Title
Oxidized organic functional groups in aerosol particles from forest emissions measured at mid-mountain and high- elevation mountain sites in Whistler, BC

Permalink
https://escholarship.org/uc/item/5bv877tc

Author
Schwartz, Rachel E.

Publication Date
2010

Peer reviewed|Thesis/dissertation

UNIVERSITY OF CALIFORNIA, SAN DIEGO

Oxidized Organic Functional Groups in Aerosol Particles from Forest Emissions
Measured at Mid-Mountain and High-Elevation Mountain Sites in Whistler, BC

A thesis submitted in partial satisfaction of the requirements for the degree
Master of Science

in

Earth Sciences

by

Rachel E. Schwartz

Committee in charge:

Lynn M. Russell, Chair
Dan Lubin
Guang Zhang

2010

The Thesis of Rachel E. Schwartz is approved, and it is acceptable in quality and form
for publication on microfilm and electronically:

_____

_____

_____
Chair

University of California, San Diego

2010

TABLE OF CONTENTS

LIST OF ABBREVIATIONS

AMS	Aerosol Mass Spectrometer
BB	Biomass Burning
BC	Black Carbon
BVOC	Biogenic Volatile Organic Compound
FTIR	Fourier Transform Infrared
HR-ToF-AMS	High-Resolution Time-of-Flight Aerosol Mass Spectrometry
IPCC	Intergovernmental Panel on Climate Change
MASL	Meters Above Sea Level
MVK/MACR	Methyl-Vinylketone / Methacrolein
OFG	Organic Functional Group
OM	Organic Mass
PMF	Positive Matrix Factorization
POA	Primary Organic Aerosol
PSCF	Potential Sources Contribution Functions
PTR-MS	Proton Transfer Reaction Mass Spectrometry
SOA	Secondary Organic Aerosol
SP2	Single Particle Soot Photometer
STXM-NEXAFS	Scanning Transmission X-Ray Microscopy with Near-Edge Absorption Fine Structure
VOC	Volatile Organic Compound
XRF	X-ray Fluorescence

LIST OF FIGURES

LIST OF TABLES

ACKNOWLEDGEMENTS

ABSTRACT OF THE THESIS

Oxidized Organic Functional Groups in Aerosol Particles from Forest Emissions
Measured at Mid-Mountain and High-Elevation Mountain Sites in Whistler, BC

by

Rachel E. Schwartz

Master of Science in Earth Sciences

University of California, San Diego, 2010

Professor Lynn M. Russell, Chair

Aerosols contribute to the largest uncertainty in climate prediction (IPCC, 2007) from both direct and indirect radiative forcing; these effects are influenced by particle size and chemistry. Although organic compounds constitute a large part of aerosols, this fraction is poorly characterized. In an effort to address the complexity of organic aerosols, aerosol particles were collected in Whistler, British Columbia, at a mid-mountain site in spring 2008 and a peak site in spring and summer 2009. The organic functional group composition of the collected aerosol was measured by Fourier transform infrared (FTIR) spectroscopy. At the mid-mountain site the organic mass (OM) project mean was $1.3 \pm 1.0\ \mu g\ m^{-3}$. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 34%, 33%, and 23% of OM,

respectively. Positive matrix factorization (PMF) analysis, which was employed with complementary elemental characterization, attributed 65% of the campaign OM to biogenic sources. The functional group composition of the biogenic factor was similar to that of secondary organic aerosol (SOA) reported from the oxidation of biogenic volatile organic compounds (BVOCs) in laboratory chamber studies, providing evidence that the magnitude and chemical composition of biogenic SOA simulated in the laboratory is similar to that found in actual atmospheric conditions. At the mountain peak site the OM project mean for all samples was 3.2 ± 3.3 μg m^{-3} and reached a maximum of 13.6 μg m^{-3} during severe wildfires. Both burning and non-burning forest emissions contributed to the significant ketone groups measured.

Chapter 1

Introduction

Aerosols are a complex constituent of the atmosphere resulting from a combination of natural and anthropogenic processes. Aerosol particles can adversely affect human health and drive many key aspects of the atmospheric and climate systems, such as cloud formation. The regulation of anthropogenic atmospheric aerosols is essential to curb unwanted effects on society. Such regulation is most effective when the system and processes are well understood; yet aerosols contribute to the largest uncertainty in climate prediction and the mechanisms that lead to adverse health effects from aerosols have not been resolved (IPCC, 2007; Pöschl, 2005). These uncertainties mandate further research to ensure responsible regulation.

Organic compounds compose up to 90% of the fine particle aerosol mass. Despite its importance, the organic fraction of the aerosol is poorly characterized (Lim and Turpin, 2002; Fuzzi et al., 2006). Recently, there has been intense interest in the characterization of the organic aerosol fraction (Kanakidou et al., 2005; Fuzzi et al., 2006; DeGouw and Jimenez, 2009). Organic aerosol particles enter the atmosphere through direct emission from a source or secondary formation in the atmosphere from gaseous precursors, volatile organic compounds (VOCs). Such aerosols are classified as primary organic aerosol (POA) and secondary organic aerosols (SOA), respectively.

Particle sources are wide ranging and include both anthropogenic and natural sources. Anthropogenic sources include industry, vehicular, ships, fossil fuel

combustion, and biomass burning (BB). Natural sources include biogenic (from the biosphere), marine (sea spray), and dust. SOA formation and sources are currently not well understood which hinders regulation efforts (DeGouw and Jimenez, 2009). Often, the line between anthropogenic and natural sources becomes blurred. For example, as land usage increases desertification, dust particulate matter will increase, or BB aerosol increases as natural forest fires grow larger than usual due to forest practices. The spatial scale of a given source may be local or near global. Asian dust transported to North America is an example of long range transport. Aerosol particles from these different sources result in aerosols with very different chemical composition. The aerosol chemistry then determines how these particles will interact in the environment, e.g. their lifetime, direct light scattering or absorbing properties, and ability to act as a cloud condensation nuclei. Aerosol chemistry occurs in a dynamic environment; aging of particles, often involving oxidation, occurs on multiple timescales. Figure 1 from Pöschl (2005) highlights the interdependencies between aerosol sources, composition, properties, transformations, and climate and health effects. In the atmosphere, the interactions of aerosol derived from varying sources are inevitable. Thus, separating and apportioning measured ambient aerosol to a source is a difficult task. Furthermore, we must not just identify and quantify aerosol sources, but also understand the complex interplay of the aerosols of different sources in the atmosphere if effective mitigation strategies for air pollution and climate are to be devised.

The contribution of a given aerosol source to the atmosphere is not static and

the feasibility of regulation is source dependent (i.e. it is easier to regulate some industries than the biosphere). Globally, biogenic VOC (BVOC) emissions may be 10 times greater than anthropogenic VOC emissions (Seinfeld and Pandis, 2006). SOA formation pathways from biogenic precursors, such as isoprene and terpenes, have been presented from smog chamber studies (Surratt et al., 2006; Clayes et. al., 2004; Carlton et al., 2009); yet which pathways are the most significant and relevant for atmospheric conditions remain unknown (Kanakidou et al., 2005). Lab studies can provide insight into common pathways and yields; but they often use unrealistically high concentrations to account for wall losses and other lab constraints such as time. By 2100, Tsigaridis and Kanakidou (2007) predict the global SOA burden will double, with the increase mostly due to SOA from BVOC oxidation. The authors contribute the main biogenic SOA change to oxidants and primary aerosol from human activities. Increased temperatures can raise the SOA from biogenic sources exponentially (Helmig et al., 2006). For a doubling of CO_2 (not accounting for increase in temperature), Kulmala et al. 2004 estimates a 10% increase in BVOC emissions. A change in emissions will non-linearly influence particle concentrations and the time scale of growth processes. Current uncertainties in biogenic SOA formation from BVOCs and the predicted changes in BVOC emissions, compound to make the study of biogenic SOA essential to any predictive modeling and regulation.

Forest fires present a complex issue for climate science and climate prediction. Large, uncontrollable fires are a worldwide phenomenon that often carries tremendous economical, environmental, and human costs. These fires are expected to increase

with climate change (IPCC, 2007). Fires account for a substantial amount of CO_2 emissions, half as much fossil fuel burning. While in general aerosols have a cooling effect on the planet, black carbon (BC) is a strong absorber and creates an opposite warming effect. In fact, BC may cause the second strongest warming effect only behind CO_2 (Ramanthan and Carmichael, 2008). About 40% of BC emissions are attributed to open BB (Ramanthan and Carmichael, 2008). Yet, since organic carbon is emitted simultaneously with BC in fires the net climatic forcing is uncertain. Bond et al. (2004) name BB as the largest (42%) combustion source of primary organic carbon ahead of fossil fuel (38%) and biofuel (20%) combustion.

The wealth of organic species makes predicting the organic contribution to aerosol properties difficult. Classifying organic composition by functional group is a useful approach to tackle this complexity since degree of oxidation and bond types relate to solubility. Organic functional group concentrations have been measured by Fourier Transform Infrared (FTIR) spectroscopy in locations across the world including urban (Houston, Mexico City), coastal (off Chile, Scripps Pier), Arctic (Barrow, Alaska; North Atlantic Ocean), and forested (Whistler, BC; Northeast US) sites (Russell et al., 2009a; Liu et al., 2009; Hawkins et al., 2010; Hawkins and Russell, 2010; Shaw et al., 2010; Russell et al., 2009b; Schwartz et al., 2010; Bahadur et al.. 2010). Unlike other techniques that focus on tracer identification (such as levoglucosan for BB) and quantification only, FTIR spectroscopy has been shown to measure close to 100% of organic mass (OM) (Maria et al., 2002, 2003; Russell, 2003; Gilardoni et al., 2007; Russell et al., 2009b). In addition, FTIR spectroscopy allows for

identification and quantification of carbonyl groups, a functional group of interest for biogenic and BB aerosols. Calogirou et al. (1999) in a review of terpene oxidation products (i.e. biogenic) note that FTIR spectroscopy is "particularly suited for detection of aldehydes, ketones [carbonyls]…".

