning of the experiment. In Experiments 4 and 5 the cooking emissions were exposed to 275 ppb and 250 ppb of ozone respectively, 4 hrs after their injection.

### 5.3.1 SP-AMS collection efficiency and shape of the particles

Quartz filter samples were collected in Experiment 5 during four periods to measure the organic carbon (OC) and elemental carbon (EC) in the chamber. The first two periods were before the ozone injection ( $t_1=0.7-0.8$  hr and  $t_2=2.7-3$  hr) and the next two after the injection ( $t_3=5.3-5.6$  hr and  $t_4=6.7-7.2$  hr). The COA mass was calculated using the OC concentration on the filters and the OM:OC ratio, measured by the SP-AMS. The COA mass measured by the filters and the online measurement of the SP-AMS were combined (Figure A.3.1) to calculate the cooking OA collection efficiency ( $CE_{OA}$ ) of the SP-AMS. Using the Aiken et al. (2008) method the  $CE_{OA}$  for the fresh emissions was 0.78 and 1.1, while for the aged 0.98 and 0.85. An average  $CE_{OA}$  of 0.93 was estimated. According to the method suggested by Canagaratna et al. (2015) the  $CE_{OA}$  for the fresh emissions were 0.74 and 1.05, while for the aged aerosol 0.93 and 0.81. The average  $CE_{OA}$  was 0.88. For our further analysis an overall average  $CE_{OA}$  equal to 0.9 will be assumed for the COA.

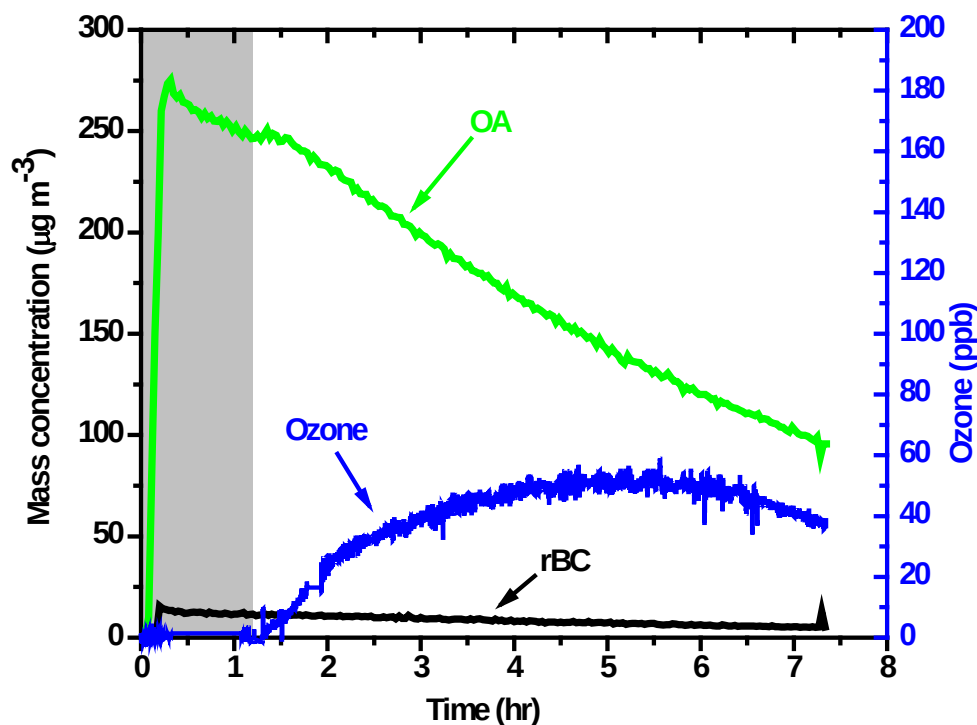
The EC measurements were compared with the rBC measurements for Experiment 5 during the four sampling. The estimated  $CE_{BC}$  values were 0.33, 0.48, 0.45, 0.38 resulting in an average  $CE_{BC}$  equal to 0.41. Beam width probe analysis (Huffman et al., 2005; Willis et al., 2014) was used in Experiments 1 and 3 to also calculate the  $CE_{BC}$  of the SP-AMS. For Experiment 1 the probe was used at  $t=7.6-9$  hr and for Experiment 3 at  $t=7.2-10$  hr. The results suggest a  $CE_{BC}=0.48$  for Experiment 1 and  $CE_{BC}=0.54$  for Experiment 3 with an average of 0.51. For our further analysis an overall average  $CE_{BC}$  equal to 0.44 will be assumed.



Nuclepore filters (polycarbonate 25 mm filters, 200 nm, Whatman) were collected in Experiment 5 for Scanning Electron Microscopy (SEM) analysis in order to investigate the shape of the particles from cooking emissions. The filters were collected in two periods before the ozone injection ( $t=0.6$  hr) and after the ozone injection ( $t=5.3$  hr). The sampling time was 20 minutes at a flow rate of  $8 \text{ L min}^{-1}$ . Figure A.3.2 suggests that the particles were not exactly spherical.

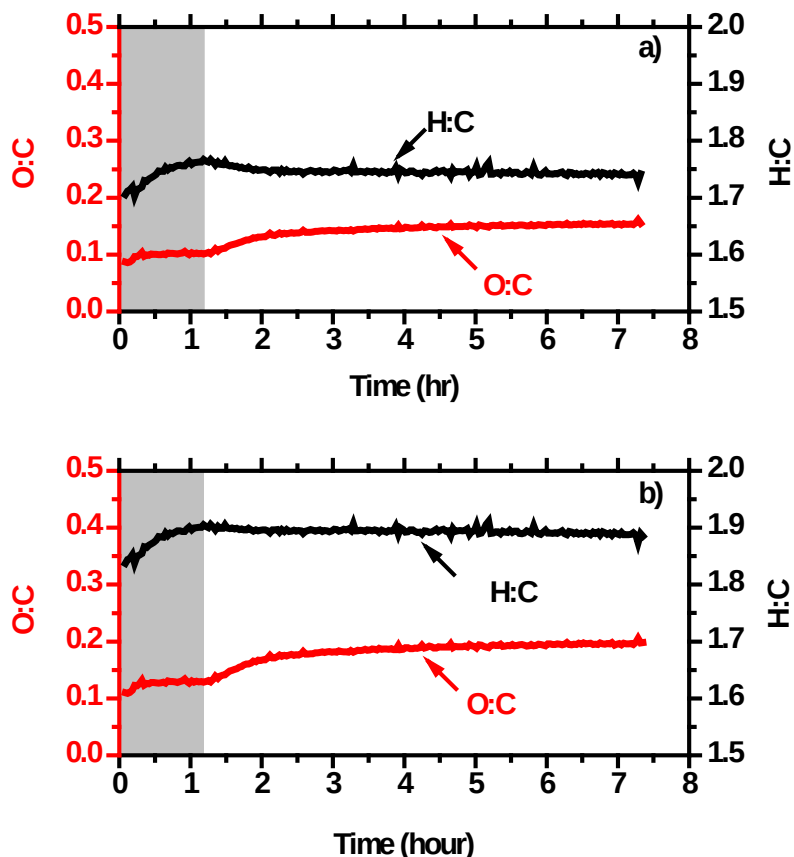
### 5.3.2 Chemical aging of COA

In Experiment 1 the initial OA concentration was approximately  $275 \mu\text{g m}^{-3}$  while the rBC was equal to  $13.9 \mu\text{g m}^{-3}$  (Figure 5.1). The rBC concentration was 5% of the OA while the levels of the other chemical components of the particles were negligible ( $<0.5\%$ ). The concentration of the OC and rBC decreased during the experiment due to losses of the particles on the walls of the smog chamber. Approximately 1 hr after the injection, the UV lights were turned on initiating the chemical aging processes. The photochemistry led to the immediate production of ozone, which reached a maximum of 56 ppb, 4 hours later. The aging caused a 17% increase of the OA/rBC.



**Figure 5.1:** The timeseries of the organic aerosol, black carbon, and ozone concentrations for Experiment 1. The shaded region indicates the period during which the chamber was dark.

The elemental ratios of the OA were calculated using SP-AMS measurements and both the methods of Aiken et al. (2008) and Canagaratna et al. (2015) (values in parenthesis). The fresh OA emissions had an O:C ratio equal to 0.1(0.13) and a H:C ratio of 1.76(1.89). The chemical aging of the OA resulted in the increase of the O:C ratio to 0.15(0.2) and in the decrease of the H:C ratio to 1.74(1.88) (Figure 5.2).



**Figure 5.2:** The timeseries of the elemental ratios of COA for Experiment 1 calculated using a) Aiken et al. (2008) and b) Canagaratna et al. (2015) methods. The red line represents the oxygen over carbon ratio and the black the hydrogen over carbon ratio of the COA. The shaded region indicates the period during which the chamber was dark.

In a similar experiment (Experiment 2) the initial concentration of OA was  $310 \mu\text{g m}^{-3}$  OA and the rBC was  $3.5 \mu\text{g m}^{-3}$ . The O:C and H:C ratios were 0.09(0.12) and 1.86(2.01). The photochemistry led to only a 1% increase of the OA/rBC and 9 ppb of ozone were produced. The O:C and H:C ratios changed to 0.14(0.18) and 1.82(1.97).

In Experiment 3 the initial concentration of the emissions was  $163 \mu\text{g m}^{-3}$  OA and  $4.4 \mu\text{g m}^{-3}$  rBC. The O:C and H:C ratios were 0.08(0.11) and 1.86(2). Approximately 1 hr later, ozone was injected in the chamber to initiate the chemical aging. The ozone concentration initially was

180 ppb. Ten minutes after the ozone injection the OA/rBC increased by 16%. The elemental ratios changed to O:C=0.13(0.16) and H:C=1.84(1.99).

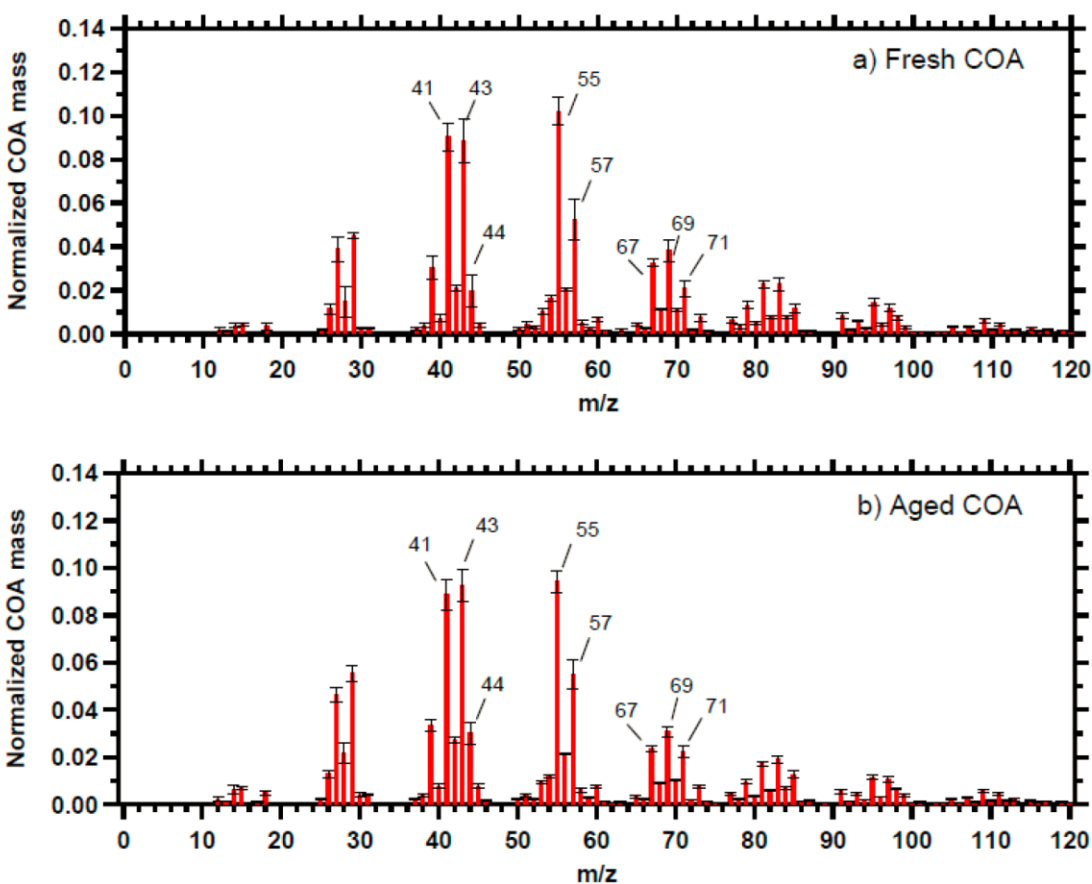
In Experiment 4 the composition of the fresh emissions was OA= 263  $\mu\text{g m}^{-3}$  and rBC =5.2  $\mu\text{g m}^{-3}$ . The initial O:C and H:C ratios were 0.1(0.13) and 1.83(1.97) accordingly. Approximately 4 hrs later, ozone was injected in the chamber to initiate the chemical aging. The exposure of the cooking emissions to 275 ppb of ozone led to a 22% increase of the OA/rBC. The elemental ratios changed to O:C=0.15(0.19) and H:C=1.79(1.94).

In Experiment 5 the initial OA concentration was equal to 261  $\mu\text{g m}^{-3}$  while the rBC was equal to 6.4  $\mu\text{g m}^{-3}$  (Figure A.3.3). The exposure of the emissions to 250 ppb of ozone in the chamber led to a 6% increase of the OA/rBC. The fresh COA emissions had an O:C ratio equal to 0.13(0.17) and an H:C ratio of 1.78(1.92). After the injection of ozone the ratios changed, the O:C ratio was equal to 0.17(0.22) and the H:C ratio was equal to 1.76(1.92) (Figure A.3.4).

In summary, the fresh COA emissions had an average O:C ratio equal to  $0.1 \pm 0.02$  ( $0.13 \pm 0.02$ ) and an average H:C ratio equal to  $1.82 \pm 0.05$  ( $1.96 \pm 0.05$ ). The chemical aging with UV light or ozone injection resulted in a small to moderate OA mass increase. The exposure of the emissions to UV light led to an increase of the OA/rBC ranging from 1% to 17% and a production of ozone ranging from 9 to 56 ppb. For the aged COA the average O:C ratio was equal to  $0.15 \pm 0.01$  ( $0.19 \pm 0.02$ ), and the average H:C ratio was equal to  $1.78 \pm 0.02$  ( $1.93 \pm 0.02$ ). When ozone was injected in the system there was more OA mass production. The OA/rBC increased from 6% to 22%. After the ozone injection, the average O:C ratio was equal to  $0.15 \pm 0.02$  ( $0.19 \pm 0.03$ ) and the average H:C ratio was equal to  $1.79 \pm 0.04$  ( $1.95 \pm 0.04$ ). The elemental ratios of the COA after injection of ozone were similar to those in the photooxidation experiments suggesting that the same oxidation state of the COA was achieved in both cases.

### 5.3.3 COA composition

Average mass spectra of the fresh and aged COA from all five experiments were compared using the angle  $\theta$  between the corresponding vectors as described in Kostenidou et al. (2009) (Figure 5.3). For the fresh emissions the  $\theta$  angle ranged from  $4^\circ$  to  $13^\circ$ , suggesting that the fresh COA emission had similar composition from the AMS' point of view, but there was some variability from experiment to experiment. Similarly, for the mass spectra of the aged COA the  $\theta$  angle ranged from  $2^\circ$  to  $8^\circ$ .

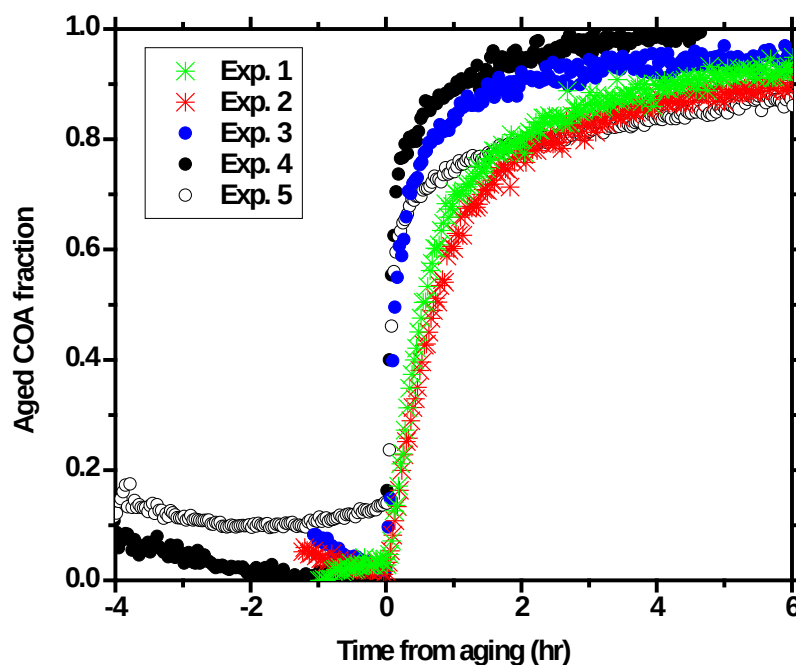


**Figure 5.3:** The average mass spectra for the fresh and aged COA.

The average mass spectra were also compared with previous studies. Mohr et al. (2009) studied the emissions of grilled fatty (20% fat) and lean burgers (7%) using a propane grill. The  $\theta$  angle

between the AMS spectrum of the fresh COA of this study and the lean burgers or the fatty burgers was  $14^\circ$ . The  $\theta$  angles between the spectra of the aged COA of this study and the fatty burgers or the lean burgers were  $19^\circ$  and  $17^\circ$  respectively.

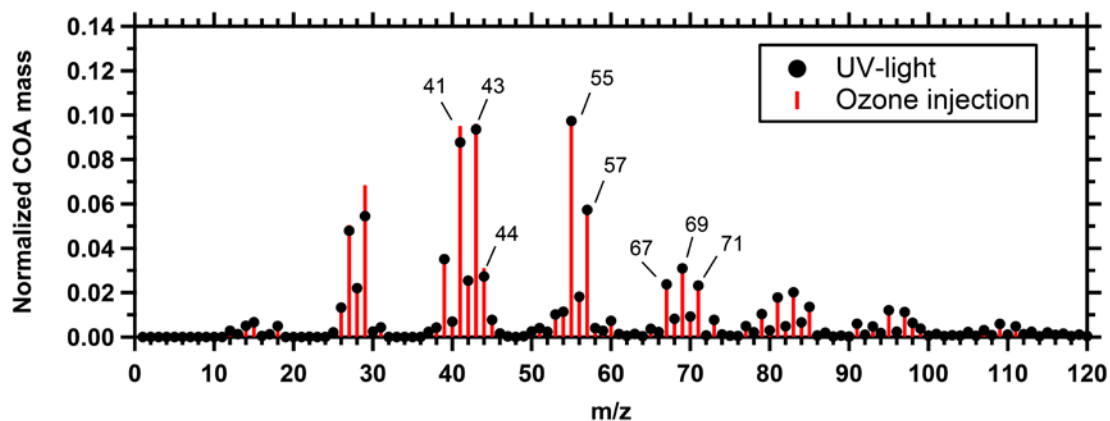
To investigate the changes in the OA composition in more detail, positive matrix factorization (PMF) was used for each experiment separately. The details of the method of analyzing AMS data using PMF is described in Lanz et al. (2007) and Ulbrich et al. (2009). A two factor solution was chosen to describe the evolution of the COA composition in all experiments. The factors that were identified corresponded to “fresh” and “aged” COA.



**Figure 5.4:** The timeseries of the aged COA fraction of the total COA for all experiments.

The temporal evolution of the aged COA mass fractions calculated by the PMF for all experiments is presented in Figure 5.4. In Experiments 3-5 in which ozone was used to initiate the chemical aging the production of the aged COA is faster than in the experiments in which UV light was used (Experiments 1-2). In all experiments, after 1 hr of chemical aging, the mass

fraction of aged COA ranged from 70 to 90%, suggesting that the conversion is rapid. The  $\theta$  angle, between the aged COA mass spectra calculated in the different experiments varied from 2-8°. There was little difference between the aging experiments using UV and ozone and the corresponding angle was 4.5° (Figure 5.5).



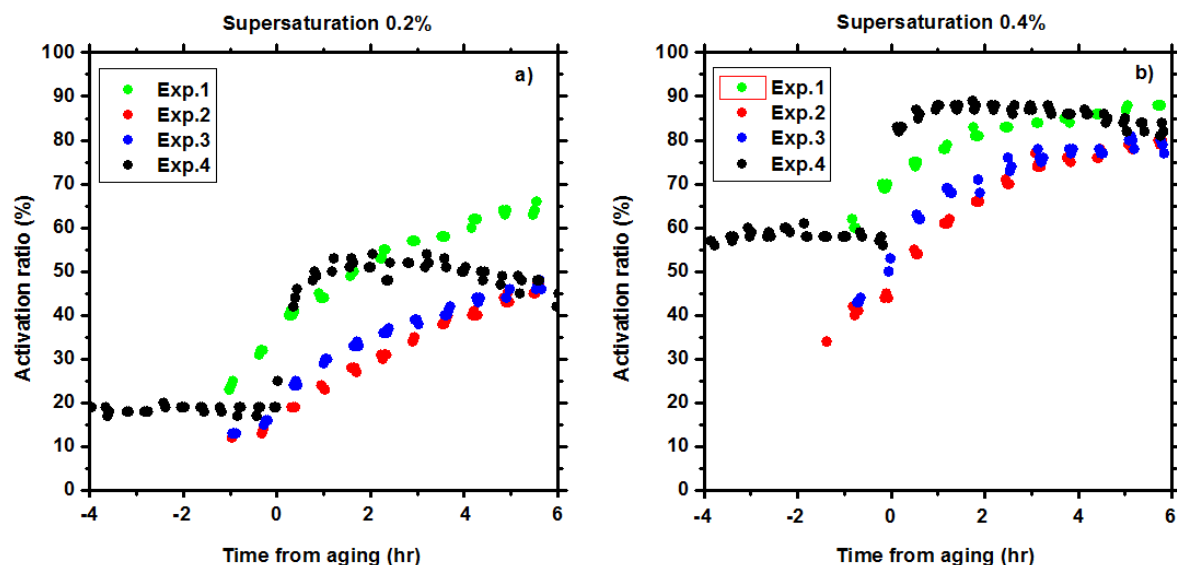
**Figure 5.5:** The average mass spectra of the aged COA retrieved from the PMF analysis for the systems where UV light and ozone injection initiated the chemical aging.