Whistler Mountain, shown in Fig. 1.2, is located about 120 km from Vancouver, in the southern Pacific Ranges of the Coastal Mountains in British Columbia, Canada. Whistler Village sits at an elevation of 620 m above sea level (asl) and Whistler Peak reaches 2182 masl. According to the BC Ministry of Forests and Range, Whistler belongs to the Squamish Forest District of the Coast Forest Region. The region includes four biogeoclimatic ecosystem classification zones: Interior Douglas-fir Transitional Zone, Alpine Tundra Zone, Mountain Hemlock Zone, and Coastal Western Hemlock Zone. The dominant vegetation of each zone is unique; climate is the largest factor controlling the ecosystem zone (Meidinger and Pojar, 1991). Trees up to about 1850 masl line the valleys surrounding Whistler Mountain. In general, the forests are largely coniferous, dominated by fir and hemlock. Whistler Valley as seen from Whistler Peak in March 2009 is shown in Fig. 1.3. Forest fires are both natural and human influenced events in forested regions. Based on the 1997 – 2008 fire seasons, the BC Wildlife Management Branch reports an average of 1,848 fires per season in BC. In a given year about 57% of forest fires were caused by lightening, with the reaming fires attributed the humans activity. Whistler Peak is influenced by long range transported particles from Asia in the early-spring, by

biogenic aerosols in the late-spring and summer (Leaitch et al., 2009), and occasionally by biomass burning aerosols in summer.

In an effort to address the complexity of organic aerosol composition and, in particular, the impact of forest emissions on the global aerosol burden, aerosol particles were collected in Whistler, British Columbia, at a mid-mountain site in spring 2008 and a peak site in spring and summer 2009. The organic functional group composition of the collected aerosol was measured by FTIR spectroscopy. Whistler is an ideal location to study the influence of forest emissions on aerosol particles because of its natural surroundings and distance from large urban centers. In addition, other studies have used this location to study both local emissions and aged long range transported aerosol; Environment Canada carries out ongoing measurements at Whistler Peak, and the mountain terrain allows for multiple sampling sites varying in altitude. Sampling over two seasons and across multiple years allows us to examine the impact of a wide variety of conditions, including forest fires, on the resulting ambient organic particles.

In Chapter 2, the ambient measurements from the mid-mountain May to June 2008 study are discussed. A portion of the measured OM is attributed to biogenic sources based on correlations with biogenic gaseous precursors. The composition of the biogenic fraction is discussed and compared to the composition of biogenic organic aerosol from controlled laboratory chamber studies. In Chapter 3, the ambient measurements from the peak March to September 2009 study are discussed. In addition to non-burning biogenic sources similar to that observed in the mid-mountain

study, biomass burning is identified as a source of organic aerosol. During March and April the observed OM concentrations are significantly lower than during the following warmer months for which the forest emissions contribute a large fraction of the measured OM. A conclusion and summary of the proceeding chapters is presented in Chapter 4.

Figures

Aerosol Composition
- *particle number and mass concentration, size distribution, shape, structure, electric charge*
- *chemical composition (particle and gas phase)*

Aerosol Sources
- *primary emissions and secondary formation*
- *natural and anthropogenic*
- *air quality control and regulations*

Composition-Dependent Properties
- *chemical reactivity and biological activity*
- *hygroscopicity, CCN and IN activity*
- *optical properties*

Atmospheric Interactions & Transformation
- *physical and chemical*
- *gases and radiation*
- *clouds and precipitation*

Climate & Health Effects
- *energy budget, hydrological cycle, biosphere*
- *respiratory, cardiovascular, infectious, allergic diseases*

Figure 1.1: Interdependence and feedback between aerosol sources, composition, properties, interactions, and effects to society through climate and health are shown (Pöschl, 2005).
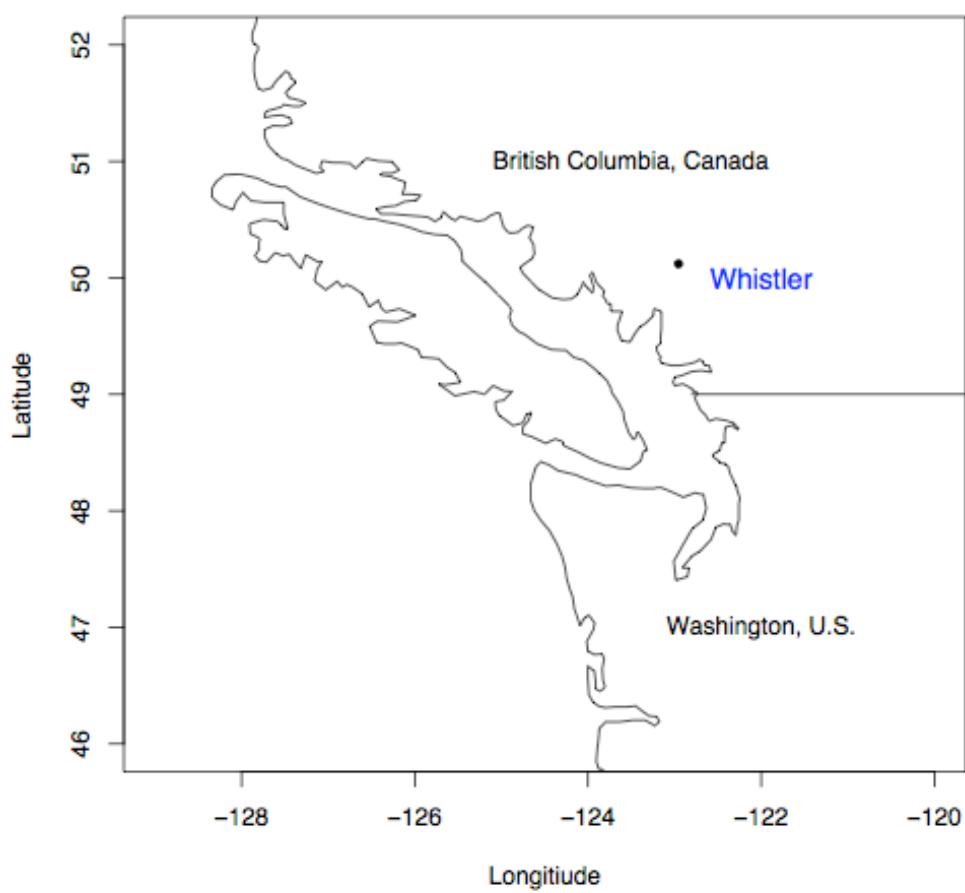
Figure 1.2: A map showing the location of Whistler, the sampling location for the mid-mountain and peak sampling projects.

Figure 1.3: View of Whistler Valley from the Whistler Peak sampling site from March 2009.

References

Bahadur, R., Uplinger, T., Russell, L.M., Sive, B.C., Cliff, S.S., Millet, D.B., Goldstein, A., and Bates, T.S.: Phenols in Northeastern US Submicron Aerosol Particles from Seawater Sources, Environ. Sci. Technol., in press, 2010.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research–Atmospheres 109 (D14), 14203–14203, 2004.

Calogirou, A., Larsen B. R., Kotzias, D.: Gas-phase terpene oxidation products: a review, Atmos. Environ., 33, 1423-1439, 1999.

Carlton, A. G., Wiedinmyer, C., Kroll, J. H.: A review of Secondary Organic Aerosol (SOA) formation from isoprene Atmos. Chem. Phys., 9, 4987-5005, 2009.

Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencser, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, Atmos. Environ., 38, 4093–4098, 2004.

DeGouw. J; Jimenez, J. L.: Organic Aerosols in the Earth's Atmosphere. Environ. Sci. Technol., 43, 20, 7614–7618, doi: 10.1021/es9006004, 2009.

Fuzzi, S., Andreae, M. O., Huebert, B. J., Kulmala, M., Bond, T. C., Boy, M., Doherty, S. J., Guenther, A., Kanakidou, M., Kawamura, K., Kerminen, V.-M., Lohmann, U., Russell, L. M., and Pöschl, U.: Critical assessment of the current state of scientific knowledge, terminology, and research needs concerning the role of organic aerosols in the atmosphere, climate, and global change, Atmos. Chem. Phys., 6, 2017–2038, 2006.

Gilardoni, S., Russell, L. M., Sorooshian, A., Flagan, R. C., Seinfeld, J. H., Bates, T. S., Quinn, P. K., Allan, J. D., Williams, B., Goldstein, A. H., Onasch, T. B., and Worsnop, D. R.: Regional variation of organic functional groups in aerosol particles on four US east coast platforms during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign, J. Geophys. Res.-Atmos., 112, D10S27, doi:10.1029/2006JD007737, 2007.

Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates T. S.: Carboxylic Acids, Sulfates, and Organosulfates in Processed Continental Organic Aerosol over the Southeast Pacific Ocean during VOCALS-REx 2008, Geophys. Res. Lett., in press, doi:10.1029/2009JD013276, 2010.

Hawkins, L. N. and Russell L. M.: Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires, in review, available for review at http://aerosols.ucsd.edu/publications.html), 2010.

Helmig, D, Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J. and Sakulyanontvittaya, T.: Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US Atmospheric Environment, 40, 22, 4150-4157, 2006.

IPCC: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.

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., Putaud, J. 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.

Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, U., Aalto, P., Keronen, P., Hakola, H., Bäck, J., Hoffmann, T., Vesala, T., and Hari, P.: A new feedback mechanism linking forests, aerosols, and climate, Atmos. Chem. Phys., 4, 557–562, 2004.

Leaitch, W. R, Macdonald, A. M., Anlauf, K. G., Liu, P. S. K., Toom-Sauntry, D., Li, S.-M., Liggio, J., Hayden, K., Wasey, M. A., Russell, L. M., Takahama, S., Liu, S., van Donkelaar, A., Duck, T., Martin, R. V., Zhang, Q., Sun, Y., McKendry, I., Shantz, N. C., and Cubison, M.: Evidence for Asian dust effects from aerosol plume measurements during INTEX-B 2006 near Whistler, BC, Atmos. Chem. Phys., 9, 3523-3546, 2009.

Lim H., Turpin B.J.: Origins of Primary and Secondary Organic Aerosol in Atlanta: Results of Time-Resolved Measurements during the Atlanta Supersite Experiment, Environ. Sci. Technol., 36, 21, 4489–4496, 2002.

Liu, S., Takahama, S., Russell, L. M., Gilardoni, S., and Baumgardner, D.: Cluster and Positive Matrix Factorization Analysis of Organic Functional Groups in Fine Particles During the MILAGRO 2006 Campaign, Atmos. Chem. Phys., 9, 6849-6863, 2009.

Maria, S. F., Russell, L. M., Turpin, B. J., and Porcja, R. J.: FTIR measurements of

functional groups and organic mass in aerosol samples over the Caribbean, Atmos. Environ., 36(33), 5185–5196, 2002.

Maria, S. F., Russell, L. M., Turpin, B. J., Porcja, R. J., Campos, T. L., Weber, R. J., Huebert, B. J.: Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types. Journal of Geophysical Research–Atmospheres 108, 8637, 2003.

Meidinger, D. and Pojar, J.: Ecosystems of British Columbia, BC Research Branch, Ecosystems, Special Report Series, 1991.

Pöschl, U.: Atmospheric Aerosols : Composition, Transformation, Climate and Health Effects. Angew. Chem. Int. Ed., 44, 7520 – 7540, 2005, doi: 10.1002/anie.200501122.

Ramanthan V. and Carmichael G.: Global and regional climate changes due to black carbon, Nature Geoscience 1, 221 – 227, 2008.

Russell, L. M.: Aerosol organic-mass-to-organic-carbon ratio measurements, Environmental Science & Technology, 37 (13), 2982–2987, 2003.

Russell, L. M., Bahadur, R., Hawkins, L. N., Allan, J., Baumgardner, D., Quinn, P. K., and Bates, T. S.: Oxygenated Fraction and Mass of Organic Aerosol from Direct Emission and Atmospheric Processing Collected on the R/V Ronald Brown during TEXAQS/GoMACCS 2006. Atmos. Environ., 43, 6100-6105, doi10.1016/j.atmosenv.2009.09.036, 2009a.

Russell, L. M., Bahadur, R., Hawkins, L. N., Allan, J., Baumgardner, D., Quinn, P. K., and Bates, T. S.: Organic Aerosol Characterization by Complementary Measurements of Chemical Bonds and Molecular Fragments, Atmos. Environ., 43, 6100-6105, doi10.1016/j.atmosenv.2009.09.036, 2009b.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates T. S., Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proc. Nat. Acad. Sci. U.S.A., in press, 2010.

Schwartz, R. E., Russell, L. M., Sjostedt, S. J., Vlasenko, A., Slowik, J. G., Abbatt, J. P. D., Macdonald, A.M., Li, S-M., Liggio, J., Toom-Sauntry, D., and Leaitch, W. R.: Biogenic Oxidized Organic Functional Groups in Aerosol Particles from a Mountain Forest Site and their Similarities to Laboratory Chamber Products, Atmos. Chem. Phys. Discuss., 10, 1–34, 2010.

Seinfeld, J. H., and Pandis, S. N., Atmospheric Chemistry and Physics Second Edition, Wiley-Interscience, New York, NY, USA, 43–46, 2006.

Shaw, P. M., Russell, L. M., Jefferson, A. and Quinn, P. K.: Arctic Organic Aerosol Measurements show Particles from Mixed Combustion in Spring Haze and from Frost Flowers in Winter, submitted, available for review at http://aerosols.ucsd.edu/publications.html), 2010.

Surratt. J.D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical Composition of Secondary Organic Aerosol Formed from the Photooxidation of Isoprene, J. Phys. Chem. A, 110, 9665-9690, DOI:10.1021/jp061734m, 2006.

Tsigaridis, K. and Kanakidou, M.: Secondary organic aerosol importance in the future atmosphere. Atmos. Environ. 41, 4682–4692, doi:10.1016/j.atmosenv.2007.03.045, 2007.

Chapter 2

Biogenic Oxidized Organic Functional Groups in Aerosol Particles from a Mountain Forest Site and their Similarities to Laboratory Chamber Products

2.1 Abstract

Submicron particles collected at Whistler, British Columbia, at 1020 masl during May and June 2008 on Teflon filters were measured by Fourier transform infrared (FTIR) and X-ray fluorescence (XRF) techniques for organic functional groups (OFG) and elemental composition. Organic mass (OM) ranged from less than 0.5 to 3.1 μg m^{-3}, with a project mean and standard deviation of 1.3 ± 1.0 μg m^{-3} and 0.21 ± 0.16 μg m^{-3} for OM and sulfate, respectively. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 34%, 33%, and 23% of OM, respectively. Ketone, amine and organosulfate groups constituted 6%, 5%, and < 1% of the average organic aerosol composition, respectively. Measurements of volatile organic compounds (VOC), including isoprene and monoterpenes from biogenic VOC (BVOC) emissions and their oxidation products (methyl-vinylketone / methacrolein, MVK/MACR), were made using co-located proton transfer reaction mass spectrometry (PTR-MS). We present chemically-specific evidence of OFG associated with BVOC emissions. Positive matrix factorization (PMF) analysis attributed 65% of the campaign OM to biogenic sources, based on the correlations of one factor to monoterpenes and MVK/MACR. The remaining fraction was attributed to anthropogenic sources based on a correlation to sulfate. The functional group composition of the biogenic factor (consisting of 32% alkane, 25% carboxylic acid,

21% organic hydroxyl, 16% ketone, and 6% amine groups) was similar to that of secondary organic aerosol (SOA) reported from the oxidation of BVOCs in laboratory chamber studies, providing evidence that the magnitude and chemical composition of biogenic SOA simulated in the laboratory is similar to that found in actual atmospheric conditions. The biogenic factor OM is also correlated to dust elements, indicating that dust may act as a non-acidic SOA sink. This role is supported by the organic functional group composition and morphology of single particles, which were analyzed by scanning transmission X-ray microscopy near edge X-ray absorption fine structure (STXM-NEXAFS).

2.2 Introduction

There is strong evidence that biogenic volatile organic compounds (BVOC) produce a large fraction of secondary organic aerosol (SOA). Globally, BVOC emissions may be 10 times greater than anthropogenic VOC emissions (Seinfeld and Pandis, 2006). Oxidation of BVOC yields a large biogenic contribution to SOA, with estimates ranging from 12 to 70 Tg/yr (Hallquist et al., 2009). There are many uncertainties in the estimates of SOA from BVOC, including the BVOC emissions, reaction yields, and oxidant levels (Simpson et al., 2007). Models predict that by 2100 the global SOA burden will double, as a result of increased biogenic SOA as well as human activities (Tsigaridis and Kanakidou, 2007). The influence of biogenic sources on global SOA is large and is also expected to increase with predicted changes in temperature, vegetation, and CO_2 levels (Tsigaridis and Kanakidou, 2007). On average

60 ± 10% of organic carbon (OC) in Europe during the summer has been attributed to biogenic sources, and it is suggested that biogenic SOA far exceeds anthropogenic SOA in the summer even in urban centers such as Zürich (Szidat et al., 2006). The importance of BVOC oxidation to particle mass and number has been demonstrated by a number of studies influenced by a variety of different forested regions (Leaitch et al., 1999; Kulmala et al., 2001; Sellegri et. al., 2004; Rissanen et al., 2006; Russell et al., 2007). A peak biogenic SOA concentration of 15 μg m^{-3} (the largest to date) was reported at a rural site north of Toronto in Ontario, Canada (Slowik et al., 2009).

Laboratory chamber studies have identified several products of isoprene oxidation and a suite of products of monoterpene oxidation; these products include carbonyls (both ketones and aldehydes), organic acids and hydroxyls, including triols and tetrols (Surratt et al., 2006; Kroll et al., 2006), and small amounts of organosulfates (Surratt et al., 2008). Significant progress has been made on understanding the proposed chemical mechanisms of the pathways for oxidation of BVOCs to form SOA (Surratt et al., 2009; Paulot et al., 2009). These controlled experiments have been run under a variety of conditions (varying oxidant concentrations, light, seed aerosol, relative humidity, and temperature), although almost always with only a single oxidant (Hallquist et al., 2009; Kanakidou et al., 2005). From measured stable products, likely pathways and intermediates have been proposed and varying yields have been calculated. In addition, the chemical composition of laboratory-produced biogenic SOA has been observed to change for some time after SOA formation has slowed (Sax et al., 2005).