These results suggest that the aged COA chemical composition is similar in the five experiments and does not depend on the chemical aging method.

### 5.3.4 CCN activity

The number size distributions for Experiments 1-4 are shown in Figure A.3.5. For the fresh emissions, the number mode diameter ranged from 87 to 127 nm, with Experiment 4 having the largest diameter. For the aged emissions the mode diameter ranged from 121 nm to 140 nm, with Experiment 1 having the largest diameter. The COA CCN activity was measured during Experiments 1-4. The activation diameters and activated fractions (CN/CCN) were calculated at supersaturations 0.2% and 0.4% using the Scanning Mobility CCN Analysis

(SMCA) method (Moore et al., 2010). At supersaturation 0.2% the activated fraction of the fresh COA was 0.12-0.23, while at 0.4% it was 0.34-0.62. The aging process made the OA more CCN active. At  $ss=0.2\%$  the activated fraction was 0.45-0.64, while at  $ss=0.4\%$  the activated fraction was 0.77-0.88 (Figure 5.6). Part of this increase in CCN activity was due to the growth of the particles and part was due to the change in chemical composition due to the aging. The activated fraction depends on both the aerosol size distribution and chemical composition, while the activation diameter only on the chemical composition.

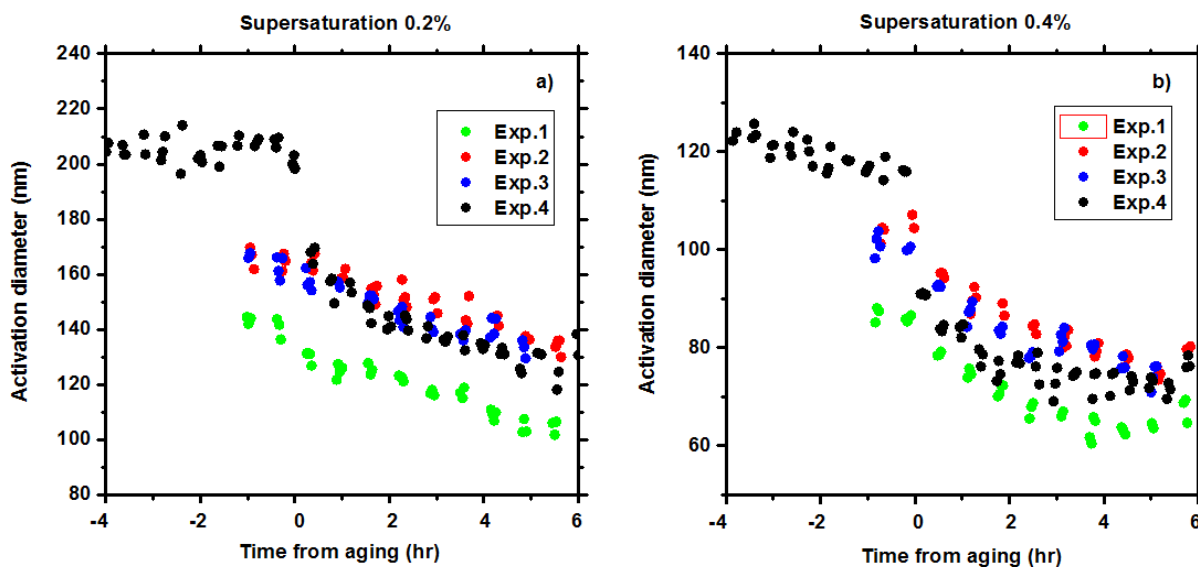


**Figure 5.6:** The activation ratios timeseries for Experiments 1-4 for supersaturation equal to: a) 0.2% and b) 0.4%.

The fresh emissions at  $ss=0.2\%$  had an activation diameter that varied from 144 to 200 nm depending on the experiment, while at  $ss=0.4\%$  the activation diameter was in the 85-122 nm range. The small differences in fresh COA composition from experiment to experiment corresponded to rather large differences in the activation diameter for this relatively hydrophobic aerosol. After the chemical aging, the COA activation diameter decreased significantly (Figure 5.7). This change is consistent with the production of aged OA discussed in the previous section.

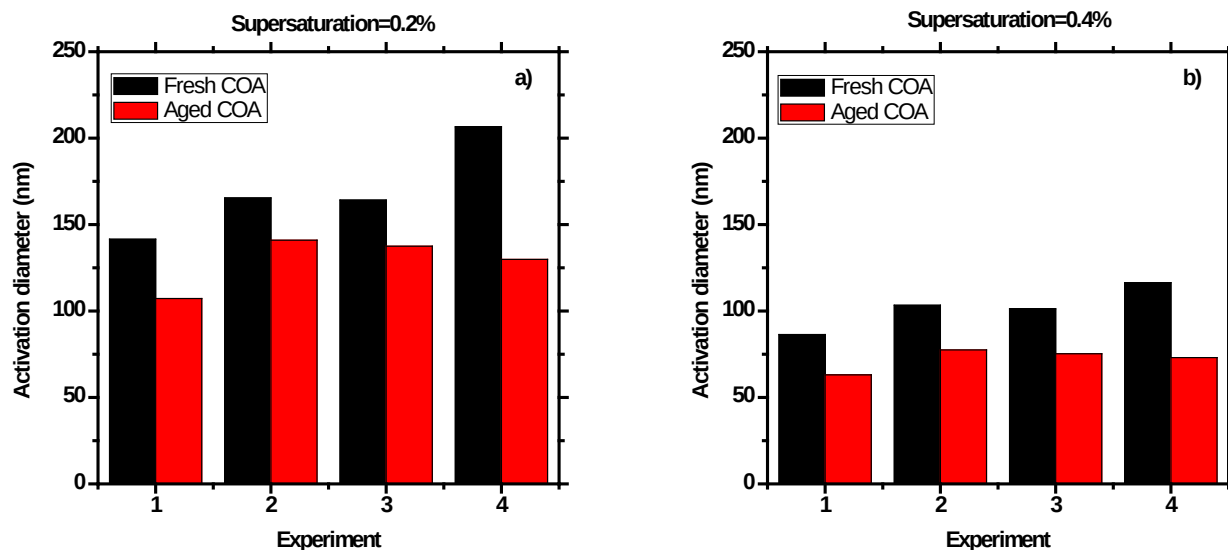


The chemical aging of the OA increased the CCN activity of COA and many smaller COA particles can be CCN after an hour of aging.



**Figure 5.7:** The activation diameter timeseries for Experiments 1-4 for supersaturation equal to: a) 0.2% and b) 0.4%.

The average activation diameters of the fresh and aged COA (after 5 hrs of chemical aging) for Experiments 1-4 are compared in Figure 5.8. For supersaturation 0.2% the activation diameter decreased by 15 to 37%. For supersaturation 0.4% the activation diameter decreased 25% to 37%. In both cases the smallest decrease of the activation diameter was in Experiment 2, in which there was the smallest OA production was observed during chemical aging. Similarly, the largest decrease of the activation diameter was in Experiment 4, in which there was the largest OA production in the chemical aging phase.



**Figure 5.8:** Average activation diameter before and after the chemical aging of COA for Experiments 1-4 for supersaturation equal to: a) 0.2% and b) 0.4%.

## 5.4 Conclusions

The effect of the chemical aging of COA on its composition and CCN activity were investigated. Cooking emissions were produced by grilling beef burgers with high fat content and the resulting particles and vapors were then exposed to oxidants for a few hours.

OA was the dominant component of the grilling particulate emissions with rBC being 1-6% of the OA and the contribution of other species being negligible. There were only small differences among the AMS fresh COA spectra in the experiments performed. The corresponding  $\theta$  angles among the vectors corresponding to the spectra ranged from  $4^\circ$  to  $13^\circ$ . The COA particles according to the SEM pictures may not have been spherical.

When the emissions were exposed to UV, 9-56 ppb of ozone were generated and the OA/rBC increased by 1% to 17%. When the COA was exposed to high concentrations of ozone (180-275 ppb) the OA/rBC increased by 6% to 26%. The O:C increased by 30% to 55% during

the aging. In all experiments the aged COA composition was similar with the  $\theta$  angles ranging from 2° to 8°.

PMF analysis was used to analyze the evolution of the chemical composition of the COA during the aging process. In all the experiments, 1 hr after the chemical aging, the “aged” COA factor was 70-90% of the total COA. The “aged” COA factor chemical composition was similar in the five experiments and did not depend on the chemical aging method.

The CCN activity of the fresh and aged COA was studied at supersaturations 0.2% and 0.4%. At supersaturation 0.2% the fresh emissions were 12-23% CCN active, while at supersaturation 0.4% the activation percentage was 34-62%. Chemical aging led to an increase of the CCN active particles to 45-64% at supersaturation 0.2%, and to 77-88% at supersaturation 0.4%. Five hours after the chemical aging the activation diameter decreased by 15-37% for supersaturation 0.2%. For supersaturation 0.4% the activation diameter decreased by 25-37%. The smallest decrease of the activation diameter occurred when there was the smallest OA production and vice versa.

## 5.5 References

Abbatt, J. P. D., Broekhuizen, K., and Kumal, P. P.: Cloud condensation nucleus activity of internally mixed ammonium sulfate/organic acid aerosol particles, *Atmos. Environ.*, 39, 4767–4778, 2005.

Aiken, A. C. , DeCarlo, P. F., Kroll, J. H., Worsnop, D. R., Huffman, J. A., Docherty, K. S., Ulbrich, I. M., Mohr, C., Kimmel, J. R., Sueper, D., Sun, Y., Zhang, Q., Trimborn, A., Northway, M., Ziemann, P. J., Canagaratna, M. R., Onasch, T. B., Alfarra, M. R., Prevot, A. S. H., Dommen, J., Duplissy, J., Metzger, A., Baltensperger, U. and Jimenez, J. L.; O/C and OM/OC ratios of primary, secondary, and ambient organic aerosols with High-Resolution Time-of-Flight Aerosol Mass Spectrometry, *Environ. Sci. Technol.*, 42, 4478–4485, 2008.

Asa-Awuku, A., Engelhart, G. J., Lee, B. H., Pandis, S. N., and Nenes, A.: Relating CCN activity, volatility, and droplet growth kinetics of  $\beta$ -caryophyllene secondary organic aerosol, *Atmos. Chem. Phys.*, 9, 795–812, 2009.

Canagaratna, M. R., Jimenez, J. L., Kroll, J. H., Chen, Q., Kessler, S. H., Massoli, P., Hildebrandt Ruiz, L., Fortner, E., Williams, L. R., Wilson, K. R., Surratt, J. D., Donahue, N. M., Jayne, J. T., and Worsnop, D. R.: Elemental ratio measurements of organic compounds using aerosol mass spectrometry: characterization, improved calibration, and implications, *Atmos. Chem. Phys.*, 15, 253–272, 2015.

Carrico, C. M., Bergin, M. H., Shrestha, A., Dibb, J. E., Gomes, L., and Harris, J.M.: The importance of carbon and mineral dust to seasonal aerosol properties in the Nepal Himalayas, *Atmos. Environ.*, 37, 2811–2824, 2003.

Cavalli, F., Viana, M., Yttri, K. E., Genberg, J., and Putaud, J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol, *Atmos. Meas. Tech.*, 3, 79–89, , 2010.

Chow, J. C., Watson, J. G., Fujita, E. M., Lu, Z., and Lawson, D. R.: Temporal and spatial variations of PM<sub>2.5</sub> and PM<sub>10</sub> aerosol in the southern California air quality study, *Atmos. Environ.*, 28, 2061–2080, 1994.

Clement, A. C., Burgman, R., and Norris, J. R.: Observational and model evidence for positive low-level cloud feedback, *Science*, 325, 460–464, 2009.

Corrigan, C. E., and Novakov, T.: Cloud condensation nucleus activity of organic compounds: a laboratory study, *Atm. Environ.*, 33, 2661–2668, 1999.

Cruz, C. N., and Pandis, S. N.: A study of the ability of pure secondary organic aerosol to act as cloud condensation nuclei, *Atmos. Environ.*, 31, 2205–2214, 1997.

Cruz, C. N., and Pandis, S. N.: Deliquescence and hygroscopic growth of mixed inorganic-organic atmospheric aerosol, *Environ. Sci. Technol.*, 34, 4313–4319, 2000.

Drinovec, L., Mocnik, G., Zotter, P., Prévôt, A. S. H., Ruckstuhl, C., Coz, E., Rupakheti, M., Sciare, J., Müller, T., Wiedensohler, A., and Hansen, A. D. A.: The “dual-spot” Aethalometer: an improved measurement of aerosol black carbon with real-time loading compensation, *Atmos. Meas. Tech.*, 8, 1965–1979, 2015.

Engelhart, G. J., Asa-Awuku, A., Nenes, A., and Pandis, S. N.: CCN activity and droplet growth kinetics of fresh and aged monoterpene secondary organic aerosol, *Atmos. Chem. Phys.*, 8, 3937–3949, 2008.

Engelhart, G. J., Moore, R. H., Nenes, A., and Pandis, S. N.: Cloud condensation nuclei activity of isoprene secondary organic aerosol, *J. Geophys. Res.*, 116, D02207, 2011.

Goldstein, A. H.: Hygroscopicity of secondary organic aerosols formed by oxidation of cycloalkenes, monoterpenes, sesquiterpenes, and related compounds, *Atmos. Chem. Phys.*, 6, 2367–2388, 2006.

Hänel, G., and Zankl, B.: Aerosol size and relative humidity: Water uptake by mixtures of salts, *Tellus*, 31, 478–486, 1979.

Hansson, H. C., Rood, M. J., Koloutsou-Vakakis, S., Hameri, K., Orsini, D., and Wiedensohler, A.: NaCl aerosol particle hygroscopicity dependence on mixing with organic compounds, *J. Atmos. Chem.*, 31, 321–346, 1998.

Heald, C. L., Jacob, D. J., Turquety, S., Hudman, R. C., Weber, R. J., Sullivan, A. P., Peltier, R. E., Atlas, E. L., deGouw, J. A., Warneke, C., Holloway, J. S., Newman, J. A., Flocke, F. M., and Seinfeld, J. H.: Concentrations and sources of organic carbon aerosols in the free troposphere over North America, *J. Geophys. Res.*, 111, D23S47, 2006.

Henning, S., Rosenorn, T., D'Anna, B., Gola, A. A., Svenningsson, B., and Bilde, M.: Cloud droplet activation and surface tension of mixtures of slightly soluble organics and inorganic salt, *Atmos. Chem. Phys.*, 5, 575–582, 2005.

Huff-Hartz, K. E. H., Tischuk, J. E., Chan, M. N., Chan, C. K., Donahue, N. M., and Pandis, S. N.: Cloud condensation nuclei activation of limited solubility organic aerosol, *Atmos. Environ.*, 40, 605–617, 2006.

Huffman, J., Jayne, J. T., Drewnick, F., Aiken, A. C., Onasch, T. B., Worsnop, D. R., Jimenez, J., Design, modeling, optimization, and experimental tests of a particle beam width probe for the aerodyne aerosol mass spectrometer, *Aerosol Sci. Tech.*, 39, 1143–1163, 2005.

King, S. M., Rosenorn, T., Shilling, J. E., Chen, Q., Wang, Z., Biskos, G., McKinney, K. A., Pöschl, U., and Martin, S. T.: Cloud droplet activation of mixed organic-sulfate particles produced by the photooxidation of isoprene, *Atmos. Chem. Phys.*, 10, 3953–3964, 2010.

Kostenidou, E., Lee, B. H., Engelhart, G. J., Pierce, J. R., and Pandis, S. N.: Mass spectra deconvolution of low, medium, and high volatility biogenic secondary organic aerosol, *Environ. Sci. Technol.*, 43, 4884–4889, 2009.

Lambe, A. T., Onasch, T. B., Massoli, P., Croasdale, D. R., Wright, J. P., Ahern, A. T., Williams, L. R., Worsnop, D. R., Brune, W. H., and Davidovits, P.: Laboratory studies of the chemical composition and cloud condensation nuclei (CCN) activity of secondary organic aerosol (SOA) and oxidized primary organic aerosol (OPOA), *Atmos. Chem. Phys.*, 11, 8913–8928, 2011.

Lanz, V. A., Alfarra, M. R., Baltensperger, U., Buchmann, B., Hueglin, C., and Prévôt, A. S. H.: Source apportionment of submicron organic aerosols at an urban site by factor analytical modelling of aerosol mass spectra, *Atmos. Chem. Phys.*, 7, 1503–1522, 2007.

Malm, W. C., Schichtel, B. A., Pitchford, M. L. Ashbaugh, L. L., and Eldred, R. A.: Spatial and monthly trends in speciated fine particle concentration in the United States, *J. Geophys. Res.*, 109, D03306, 2004

.

Mohr, C., Huffman, J. A., Cubison, M. J., Aiken, A. C., Docherty, K. S., Kimmel, J. R., Ulbrich, I. M., Hannigan, M. P., and Jimenez, J. L.: Characterization of Primary Organic Aerosol Emissions from Meat Cooking, Trash Burning, and Motor Vehicles with High-Resolution Aerosol Mass Spectrometry and Comparison with Ambient and Chamber Observations, *Environ. Sci. Technol.*, 43, 2443–2449, 2009.

Moore, R., Nenes, A., and Medina, J.: Scanning Mobility CCN Analysis – A method for fast measurements of size resolved CCN distributions and activation kinetics, *Aerosol Sci. Technol.*, 44, 861–871, 2010.

Murphy, D. M., Anderson, J. R., Quinn, P. K., McInnes, L. M., Brechtel, F. J., Kreidenweis, S. M., Middlebrook, A. M., Posfai, M., Thomson, D. S., and Buseck, P. R.: Influence of sea-salt on aerosol radiative properties in the Southern Ocean marine boundary layer, *Nature*, 392, 62–65, 1998.

Onasch, T. B., Trimborn, A., Fortner, E. C., Jayne, J. T., Kok, G. L., Williams, L. R., Davidovits, P., and Worsnop, D. R.: Soot particle aerosol mass spectrometer: Development, validation, and initial application, *Aerosol Sci. Technol.*, 46, 804–817, 2012.

Pruppacher, H. R., and Klett J. D.: *Microphysics of Clouds and Precipitation*, D. Reidel Publishing, London, 1978.

Raymond, T. M. and Pandis, S. N.: Cloud activation of singlecomponent organic aerosol particles, *J. Geophys. Res.*, 107, 4787, 2002.

Riipinen, I., Rastak, N., and Pandis, S. N.: Connecting the solubility and CCN activation of complex organic aerosols: a theoretical study using solubility distributions, *Atmos. Chem. Phys.*, 15, 6305–6322, 2015.

Roberts, G. C., and Nenes, A.: A continuous-flow streamwise thermal-gradient CCN chamber for atmospheric measurements, *Aerosol Sci. Technol.*, 39, 206–221, 2005.

Rogge W. F., Hildemann L. M., Mazurek M. A., Cass, G. R., Simoneit B. R. T: Sources of fine organic aerosol. 1. Charbroilers and meat cooking operations, *Environ. Sci. Technol.*, 1991, 25, 1112–1125, 1991.

Rose, D., Gunthe, S. S., Mikhailov, E., Frank, G. P., Dusek, U., Andreae, M. O., and Pöschl, U.: Calibration and measurement uncertainties of a continuous-flow cloud condensation nuclei counter (DMT-CCNC): CCN activation of ammonium sulfate and sodium chloride aerosol particles in theory and experiment, *Atmos. Chem. Phys.*, 8, 1153–1179, 2008.

Rosenfeld, D., Lohmann, U., Raga, G. B., O'Dowd, C. D., Kulmala, M., Fuzzi, S., Reissell, A., and Andreae, M. O.: Flood or drought: How do aerosols affect precipitation?, *Science*, 321, 1309–1313, 2008.

Saxena, P., Hildemann, L. M., McMurry, P. H., and Seinfeld, J. H.: Organics alter hygroscopic behavior of atmospheric particles, *J. Geophys. Res.*, 100, 18755–18770, 1995.

Schauer, C., Rogge, W. F., Hildemann, L. M., Mazurek, M. A., and Cass, G. R.: Source apportionment of airborne particulate matter using organic compounds as tracers, *Atmos. Environ.*, 30, 3837–3855, 1996.

Schauer, J. J., and Cass, G. R.: Source apportionment of wintertime gas-phase and particle-phase air pollutants using organic compounds as tracers, *Environ. Sci. Technol.*, 34, 1821–1832, 2000.



Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources. 1. C1 through C29 organic compounds from meat charbroiling, *Environ. Sci. Technol.*, 33, 1566–1577, 1999.