However, there is very little evidence that these products identified in the laboratory are formed and persist in the real atmosphere. The pathways that are the most significant and relevant for atmospheric conditions remain unknown (Kanakidou et al., 2005; Hallquist et al., 2009). Laboratory chamber studies have provided quantitative information on specific pathways and yields, but they typically use controlled conditions with a single oxidant and no competing reactants – an idealized situation rarely encountered in the atmosphere. In addition, as a result of the sensitivity of aerosol formation to the concentration of NO_x, the mass yields determined in the lab may not accurately represent those of ambient aerosol (Seinfeld and Pandis, 2006). Further ambient measurements of biogenic SOA are necessary to guide the myriad of results arising from chamber studies by providing constraints of real atmospheric conditions. However, the complexity of multiple atmospheric variables (such as transport times, mixing efficiencies, and multiple co-located sources) and their interplay in ambient conditions, as well as the multitude of different organic compounds, make ambient organic identification more challenging and often more limited than controlled laboratory studies (Goldstein and Galbally, 2007). Some methods such as gas chromatography-mass spectrometry can identify specific chemical biogenic SOA tracers but are limited to identifying only a fraction (at best < 25%) of the atmospheric aerosol (Cahill et al., 2006). *In situ* atmospheric measurements have provided evidence that biogenic SOA has high ratios of oxygen to carbon. The large concentrations of biogenic SOA measured at Egbert, Canada, were constrained by a lower limit of oxygenated organic aerosol (OOA-2, O/C ~0.46) and

an upper limit of the weighted sum of OOA-1 (O/C ~ 0.81) and OOA-2, where Slowik et al. (2009) approximate the O/C ratio from the fraction of m/z 44 (CO_2^+ ion) in the total organic mass spectrum, as presented by Aiken et al. (2008).

In this chapter, we use an expanded suite of instrumentation and statistical techniques to present chemically-specific evidence for organic functional groups (OFG) associated with biogenic VOC emissions. The suite of gas and particle phase measurements at a mid-mountain site in the forests of Whistler, British Columbia, in May and June of 2008 are used to identify the sources and composition of the organic mass during this study, providing an opportunity to compare products observed in laboratory chamber studies to those formed under atmospheric conditions.

2.3 Methods

Atmospheric particles and gases were sampled by a suite of co-located instruments during a one-month campaign at a site in Whistler, BC, at 1020 m above sea level (asl). The valleys surrounding Whistler Mountain are lined by trees up to about 1850 m asl. The forests are largely coniferous, dominated by firs and hemlock. The measurements at the Children's Learning Center (CLC) building on Whistler mountain included Fourier transform infrared (FTIR), high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), proton-transfer reaction mass spectrometry (PTR-MS), X-ray fluorescence (XRF), single particle soot photometer (SP2), Scanning Transmission X-Ray Microscopy with Near-Edge Absorption Fine Structure (STXM-NEXAFS), gas phase (CO, O_3, NO_x), and meteorological

conditions from 16 May to 16 June 2008. In addition, Environment Canada (EC) maintains measurements of ozone, CO, particle size distributions (0.01- 20 μm), ionic composition, light scattering, and light absorption at Whistler Peak at 2182 m asl (Leaitch et al., 2009).

FTIR provides organic functional group concentrations through chemical bond-based measurements (Russell et al., 2009a). Submicron particles were collected on 37 mm Teflon filters (Pall Inc.) downstream of a 1-μm, sharp-cut cyclone (SCC 2.229 PM1, BGI Inc.). Overlapping duplicate samples of approximately 12 and 24 hr duration were collected to provide redundant and higher loading samples. Filter changes generally occurred each morning (between 6 and 8 am PST) and each evening (between 5 and 8 pm PST). Back filters were collected to monitor VOC adsorption and handling artifacts, although the FTIR absorption of these filters was below detection limit in all cases. The standard deviation of the collected blanks was added to the calculation of the sample precision. FTIR spectra, measured with a Tensor 27 spectrometer (Bruker, Billerica, MA), were fit with polynomial baselines and peaks associated with each OFG, including alkane, carboxylic acid, organic hydroxyl, amine, organosulfate, and non-acidic carbonyl (ester or ketone) group concentrations (Maria et al., 2002; Gilardoni et al., 2007; Russell et al., 2009a). Alkene, aromatic, phenol, and organonitrate groups were below detection limit for all samples collected during this project.

High resolution time-of-flight Aerosol Mass Spectrometry (HR-ToF-AMS, Aerodyne Research Inc., Billerica, MA) provides real-time measurements of non-

refractory compounds including sulfate, nitrate, and organic mass through production of mass fragments by electron impact and detected by their mass to charge ratio (m/z) (Jayne et al., 2000; DeCarlo et al., 2006; Canagaratna et al., 2007). The AMS was operated in two modes: V and W-mode. The high mass resolution of W-mode (3000-5000) allowed fragments of nominally the same m/z to be quantified separately, thereby enabling a distinction between hydrocarbon (C_xH_y) and oxygenated hydrocarbon ($C_xH_yO_z$). W-mode data analysis (*i.e.* quantification of individual m/z with better than unit mass resolution) for this study was completed using a custom algorithm that incorporated a peak fitting procedure, typical AMS correction factors, and the correction for O/C suggested by Aiken et al. (2008).

Mixing ratios of selected VOCs were measured using high-sensitivity PTR-MS acquired from IONICON Analytik (Innsbruck, Austria). PTR-MS measures VOC concentrations from mass fragments of VOCs with a proton affinity higher than that of water, including monoterpenes and isoprene which are taken to be representative of BVOC emissions (Guenther et al., 1995). In brief, ambient air is pumped into a drift tube where VOCs undergo proton-transfer reaction with H_3O^+ ions produced by the ion source. Species with a proton affinity higher than water form stable ions that are selected with respect to m/z and counted (de Gouw et al., 2009). The particular PTR-MS instrument and the sampling and calibration methods used here have been described previously (Vlasenko et al., 2009). One difference in operations was that a heated (350 °C) platinum glass wool catalyst (Shimadzu Scientific Instruments, Columbia, MD) was used for automatic background collection (for 14 min every 3 hr),

as opposed to the activated charcoal used in the earlier study. As previously, a 500 ppb Apel-Reimer standard was employed (with 22 calibration points), which contained isoprene, α-pinene, and limonene. We assume that all monoterpenes are detected with the same average sensitivity as that measured for the sum of α-pinene and limonene. Methanol and acetone were also measured. Similarly, we report mixing ratios for the sum of methacrolein (MACR) and methylvinylketone (MVK) that are detected at the same m/z by the PTR-MS. MVK was calibrated with the Apel-Reimer standard, and we assume MACR has the same sensitivity. Detection of other BVOCS such as pinonaldehyde was not possible because of low mixing ratios near the instrument's detection limit during the campaign.

A single particle soot photometer (SP2) (Droplet Measurement Technologies, Boulder, CO) was used to measure black carbon (BC) in particles containing BC cores larger than about 70 nm diameter (Stephens et al., 2003; Schwarz et al. 2006; Slowik et al., 2004). Briefly, an air stream that contains BC passes through an air jet and intersects an intra-cavity and continuous Nd:YAG laser beam at 1064 nm wavelength. BC particles absorb the laser light and are heated to reach incandescence. The emitted incandescence light is detected using photomultiplier detectors. The peak incandescence signal is proportional to BC mass. The detector signals from individual particles are recorded at a high frequency, allowing the signals of each particle to be recorded and stored for further analysis. BC particle number concentrations are obtained by integrating the individual particles of different sizes from 70 nm and up.

X-ray fluorescence analysis (XRF) of the same filters used for FTIR was carried out at Chester LabNet (Tigard, Oregon) and provides elemental composition of metals heavier than Na (Maria et al., 2003), including S, Si, Al, Fe, Ca, Ti, V, K, Cr, Mn, Ni, Zn, and Br. The remaining elements heavier than Na (including Na) are also detected by this method but are omitted from this discussion because more than 34 of the 49 samples were below the detection limit.

Samples of atmospheric particles were collected for Scanning Transmission X-ray Microscopy Near Edge X-ray Absorption Fine Spectra (STXM-NEXAFS) by impaction on silicon nitride windows during 12 sampling periods, each of approximately 30 to 60 min. STXM-NEXAFS provides single particle chemical composition, size, and morphology measurements (Takahama et al., 2007; 2010). Of these 12 samples, 89 particles from four windows were analyzed at the Advanced Light Source (ALS) at the Lawrence Berkeley Laboratories (LBL).

The submicron organic mass (OM) measured by FTIR and Q-AMS has been shown to agree within 20% in ambient studies with primarily non-refractory, smaller than 500 nm, particles (Russell et al., 2009b). Figure 2.1 shows the comparison between the V mode of HR-ToF-AMS and FTIR OM measurements, for which the AMS OM concentrations were averaged for the filter sampling period and only samples in which the AMS measured OM for more than 85% of the sample duration are included. The average FTIR to V-mode HR-Tof-AMS ratio is 1.6 with correlation coefficient (r) equal to 0.85. Several of the samples with higher FTIR than AMS OM concentrations also contained a significant concentration of dust (as illustrated in Fig.

2.1), suggesting that OM on submicron dust is not adequately measured by the AMS. This result is consistent with similar findings in a high-dust region reported by Hawkins et al. (2010). Samples with Si concentrations below 0.05 µg m^{-3} have a stronger correlation of r = 0.89 (V-mode) and lie closer to the 1:1 line. The submicron dust elemental concentrations (Fig. 2.2) were present in ratios similar to those found in Asia and North America (McKendry et al., 2001). The average AMS sulfur (from sulfate) to XRF sulfur ratio is 0.31 with r = 0.91. The different fractions of OM and sulfur collected by the AMS relative to offline impactors suggest that a majority of the OM is not present on the same particles as the sulfate.

2.4 Results

Whistler peak is influenced by long range transported particles from Asia in the early-spring, by biogenic aerosols in the late-spring and summer (Leaitch et al., 2009), and occasionally by biomass burning aerosols in summer. Vancouver is 100 km southwest of Whistler and is the closest large city. During the 2008 measurements at the mid-mountain site, the lack of nearby large pollution sources and specific meteorological conditions resulted in lower concentrations of atmospheric oxidants in the valley. The project means and standard deviations of NO_x and O_3 concentration, measured using a TECO 42C and TECO 49C (Thermo Electron Corporation, Waltham, MA), were 1.5 ± 1 and 28 ± 11 ppbv, respectively (as listed in Table 1). The mean NO_x is dominated by relatively short-lived increases due to local traffic and the morning breakup of the nocturnal inversion that formed below the CLC. The tall

spikes in BC number concentration, shown in Fig. 2.3d, are attributed to diesel trucks from a nearby mountain road. The lower but broader increases in BC concentration during the late mornings are related to the nocturnal inversion breakup that carried pollutants accumulated over Whistler village through the site; the latter was rapidly diluted as the boundary layer grew. These factors account for less than a 10% increase in the 12 hr average of more than 90% of the filter sampling periods. Overall these BC number concentrations are quite low (Jacobson, 2002) and there is no evidence to suggest the local truck emissions contributed more than 10% of OM.

The OFG composition is shown in Fig. 2.3a for the May and June 2008 measurement campaign. OM was composed of alkane, carboxylic acid, ketone, organic hydroxyl, and amine groups, with five samples containing detectable organosulfate groups. OM was variable throughout the project, ranging from less than 0.5 to 3.1 μg m^{-3}, with the project mean and standard deviation at 1.3 ± 1.0 μg m^{-3}. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 34%, 33%, and 23% of OM, respectively. Ketone, amine, and organosulfate groups made up 6%, 5%, and < 1% of the average organic aerosol composition, respectively.

The OFG concentrations show correlations with each other and dust, suggesting at least two distinct types of organic sources. Organic hydroxyl group fraction is mildly correlated to amine group fractions. In addition, organic hydroxyl and amine groups are strongly (r = 0.8) and mildly (r = 0.6) correlated with dust (Si), respectively, while alkane and carboxylic acid groups show no correlation ($|r| < 0.25$) to dust (Si). These differences suggest at least two distinct sources with varying OFG

signatures contributing to OM. There are weak correlations among several of the OFG and VOC. Weak correlations are consistent with both the formation of OFG from VOCs that are simultaneously removed as well as the multivariate nature of the dependence of OM on mixtures of sources, oxidants, and photochemical pathways.

A prominent feature of the time series of the summed OFG and BVOCs shown in Figs. 2.3a,b is the two large peaks in concentration during two different periods, "H1" (from 18:00 PST May 16 to 13:00 PST May 19) and "H2" (from 18:00 PST May 24 to 8:00 PST May 28). The time between and after these two periods also includes significantly increased concentrations of both monoterpenes (38 to 210 ppt) and OM (0.1 to 2.3 μg m^{-3}). The temporal variations of isoprene and monoterpene concentrations are only weakly correlated. Secondary, longer-lived oxidation products of BVOCs, such as MVK/MACR, which in general had low mixing ratio values (a factor two higher than instrument noise), also had higher concentrations during H1 and H2 (listed in Table 2.1).

An interesting feature of the local activities near the mid-mountain site was a nearly continuous background of submicron dust components ranging from about 0.02 to 0.8 μg m^{-3}. This submicron dust is probably associated with local sources because of its substantial concentration, its weak correlation with local wind speed, and the lack of evidence for free tropospheric influence of long-range transported Asian aerosols. The lack of a significant difference in day and night concentrations suggests that the submicron dust was either sufficiently long-lived that there was no temporal correlation to specific daytime activities on the mountain or that the majority of the

dust was windblown rather than activity-related. The trace metal measurements from XRF included S, Si, and Al, each with campaign average concentrations greater than 50 ng m^{-3}. Fe, Ca, Ti, V, Cr, Mn, Ni, Zn, and Br contributed from 0.4 to 34 ng m^{-3} over the study. The concentrations of crustal elements are shown in Fig. 2.3c.

We apply Positive Matrix Factorization (PMF, using PMF2 software purchased from P. Paatero, Helsinki University, based on Paatero and Tapper (1994)) to separate the fraction of the OFG that is most closely associated with the same sources as the BVOC emissions. This method has been used previously on FTIR spectra to identify and separate combustion, wood burning, marine, and other sources (Russell et al., 2009a; 2010; Liu et al., 2009; Hawkins and Russell, 2010). PMF was applied on the 80 baselined FTIR spectra collected for 12 and 24 hr samples, using an uncertainty matrix constructed as discussed in Russell et al. (2009a). Results for 2, 3, 4, 5, and 6 factor solutions with rotation parameter FPEAK of -0.4, -0.2, 0, 0.2, and 0.4 were explored. For more than four factors, two or more factors were correlated to each other, indicating that the measurements were insufficient to differentiate additional independent factors. For the four-factor solution the FPEAK range was expanded to -2 to 2, and the Q values as a function of FPEAK were examined (Ulbrich et al. 2009). The effects of rotation close to zero were small, and those further from zero provide unrealistic spectra. FPEAK = 0.2 was chosen for detailed investigation because of its low Q value and realistic spectra shape. To provide an estimate of the PMF spectra uncertainties, spectra for a range of three rotations are shown in Fig. 2.5.

The four-factor solution reproduced more than 90% of the absorbance. Three of the four factors obtained from this correlation were mildly or weakly correlated with monoterpene or isoprene concentrations and each other. Since these correlations mean that the factors were not independent, their sum is considered here as parts of a single factor (shown in Fig. 2.3e). The summed biogenic factor fraction is correlated to monoterpenes and MVK/MACR with correlation coefficients of 0.69 and 0.63, respectively, as shown in Fig. 2.4a,b. Because of the correlation to BVOC, this factor has been identified as a "biogenic" factor; it accounts for more than half of the OM (65%) during the project and is more than 80% of OM during the H1 and H2 periods of higher monoterpene and isoprene concentrations. The fourth factor from PMF was weakly anti-correlated to monoterpenes ($r = -0.44$) and mildly correlated to AMS sulfate and XRF S concentrations (Fig. 2.4d). The correlation to sulfur species suggests a fossil fuel combustion source for this OM and is referred to as the "combustion" factor. This factor may also include contributions from the port and urban areas of Vancouver as well as particles transported from Asian sources.

The average concentrations of the summed biogenic and combustion factors and their fractional composition of OFG are listed in Tables 2.1 and 2.2, respectively. The summed biogenic factor is composed of 32% (32-38%) alkane, 25% (22-25%) carboxylic acid, 21% (19-21%) organic hydroxyl, 16% (12-16%) ketone, and 6% (6-7%) amine groups, where the range is for the PMF rotations shown in Fig. 2.5. The combustion factor is largely alkane (52%, 50-57%) and carboxylic acid (30%, 24-33%) groups.

The correlation of the biogenic factor fraction with monoterpenes of $r = 0.69$ is higher than the correlation of OM with monoterpenes ($r = 0.33$). This correlation of the biogenic factor OM to monoterpenes is also higher than that of the OOA-2 factor identified from the more rapid time resolution AMS measurements at Egbert, ON (Slowik et al., 2009), because that factor was associated with both anthropogenic and biogenic sources during different time periods of the study. In addition, the Egbert site was ≥ 12 hr downwind of the main BVOC emission sources rather than in the middle of the forest as at Whistler, resulting in closer correlation between BVOC precursors and SOA reaction products. It is also possible that the 12 hr sample duration is sufficient to smear the time delay for the oxidation of monoterpenes and condensation of the oxidized products to form SOA, which we expect to be less than 10 hr in similar atmospheric conditions (Russell et al., 2007). The correlation of BVOC concentrations to the biogenic OM factor identified by PMF is stronger than the correlations to the directly-measured OFG, supporting the interpretation of this factor as representing the fraction of the OM from a biogenic source. The biogenic factor is also correlated strongly ($r > 0.75$) with elements often used as tracers for dust (Al, Si, K, Ti, and Fe). The correlation between the biogenic factor fraction and Si ($r = 0.63$) is shown in Fig. 2.4c.

The three individual parts of the summed biogenic factor show different strong, mild, and weak correlations with specific BVOC, OFG, and dust. For this reason, even though these three parts of the summed biogenic factor have sources that co-vary too much to be resolved independently, we consider the characteristics that

differentiate each part. The first part of the biogenic factor, Part 1, consists mostly of organic hydroxyl groups (69%, 68-72%) and is strongly correlated to the dust signal. To evaluate the role that the particle substrate may play in heterogeneous formation of SOA, we have also considered the correlation of the product of Si and monoterpene concentrations with this part of the biogenic factor; this correlation is strong with r = 0.93, with this correlation coefficient exceeding those of monoterpenes with the summed biogenic factor or with either of the other two parts. The second and smallest biogenic factor part, Part 2, is mildly correlated with monoterpenes (r = 0.64). This factor consists primarily of alkane (66%, 56-66%) and acid (25%, 24-32%) groups. Part 3 of the summed biogenic factor is weakly (r = 0.30) correlated with isoprene when we include samples with above detection limit (dl) isoprene measurements for more than 50% of the filter time (and OM below dl samples are included). This factor has a significant fraction of ketone groups (36%, 31-38%). In summary, the differences in the parts of the summed biogenic factor likely represent the products of different types of BVOC (namely isoprene and monoterpenes) as well as different SOA formation processes (such as condensation of organic hydroxyl group-containing products on dust instead of further oxidation to ketone or acid groups).

2.5 Discussion

Since OFG are characteristic of the organic compounds they make up, we expect the composition of the biogenic factor to resemble the composition of laboratory chamber SOA produced from oxidation of monoterpenes and isoprene.