Schauer, J. J., Kleeman, M. J., Cass, G. R., and Simoneit, B. R. T.: Measurement of emissions from air pollution sources, 4. C-1– C-27 organic compounds from cooking with seed oils, *Environ. Sci. Technol.*, 36, 567–575, 2002.

Seinfeld J. H., and Pandis S. N. (2006): *Atmospheric Chemistry and Physics: From Air Pollution to Climate Change*, 2nd edition, J. Wiley, New York.

Sloane, C.S., Watson, J.G., Chow, J.C., Pritchett, L.C., and L.W. Richards: Size-segregated fine particle measurements by chemical species and their impact on visibility impairment in Denver, *Atmos. Environ.*, 25A, 1013-1024, 1991.

Svenningsson, B., Rissler, J., Swietlicki, E., Mircea, M., Bilde, M., Facchini, M. C., Decesari, S., Fuzzi, S., Zhou, J., Mønster, J., and Rosenørn, T.: Hygroscopic growth and critical supersaturations for mixed aerosol particles of inorganic and organic compounds of atmospheric relevance, *Atmos. Chem. Phys.*, 6, 1937–1952, 2006.

Twomey, S.: The influence of pollution on the shortwave albedo of clouds, *J. Atmos. Sci.*, 34, 1149–1152, 1977.

Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.: Interpretation of organic components from positive matrix factorization of aerosol mass spectrometric data, *Atmos. Chem. Phys.*, 9, 2891–2918, 2009.

Varutbangkul, V., Brechtel, F. J., Bahreini, R., Ng, N. L., Keywood, Wolff, G. T, Ruthkosky, M. S., Stroup, D. P., Korsog, P. E.: A characterization of the principal PM-10 species in Claremont (summer) and Long Beach (fall) during SCAQS, *Atmos. Environ.*, 10, 2173-2186, 1991.

Willis, M. D., Lee, A. K. Y., Onasch, T. B., Fortner, E. C., Williams, L. R., Lambe, A. T., Worsnop, D. R., and Abbatt, J. P. D.: Collection efficiency of the soot-particle aerosol mass spectrometer (SP-AMS) for internally mixed particulate black carbon, *Atmos. Meas. Tech.*, 7, 4507–4516, 2014.

Zheng, M., Fang, M., Wang, F., and To, K. L.: Characterization of the solvent extractable organic compounds in PM<sub>2.5</sub> aerosols in Hong Kong, *Atmos. Environ.*, 34, 2691–2702, 2000.

## **Chapter 6**

### **Summary and suggestions for future work**

## 6.1 Summary

This thesis focuses on the formation and chemical aging of OA which is the most diverse and least understood component of submicron aerosols. Furthermore it explores the effects of the chemical aging of OA on different properties of the particles, such as their ability to absorb light and to act as CCN is quantified.

The formation of secondary organic aerosol from the reaction of  $\beta$ -caryophyllene with  $O_3$  and OH radicals and its chemical aging was examined. The SOA yield for the ozonolysis of  $\beta$ -caryophyllene was 27% at  $10 \mu\text{g m}^{-3}$  SOA. For the reaction of  $\beta$ -caryophyllene with OH at low  $\text{NO}_x$  the SOA yield was 20% at  $10 \mu\text{g m}^{-3}$  SOA and at high  $\text{NO}_x$  it was 38% at  $10 \mu\text{g m}^{-3}$  SOA. While the reactions under low  $\text{NO}_x$  conditions had similar SOA yields as the ozonolysis reactions, the presence of high  $\text{NO}_x$  levels leads to the production of less volatile compounds and higher yields. The magnitude of the vapor wall losses to the Teflon walls was estimated to be up to approximately 35% of the formed SOA. The average density of the SOA formed in the ozonolysis experiments was  $0.99 \pm 0.05 \mu\text{g m}^{-3}$ . The average O:C ratio of the SOA produced was  $0.31 \pm 0.04$  and the H:C ratio was  $1.5 \pm 0.03$ . Similarly, the parameters of the SOA formed from the reaction of  $\beta$ -caryophyllene with OH at low  $\text{NO}_x$  were  $\rho = 1.05 \pm 0.04 \mu\text{g m}^{-3}$ ,  $\text{O:C} = 0.24 \pm 0.02$ ,  $\text{H:C} = 1.52 \pm 0.03$  and at high  $\text{NO}_x$   $\rho = 1.19 \pm 0.1 \mu\text{g m}^{-3}$ ,  $\text{O:C} = 0.34 \pm 0.07$  and the  $\text{H:C} = 1.5 \pm 0.07$ . The exposure of the  $\beta$ -caryophyllene SOA to UV light and to hydroxyl radicals under low  $\text{NO}_x$  conditions had little or no effect on the SOA levels. The exposure of the  $\beta$ -caryophyllene SOA to OH radicals, under high  $\text{NO}_x$  conditions, led to 13-17% increase of SOA mass concentration at dry conditions, and the O:C increased by 0.04 to 0.06 units. High relative humidity (50% and 90%) did not appear to affect the fresh SOA production and its AMS spectrum. On the contrary,

the high RH conditions enhanced the chemical aging of the  $\beta$ -caryophyllene SOA by 40% and the O:C increased by 0.07 units.

In the next phase of the work, commercial BC instruments that are used widely for atmospheric measurements were compared in relatively well constrained yet complex laboratory environment using biomass burning emissions. A CE of 0.35 was estimated for the SP-AMS rBC mass by using the beam-width probe analysis. The corrected SP-AMS and SP2 rBC measurements agreed within 6% suggesting that the CE of the SP-AMS for the BC measurements was affected mainly by the shape of the particles. The eBC measurements by the optical instruments were compared with the corrected rBC measurements by the SP-AMS during high and low OA/rBC conditions. For the high OA/rBC experiments the ratio of eBC to rBC was higher (ranging from 1.46 to 2.34) than for the experiments in which OA/rBC was low (ranging from 0.8 to 0.93). The presence of high OA concentrations in the system can lead to an overestimation of the eBC by a factor of 2 or more. New MAC values were calculated for the two OA/rBC regimes for all optical instruments. At high OA/rBC ratios the MAC values were higher ( $\text{MAC}=9\text{--}23.9 \text{ m}^2 \text{ g}^{-1}$ ) than at low OA/rBC ( $\text{MAC}=4.4\text{--}8.1 \text{ m}^2 \text{ g}^{-1}$ ). The OA/rBC ratio has a significant effect in the measurements of the optical instruments, due to mainly the increase of the thickness of the OA coating of the BC core. For the low OA/rBC regime the measurements of eBC of the optical instruments were more consistent (slope ranging from 0.85 to 0.98) than for the high OA/rBC conditions (slope ranging from 0.74 to 1.58). For low OA/rBC the aethalometer gave the highest measurements and the blue PAX the lowest measurements of eBC, while for high OA/rBC the blue PAX gave the highest measurements and the MAAP the lowest measurements of eBC.

The changes that occur in the absorption of light by BC-containing particles as their non-refractory coating increases were investigated. Initially, we studied the chemical aging of the emissions from the burning of longleaf pine wood and white birch bark. The chemical aging resulted in the increase of the mass concentration and the O:C of the organic aerosol. At the same time the aerosol absorption was enhanced. For the pine wood experiments the absorption increased by as much as a factor of 1.9. For the white birch bark experiments the  $E_{\text{Abs}}$  was less than 1.05. For both types of experiments the  $E_{\text{Abs}}$  was higher after the chemical aging of the emissions with OH radicals. The calculated AAE from the aethalometer suggests that there was no brown carbon in both systems. In the second part of the study we coated the white birch bark emissions with aromatic SOA. These experiments suggested that the absorption activity of the BC core was mainly affected by the changes of the organic aerosol mass and not by the changes of the chemical composition of the organic shell. To confirm the core-shell morphology of the aging particles and the particles of the aromatic SOA-soot system we used Mie theory assuming spherical particles and a non-absorbing coating. The measurements were consistent with the corresponding Mie theory predictions.

Finally, the effect of the chemical aging of cooking OA on its composition and CCN activity was studied using emissions that were produced by grilling beef burgers with high fat content. The COA particles according to the SEM pictures may have not been spherical. OA was the dominant component of the fresh grilling particulate emissions with rBC being 1-6% of the aerosol and the contribution of other species being negligible. There were only small differences among the AMS fresh COA spectra in the experiments performed. The corresponding  $\theta$  angles among the vectors corresponding to the spectra ranged from  $4^\circ$  to  $13^\circ$ . When the emissions were exposed to UV, 9-56 ppb of ozone were generated and the OA/rBC increased by 1% to 17%.

When the COA was exposed to high concentrations of ozone (180-275 ppb) the OA/rBC increased by 6% to 26%. The O:C increased by 30% to 55% during the aging. In all experiments the aged COA composition was similar with the  $\theta$  angles ranging from  $2^\circ$  to  $8^\circ$ . PMF analysis was used to analyze the evolution of the chemical composition of the COA during the aging process. In all the experiments, 1 hr after the chemical aging, the “aged” COA factor was 70-90% of the total COA. The “aged” COA factor chemical composition was similar in the five experiments and did not depend on the chemical aging method. The CCN activity of the fresh and aged COA was studied at supersaturations 0.2% and 0.4%. At supersaturation 0.2% the fresh emissions were 12-23% CCN active, while at supersaturation 0.4% the activation percentage was 34-62%. Chemical aging led to an increase of the CCN active particles to 45-64% at supersaturation 0.2%, and to 77-88% at supersaturation 0.4%. Five hours after the chemical aging the activation diameter decreased by 15-37% for supersaturation 0.2%. For supersaturation 0.4% the activation diameter decreased by 25-37%. The smallest decrease of the activation diameter occurred when there was the smallest OA production and vice versa.

## 6.2 Suggestions for future work

Despite the progress achieved in this work regarding the formation and chemical aging of atmospheric OA, there are still many questions that need to be answered.

In this thesis we studied the chemical aging of biomass burning organic aerosol using ozone and OH radicals. There is a need to study the reaction of the corresponding emissions with the  $\text{NO}_3$  radical, which is the main atmospheric oxidant during the nighttime. These experiments will help us quantify the chemical aging of biomass burning that happens in the atmosphere during the night, which is the prime time that wood combustion is used for residential heating.

The chemical aging of COA was studied for the first time in this work. Even though we proved that the fresh and aged COA have the same mass spectra using an SP-AMS, a more in depth analysis has to be done to explore the chemical composition of the COA. Further analysis of the chemical composition of the fresh and aged COA using other mass spectrometry techniques, like high pressure liquid chromatography-mass spectrometry (HPLC-MS) would be helpful. Furthermore, experiments that measure the volatility and the water solubility of the COA must be conducted. This work will help us understand the connection between the oxidation state, the volatility, the solubility and the hygroscopicity of the OA.

The inter-comparison of BC-related instruments presented in this thesis will be a valuable tool for future studies. Even though we addressed how the measurements of the optical instruments are being affected by the changes of the concentration of the OA, there are still some parameters that need to be investigated. The effects of changes of ambient relative humidity have not been investigated in depth yet.