Table 2.2 summarizes the mass fractions of OFG in the reported SOA products from oxidation of monoterpenes, isoprene, and their mixtures. The observed ambient biogenic factor has 16% ketone groups, which is similar to the 10 - 17% ketone groups from the reported smog chamber products 10-hydroxypinonic acid, pinonaldehyde, pinonic acid, and methylglyoxal sulfates (isomer 1) (Hallquist et al., 2009). The organic hydroxyl group composition (21%) is similar to that of 3-hydroxyglutaric acid (16%), 2-hydroxymethylsuccinic acid (16%), and glyoxal sulfate (15%), as shown in Table 2. The carboxylic acid fraction (25%) is similar to that found for pinonic acid (24%). The summed biogenic OM factor, like both C5-alkene triols isomers has an average O/C of 0.6. Several compounds shown in Table 2.2 contain small contributions of OFG not identified in the Whistler biogenic factor, and no single compound exactly matches the measured biogenic OFG composition. However, there are possible combinations, such as, a 2:1 ratio of pinonic acid to methyltetrol, that nearly reconstruct the overall biogenic factor OFG composition. Multiple combinations of more than 2 compounds also resemble the overall biogenic factor OFG composition.

Certainly there are many unidentified compounds that also contribute to the chamber SOA, and Table 2.2 shows only the similarity of the OFG in the identified compounds with those in the summed biogenic factor. To compare to the overall chamber SOA composition, we see that the O/C ratio of the summed biogenic factor is slightly higher than the values for smog chamber SOA from both monoterpene and isoprene reactions (0.37 to 0.57) (Hallquist et al., 2009), but the chamber data are well

within the range of Parts 2 (0.2) and 3 (0.6). The summed biogenic factor O/C also exceeds the O/C of the OOA-2 factor (~0.46), which was during an identified biogenic period associated with biogenic SOA at Egbert (Slowik et al., 2009). The higher O/C of the Whistler biogenic SOA could easily result from differences in atmospheric oxidant concentrations as well as in sampling methodology, since the high O/C (1.2) in the organic hydroxyl group-containing Part 1 of the summed biogenic factor is likely formed on dust which is absent in chamber studies and either absent or not sampled at Egbert.

To identify the locations of the biogenic and combustion OM factors, we used Hybrid Single-Particle Lagrangian Integrated Trajectory (HYSPLIT, http://*www.arl.noaa.gov/HYSPLIT.php*) back trajectories to evaluate the probability that the times during which the OM was largely from one factor (above the 75th percentile) coincided with a particular back trajectory region. We investigated 1 and 3 day back trajectories and chose the former, since the 3-day trajectories were disproportionately affected by a few unusual samples that did not reflect the majority of the study measurements. Figure 2.6 shows the one-day HYSPLIT back trajectories and maps of potential source contribution functions (PSCF) of monoterpenes, the summed biogenic factor, and the combustion factor (Pekney et al., 2006). The PSCF calculation indicates that the source regions of monoterpenes and the summed biogenic factor largely coincide with the forested regions to the east of Whistler. The small differences in the three parts of the biogenic factor may indicate differences in BVOC emissions from the vegetation in different regions. The source region identified

for the combustion factor is southwest of Whistler, including the regions near the coastal cities of Vancouver, Seattle, and Portland, as well as the offshore shipping activities associated with their ports.

The summed biogenic factor is also correlated with the oxygenated VOCs methanol (r = 0.55) and acetone (r = 0.69). This suggests that variations in these VOCs, especially acetone, are associated with products of BVOCs that may serve as precursors to the biogenic SOA or may simply be produced simultaneously (Vereecken and Peeters, 2000). This interpretation of methanol and acetone production from local biogenic sources is supported by observed strong diurnal variations of acetone, as such variations would tend to be reduced during transport from Vancouver or some other distant anthropogenic source.

The 0.02-0.8 μg m^{-3} concentrations of submicron dust components and the correlation of these components to the biogenic factor, suggests that dust acts as a surface for the condensation of products of BVOC oxidation. The correlation between the product of crustal elements and BVOCs with the biogenic factor (r > 0.9) provides some support for this speculation. Strong correlations between the biogenic factor and the product of OM and BVOCs (r > 0.8) are consistent with the two-product model of SOA formation suggested by Odum et al. (1996), indicating that SOA condensation onto pre-existing organic particles may play a limiting role.

The weakness of the correlations with BVOCs limits our ability to develop quantitative generalizations from these results. However, if there were a 4 to 12 hr delay required to form SOA from BVOCs in the atmosphere, stronger correlations

would not be expected. This time delay is more evident during the short duration H1 and H2 events, as is expected for Eulerian sampling with a variable temporal offset from the source region. However, the 12 to 24 hr offset between the peaks in VOCs and the peaks in SOA suggests an SOA formation timescale of under a day. In addition to the delay associated with the chemical formation of biogenic SOA, there may also be an accumulation effect as the aerosol passing over the forest picks up SOA, which would also result in a lag between the peaks in BVOC and biogenic SOA concentrations.

The non-acidic carbonyl group contribution observed during this study is similar to the OM attributed to biogenic SOA in ICARTT (Bahadur et al., 2010) and to biomass burning emissions during measurements at the Scripps pier (Hawkins and Russell, 2010). This observation of ketone groups associated with both the emissions of plants and the burning of plants is enabled by the suitability of FTIR for detecting ketone groups (Calogirou et al., 1999). The high organic hydroxyl group factor, and its strong association with dust, suggests a different SOA formation pathway that has only been identified in Whistler.

In order to better understand the role of the ketone and carboxylic acid groups in biogenic SOA, we have classified the 89 particles analyzed by NEXAFS-STXM into the 14 categories presented by Takahama et al. (2007). The two most common particle types for the 89 particles were "secondary" (type "a") and "other" (types "k", "l", and "n") containing 32 and 24 particles, respectively. The remaining particles were classified as biomass burning (types "i" and "j"), combustion (types "b" – "e",

"g", "h", and "m"), and ultisol-soil (type "f"). As shown in Fig. 2.7, the "other" particles have a higher ratio of ketone to carboxylic acid groups than the "secondary" particles. The "secondary" particles also tend to be larger in size. This distinction is consistent with the results from the PMF factors of the FTIR submicron filter-based measurements that most of the ketone groups are formed from a different source or process than the carboxylic acid groups, as shown in Fig. 2.5 by the biogenic and combustion factor OFG compositions. The size differences suggest that at least some of the higher carboxylic acid group fractions may be from cloud processing, since reactions in cloud droplets may result in high SOA yields and more particle growth (Altieri et al., 2008). Conversely, the ketone group ratios are higher on many of the submicron particles since the higher contribution at smaller diameters suggests they are more likely to have formed from gas phase reactions (Maria et al., 2004).

2.6 Conclusions

The ambient OM concentrations at Whistler ranged from less than 0.5 to 3.1 $\mu g\ m^{-3}$, with two distinct periods that corresponded to high concentrations of gas phase monoterpenes and isoprene as well as OM. About 65% of OM during the month-long study and over 80% during the periods of high monoterpene and isoprene concentrations was associated with secondary biogenic OM. The OFG composition of this biogenic OM differs from those compositions associated in other field campaigns with fossil fuel combustion and marine emissions (Russell et al., 2009a; 2010; Liu et al., 2009).

These findings provide one of the most unambiguous data sets for characterizing the functional group composition of ambient biogenic SOA. The presence of alkane, carboxylic acid, ketone, and organic hydroxyl groups in biogenic SOA is qualitatively consistent with both smog chamber results and with other biogenic OFG measurements (Hallquist et al., 2009; Bahadur et al., 2010). In fact, the similarity of the quantitative contributions of OFGs in the summed biogenic factor to those in the products identified from laboratory chamber SOA provides preliminary evidence for the atmospheric importance of the production and persistence of ketone and organic hydroxyl groups rather than aldehyde or organosulfate groups. While the differences between atmospheric SOA and laboratory chamber SOA are expected given the lower levels of both oxidants and BVOCs at Whistler during the study period, the similarities provide an indication of which products are more common and more stable in the atmosphere. The absence of aldehyde groups in the ambient SOA could also result from the sampling methods, or it may indicate that aldehydes are too volatile or too unstable to persist in atmospheric particles.

Acknowledgements

Whistler-Blackcomb for site access and help with logistics, as well as Juniper Buller for assistance in collecting filters at Whistler during this campaign.

This chapter, in full, has been submitted for publication of the material as it may appear in Atmospheric Chemistry and Physics and is now posted in the online journal Atmospheric Chemistry and Physics Discussion, Schwartz, Rachel E.; Russell, Lynn M.; Sjostedt, Steve J.; Vlasenko, Alexander; Slowik, Jay G.; Abbatt, Jonathan P. D.; Macdonald, Anne Maire; Li, Shao-Meng; Liggio, John; Toom-Sauntry, Desiree; and Leaitch, W. R , "Biogenic Oxidized Organic Functional Groups in Aerosol Particles from a Mountain Forest Site and their Similarities to Laboratory Chamber Products". The thesis author was the primary investigator and author of this paper. I would like to thank all co-authors for their contributions.

Table 2. 2: OFG Fractional Composition of FTIR Factors and reported biogenic SOA from Hallquist et al. (2009) Tables 3 –5.

	O/C	Alkane Groups	Ketone Groups	Aldehyde Groups	Organic Hydroxyl Groups	Carboxlyic Acid Groups	Organo-sulfate Groups	Organo-nitrate Groups	Alkene Groups	Amine Groups	FTIR missing
PMF summed biogenic factor	0.6	32	16	0	21	25	0	0	0	6	0
Biogenic Part 1	1.1	16	0	0	69	9	0	0	0	6	0
Biogenic Part 2	0.2	66	0	0	3	25	0	0	0	7	0
Biogenic Part 3	0.6	30	36	0	15	14	0	0	0	6	0
PMF combustion factor	0.4	52	0	0	17	30	0	0	0	1	0
Monoterpenes	0.5	45	7	3	2	18	19	4	0	0	4
3-hydroxyglutaric acid[a,b,d]	1	24	0	0	16	61	0	0	0	0	0
α,α–dimethyltric-arballylic acid [a,b,c]	0.8	31	0	0	0	66	0	0	0	0	3
2,3-dihydroxypinane[d]	0.7	38	0	0	0	0	35	23	0	0	4
2,10-dihydroxy-pinane[d,e]	0.5	45	0	0	9	0	41	0	0	0	5
10-hydroxypinonic acid [d]	0.7	35	10	0	0	16	36	0	0	0	3
pinonaldehyde [f]	0.2	62	17	17	0	0	0	0	0	0	4
pinonic acid [g]	0.3	57	15	0	0	24	0	0	0	0	3
Isoprene	1.4	22	2	3	35	10	27	3	3	0	-5
2-methyltetrol[h,i,j,n]	0.8	14	0	0	92	0	0	0	0	0	-6

Table 2.2: OFG Fractional Composition of FTIR Factors and reported biogenic SOA from Hallquist et al. (2009) Tables 3 –5, Continued

|	O/C	Alkane Groups	Ketone Groups	Aldehyde Groups	Organic Hydroxyl Groups	Carboxlyic Acid Groups	Organo-sulfate Groups	Organo-nitrate Groups	Alkene Groups	Amine Groups	FTIR missing
C5-alkene triols isomer 2[j]	0.6	30	0	0	58	0	0	0	22	0	-10
glyoxal sulfate[m,n]	3	5	0	18	15	0	65	0	0	0	-3
methylglyoxal sulfates isomer 1[m,n]	2	16	16	0	14	0	60	0	0	0	-7
methylglyoxal sulfates isomer 2[m,n]	2	12	0	16	14	0	60	0	0	0	-2
C5-alkane triol 2-[d]	1.6	26	0	0	9	0	42	28	0	0	-5
2-hydroxymethyl-succinic acid[g]	1	24	0	0	16	61	0	0	0	0	0
2,3,4-trihydroxy-2-methylbutyl hydrogen sulfate[g] and 2-methyltetrol sulfate esters[d]	1.4	26	0	0	32	0	47	0	0	0	-5

[a] Jaoui et al. (2005), [b] Claeys et al. (2007), [c] Szmigielski et al. (2007b), [d] Surratt et al. (2008), [e] Iinuma et al. (2007), [f] Williams et al. (2007), [g] Hallquist et al. (2009), [h] Edney et al. (2005), [i] Böge et al. (2006), [j] Surratt et al. (2006), [k] Claeys et al. (2004b), [l] Szmigielski et al. (2007a), [m] Liggio et al. (2005a, b), [n] Surratt et al. (2007a).