# Appendix

## A.1 An inter-comparison of black carbon related instruments in a laboratory study of biomass burning aerosol

**Table A.1.1:** Initial mode diameters of the biomass burning particles

| <b>Exp.</b> | <b><math>D_{m,number}^a</math></b><br>(nm) | <b><math>D_{me,rBC}^b</math></b><br>(nm) | <b><math>D_{va,OA}^c</math></b><br>(nm) | <b><math>D_{va,rBC}^d</math></b><br>(nm) |
|-------------|--------------------------------------------|------------------------------------------|-----------------------------------------|------------------------------------------|
| 1           | 178                                        | 235                                      | 123                                     | 149                                      |
| 2           | 40                                         | 175                                      | 100                                     | 115                                      |
| 3           | 163                                        | 245                                      | 149                                     | 140                                      |
| 4           | 129                                        | 180                                      | 108                                     | 123                                      |
| 5           | 60                                         | 200                                      | 132                                     | 149                                      |
| 6           | 187                                        | -                                        | 299                                     | 299                                      |
| 7           | 203                                        | -                                        | 78                                      | 78                                       |
| 8           | 211                                        | -                                        | 154                                     | 136                                      |
| 9           | 220                                        | -                                        | 118                                     | 118                                      |
| 10          | -                                          | -                                        | 192                                     | 205                                      |
| 11          | -                                          | -                                        | 157                                     | 192                                      |
| 12          | -                                          | -                                        | 157                                     | 157                                      |

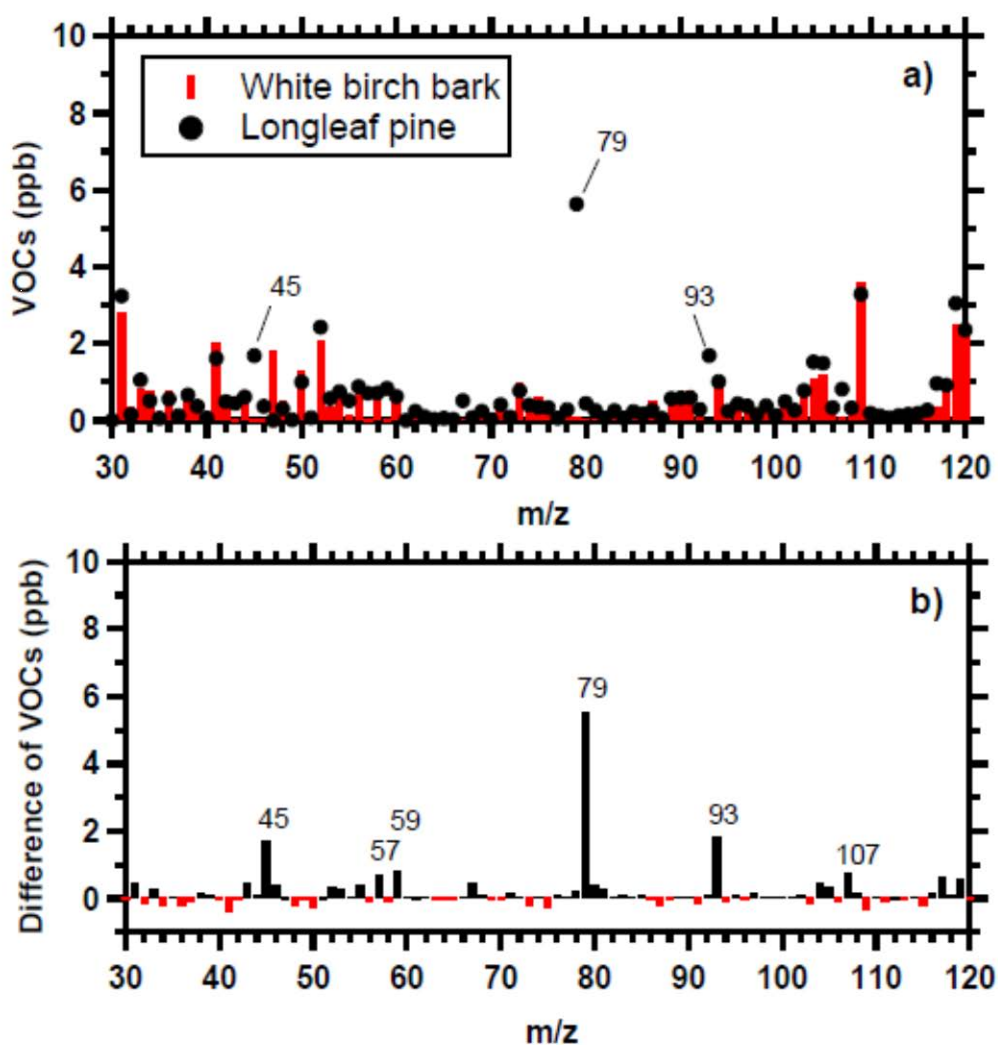
<sup>a</sup> Number mode diameter (SMPS)

<sup>b</sup> BC mass equivalent mode diameter (SP2)

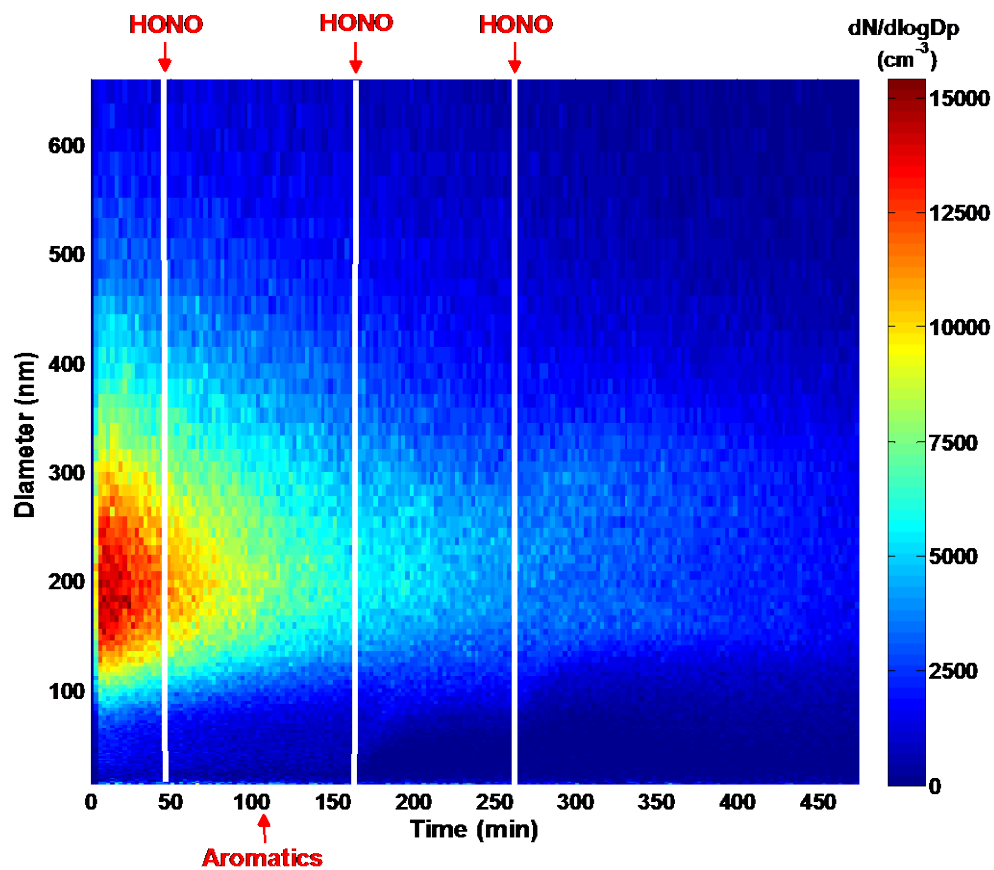
<sup>c</sup> OA vacuum aerodynamic mode diameter (SP-AMS)

<sup>d</sup> Refractory BC vacuum aerodynamic diameter (SP-AMS)

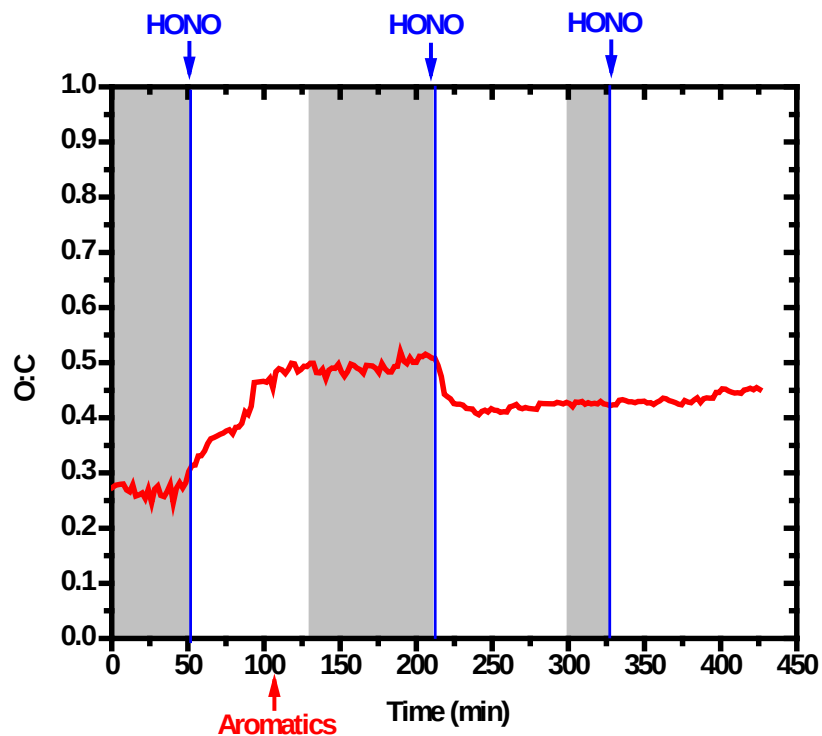
## A.2 Absorption of chemically aged biomass burning carbonaceous aerosol



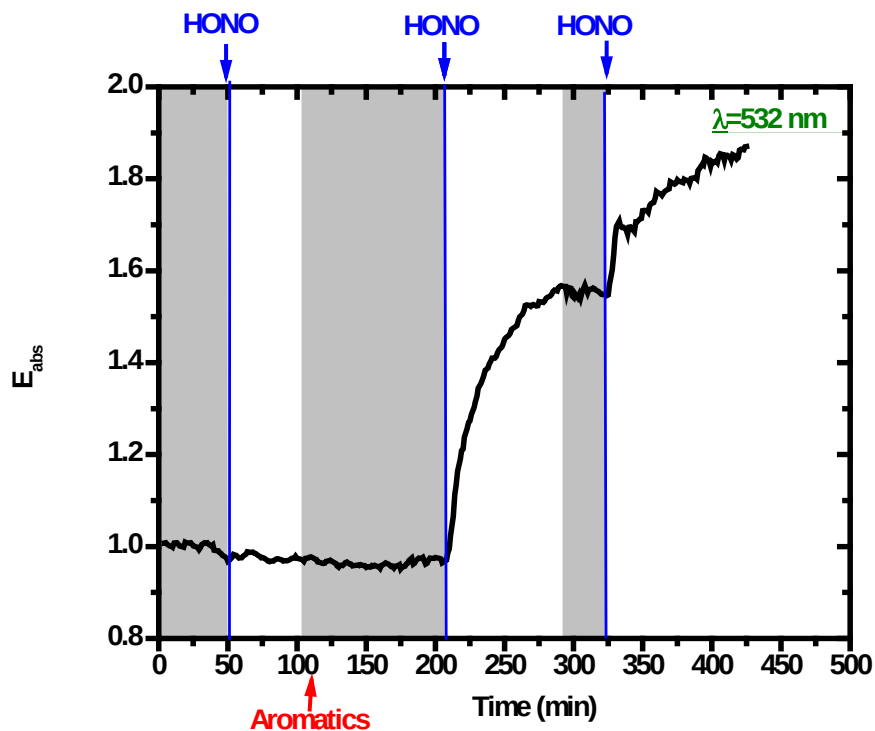
**Figure A.2.1:** a) The concentration of the VOCs of the pine wood emissions and the white birch bark emission. b) The difference of the VOCs concentration between the emissions from the burning of the two fuels. The emissions from the pine wood have higher organic vapor concentrations with the highest peak at  $m/z$  79 (benzene).



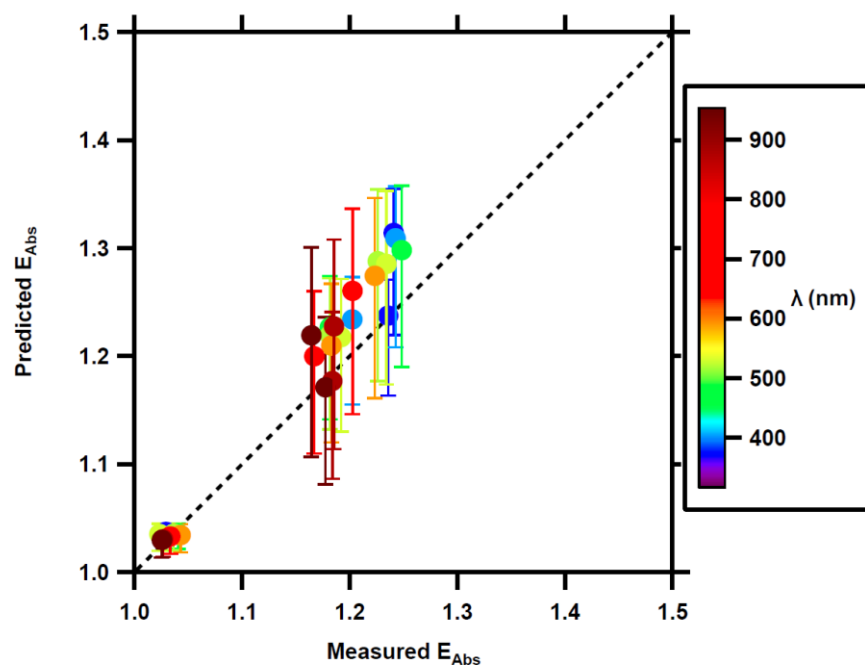
**Figure A.2.2:** The aerosol number size distributions as a function of time for Experiment 11. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber.



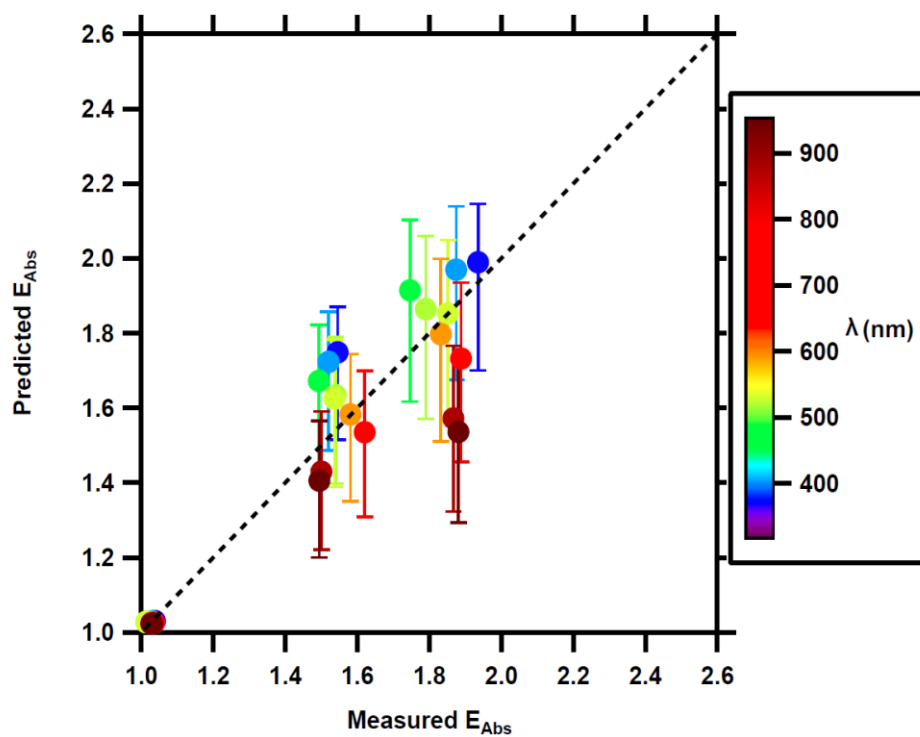
**Figure A.2.3:** The oxygen over carbon (O:C) ratio of the organic aerosol as a function of time for Experiment 15. The shaded parts indicate the periods when the UV light was off and the white ones the periods when the UV light was on. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber.



**Figure A.2.4:** The absorption enhancement of the black carbon as a function of time for Experiment 15. The shaded regions indicate the periods during which the chamber was dark. Also shown, the times when the aromatic VOCs and HONO were injected in the chamber.



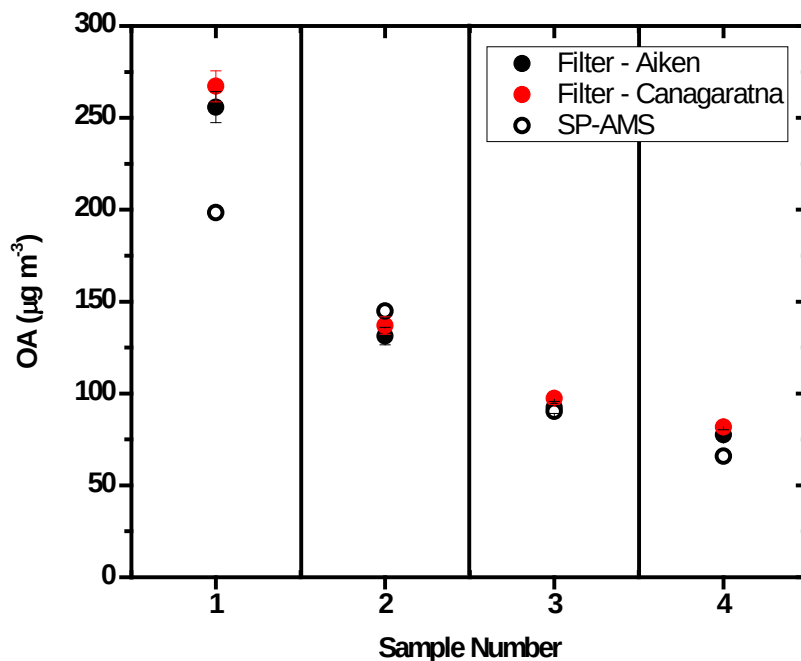
**Figure A.2.5:** Predicted (Mie theory) and observed absorption enhancement,  $E_{Abs}$ , for all three periods of Experiment 12.



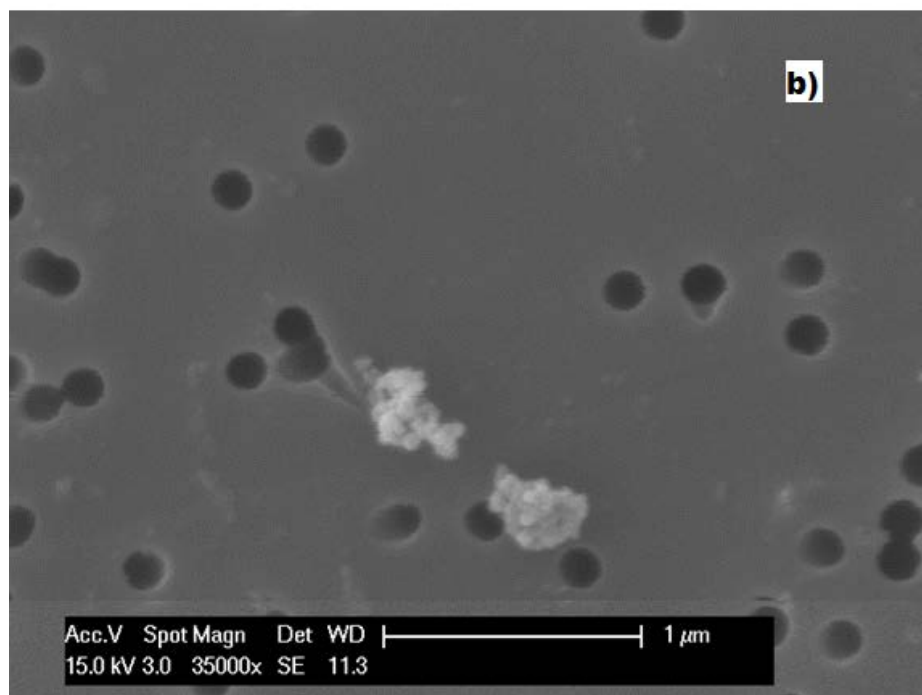
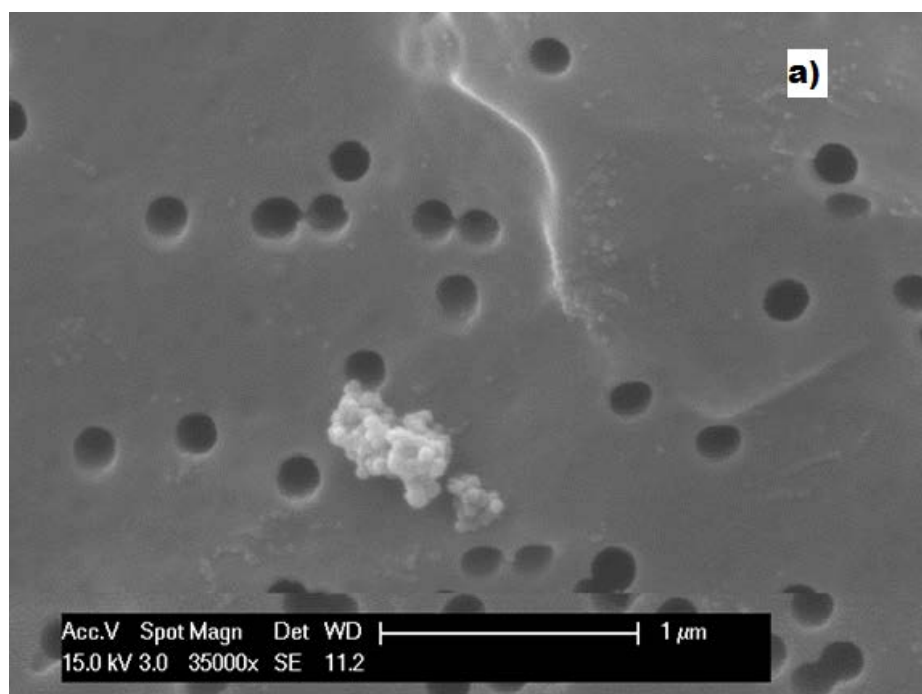
**Figure A.2.6:** Predicted (Mie theory) and observed absorption enhancement,  $E_{Abs}$ , for all three periods of Experiment 13.



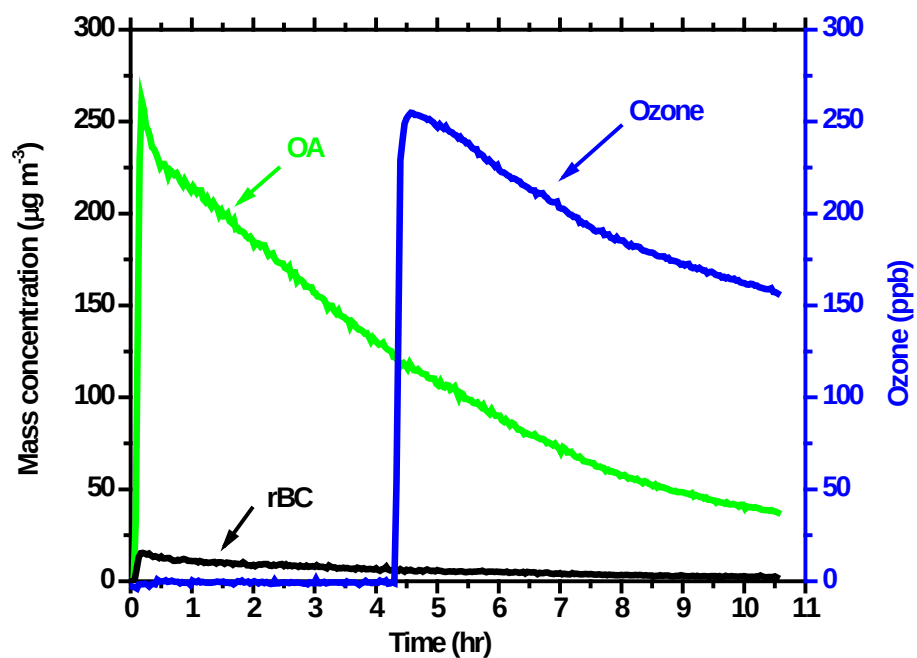
### A.3 Chemical composition and CCN activity of fresh and chemically-aged cooking organic aerosol



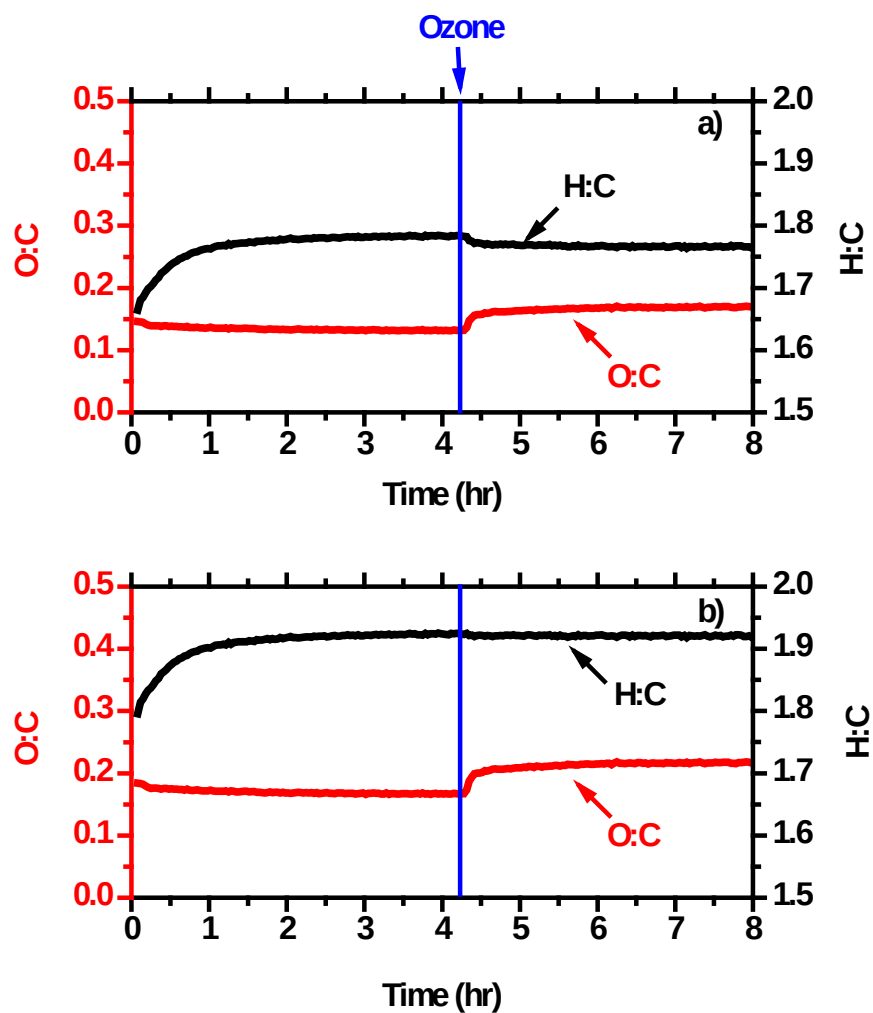
**Figure A.3.1:** Comparison of the OA concentration measured using filters (with the OM:OC calculated according to the Aiken et al. (2008) and Canagaratna et al. (2015) algorithms) and the online measurement of the SP-AMS for Experiment 5.



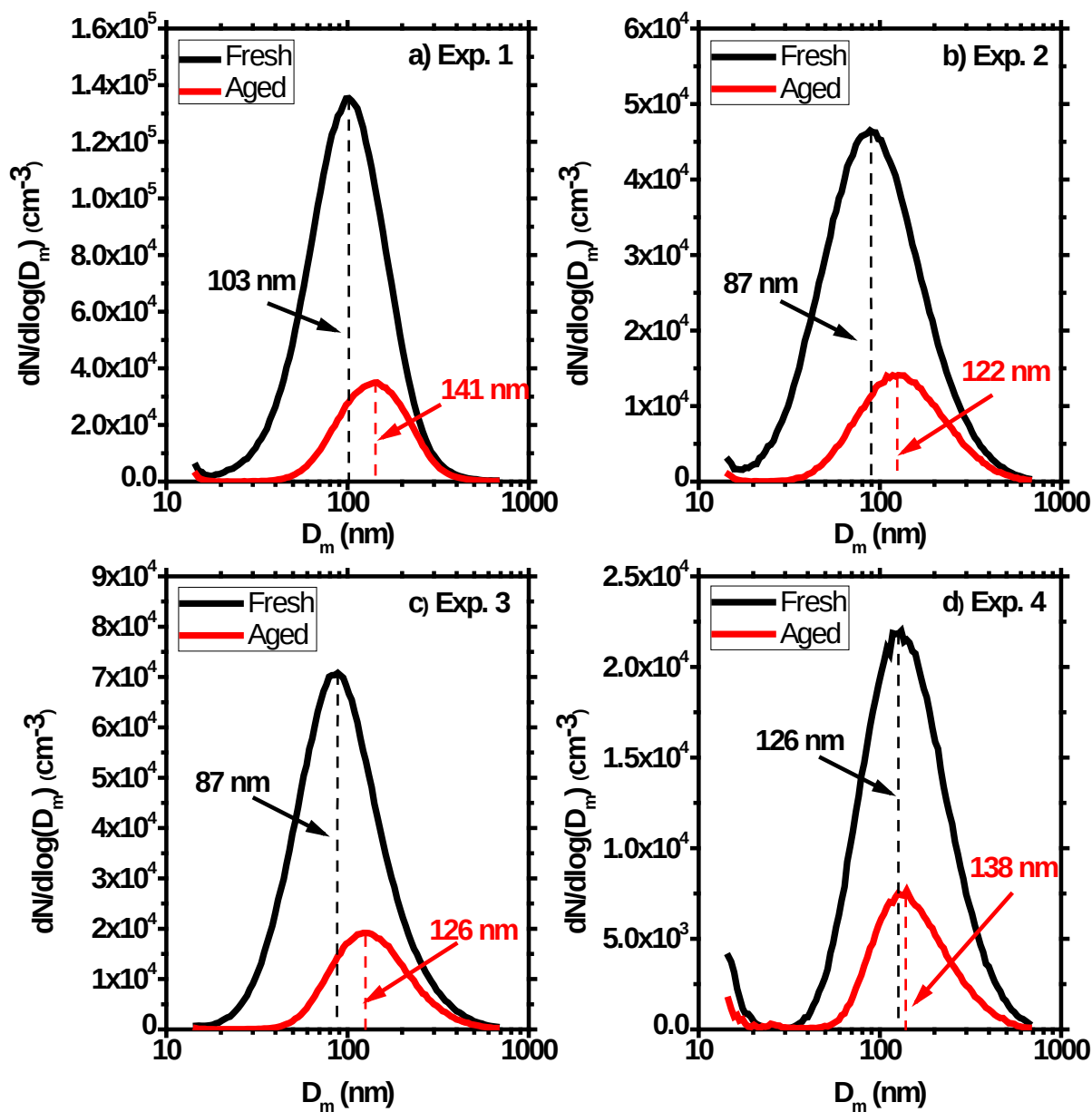
**Figure A.3.2:** SEM photographs of COA collected during Experiment 5.



**Figure A.3.3:** Measured organic aerosol and black carbon, and ozone concentrations for Experiment 5.



**Figure A.3.4:** The timeseries of the elemental ratios of COA for Experiment 5 calculated using the: a) Aiken et al. (2008) and b) Canagaratna et al. (2015) methods. The red line represents the oxygen over carbon ratio and the black the hydrogen over carbon ratio of the COA. Also shown the time of ozone injection in the chamber.



**Figure A.3.5:** Number size distributions of the fresh and aged (after 5 hrs of aging) cooking organic aerosol for Experiments 1-4. Also shown the mode diameters of the distributions.