Figures
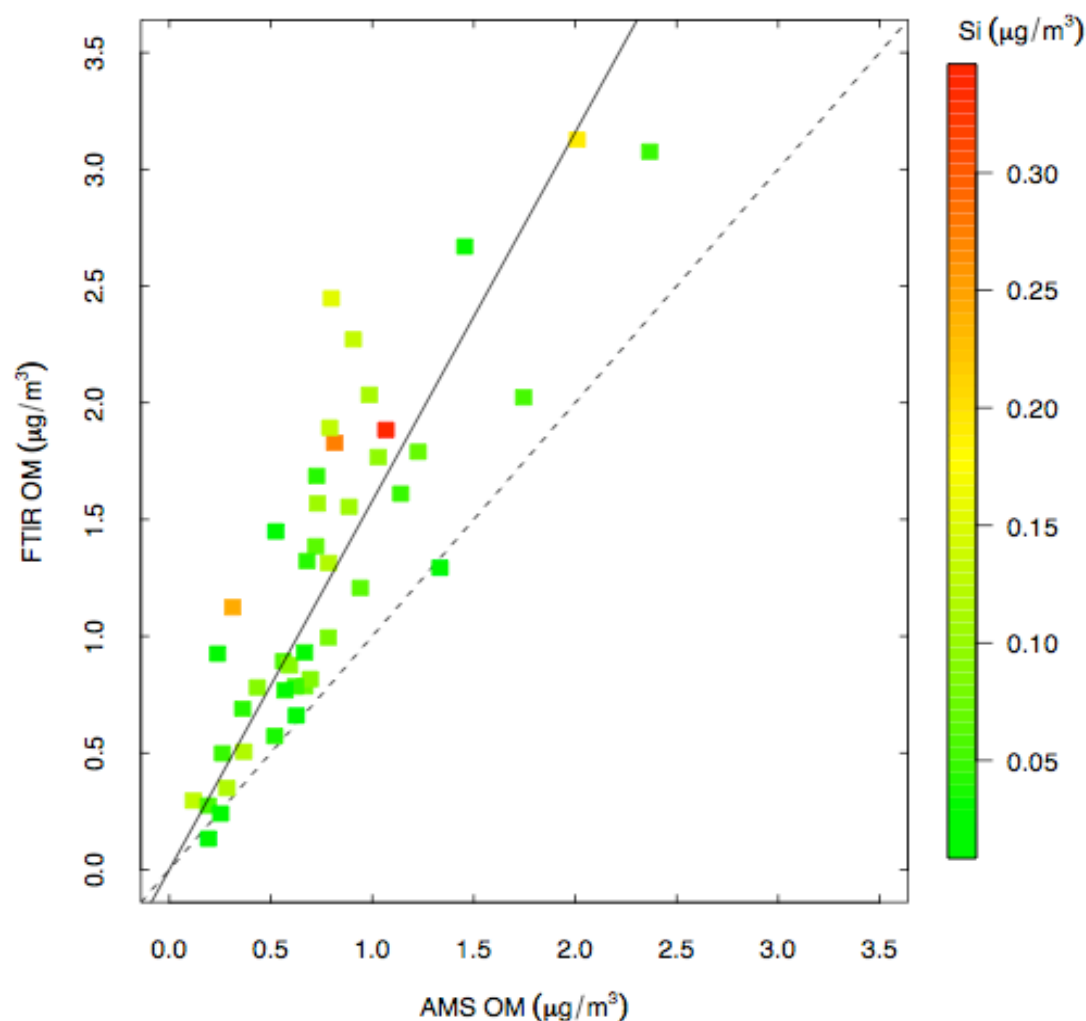
Figure 2.1: Comparison of V mode HR- Tof-AMS and FTIR OM concentrations. Five-minute resolution HR-Tof-AMS data was averaged over each filter sampling period and only filter periods in which the AMS was collecting measurements for at least 85% of the sample period (with a 50% duty cycle in V mode) were used here. 1:1 line is shown by a dashed line. Linear regression produces a fit through the origin with slope of 1. 6 and r = 0.85.
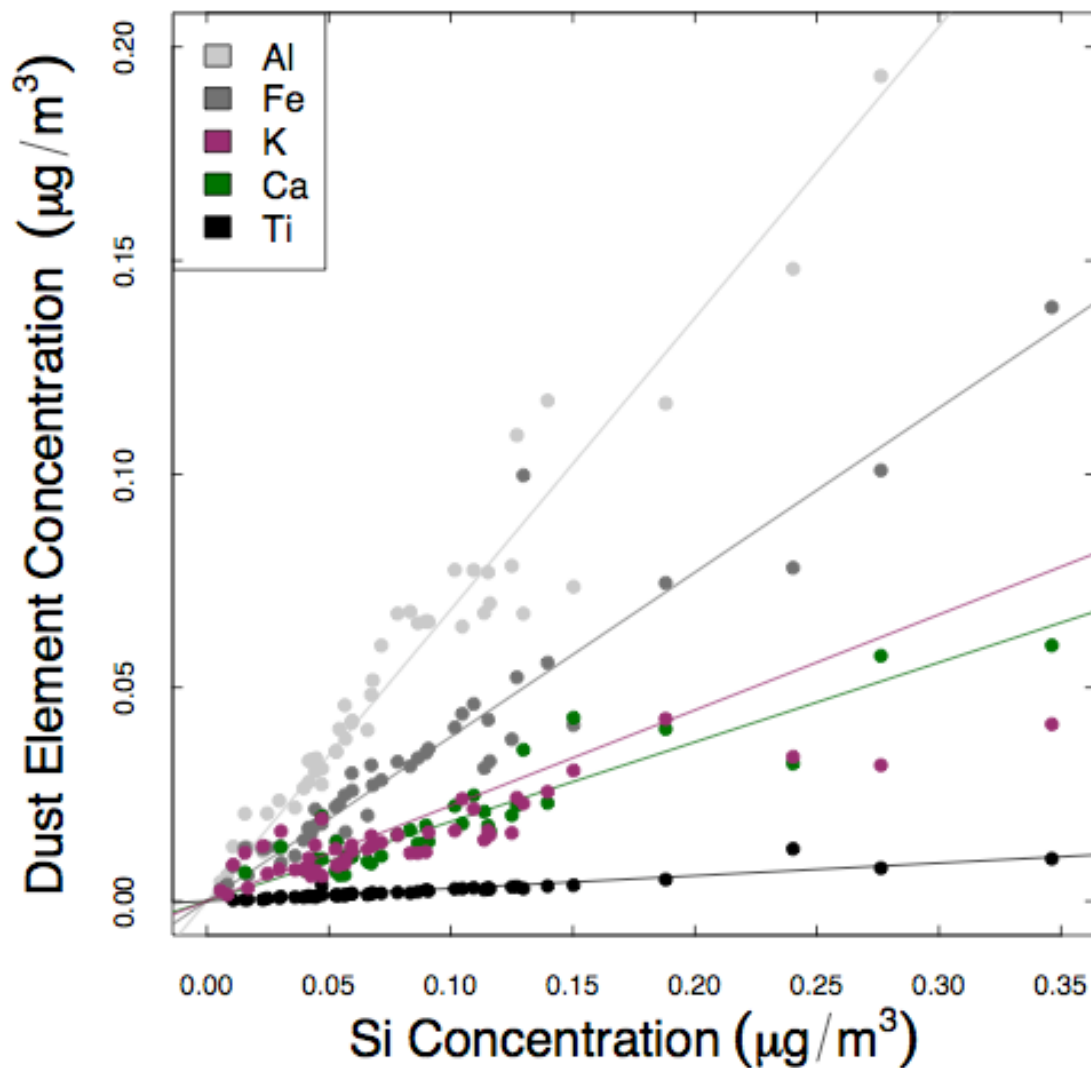
Figure 2.2: Comparison of concentrations of several dust markers (Al, Fe, K, Ca, Ti) with Si for all above detection limit12 hr samples collected during the project. All 5 dust markers had strong correlations with Si and slopes of 0.68, 0.38, 0.22, 0.18, and 0.03 for Al, Fe, K, Ca, Ti, respectively.
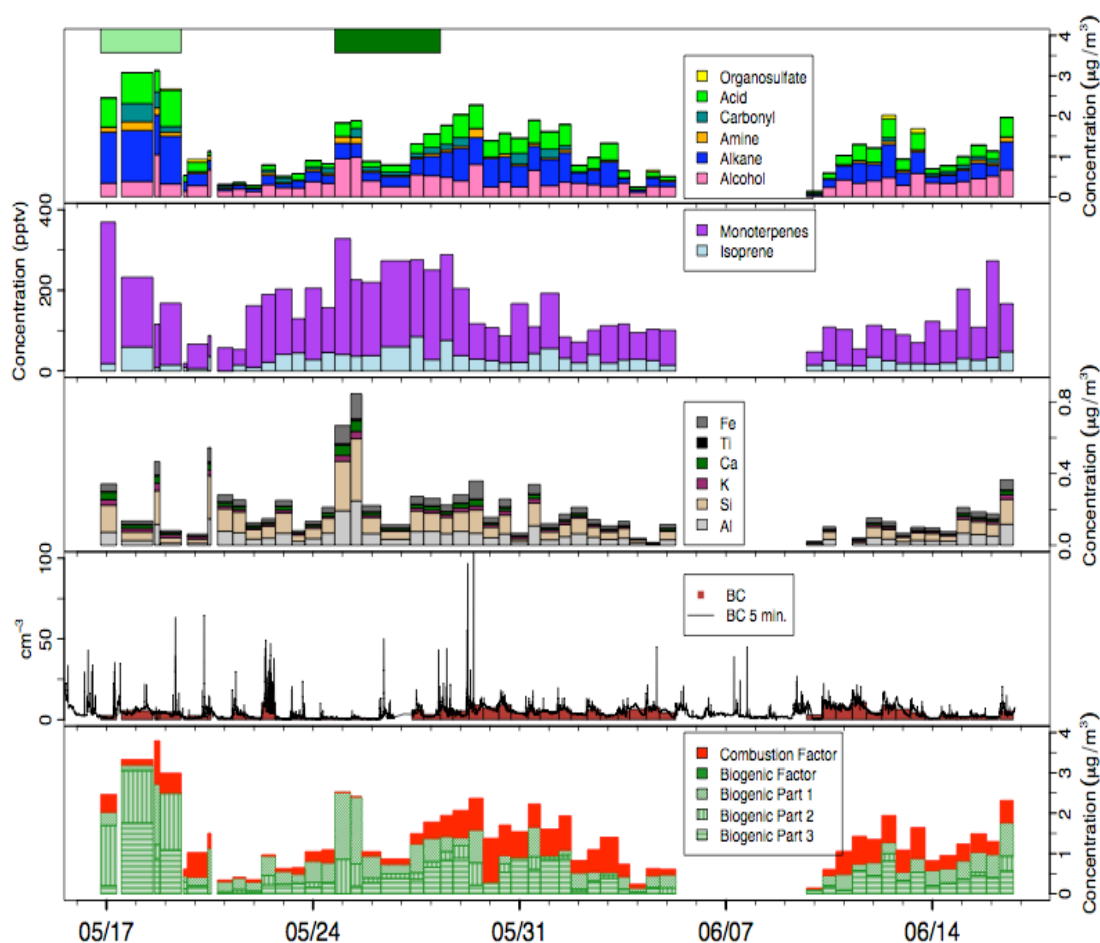
Figure 2.3: Time series of measured and calculated submicron aerosol components with H1 (light green) and H2 (dark green) marked by top colored bars: a) Time series of OM and OFG as stacked bars: organic hydroxyl (pink), alkane (blue), ketone (teal), amine (orange), acid (green), organosulfate (yellow) group concentrations; b) shows the sum of isoprene (light blue) and monoterpenes (purple) concentration; c) dust components Al (light grey), Si (tan), K (maroon), Ca (dark green) , Ti (black), Fe(dark grey); d) Time series of 5 min. average BC measurements (black) and ~12 hour averages (brown); e) Time series of OM reconstructed from four-factor PMF.
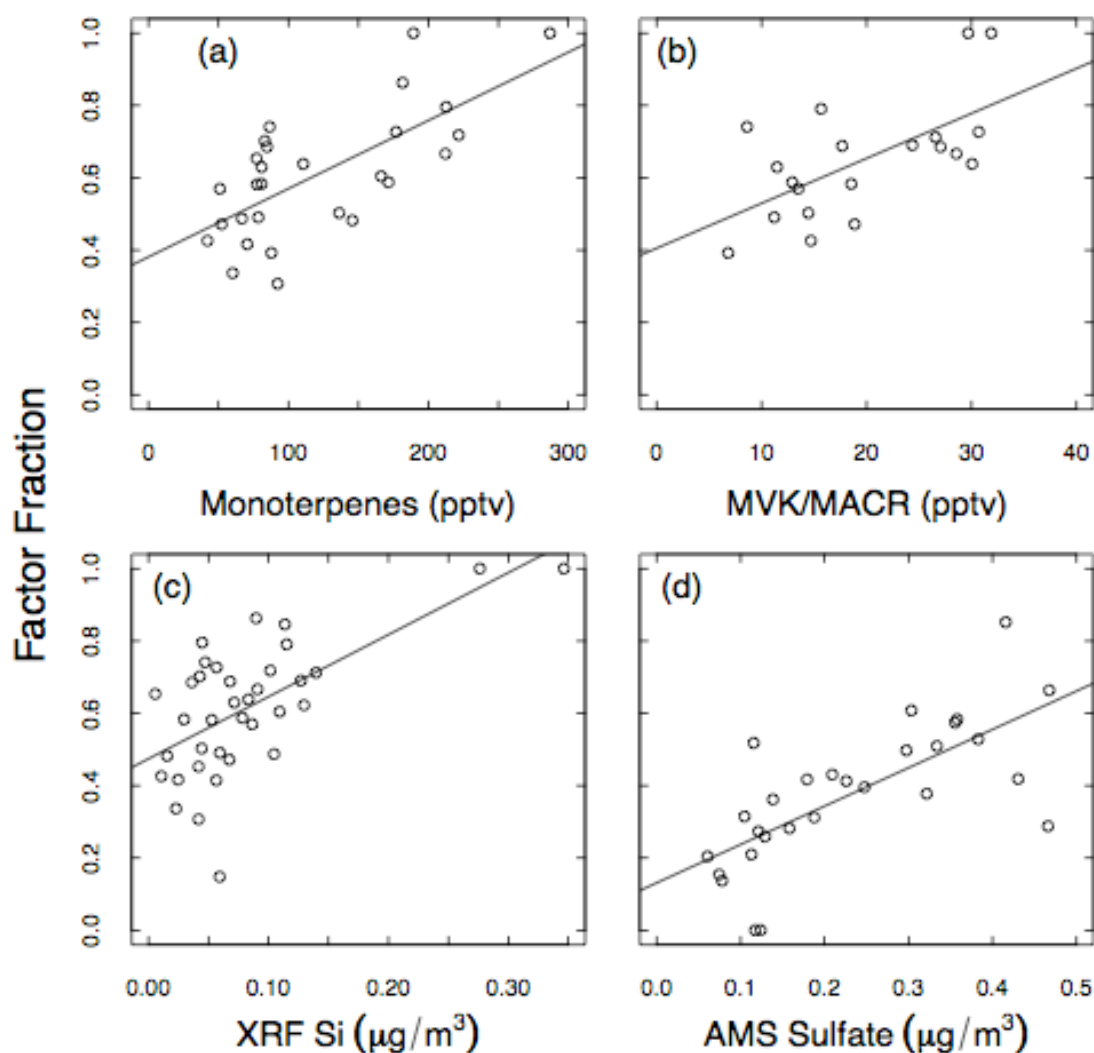
Figure 2.4: Comparison of PMF fractions and important tracers. Biogenic factor fraction and a) monoterpenes, b) MVK/MACR c) Si, and Combustion factor fraction and d) sulfate. Comparison includes 12 hr samples with OM above detection, with four samples during 17-18 May omitted because the flow control was not operating during this time and PTR-MS measurements when the VOC were measured above dl for more than 80% of the filter time. (OM concentrations are BDL if less than 80% of the mass from the functional groups was above detection limit.)
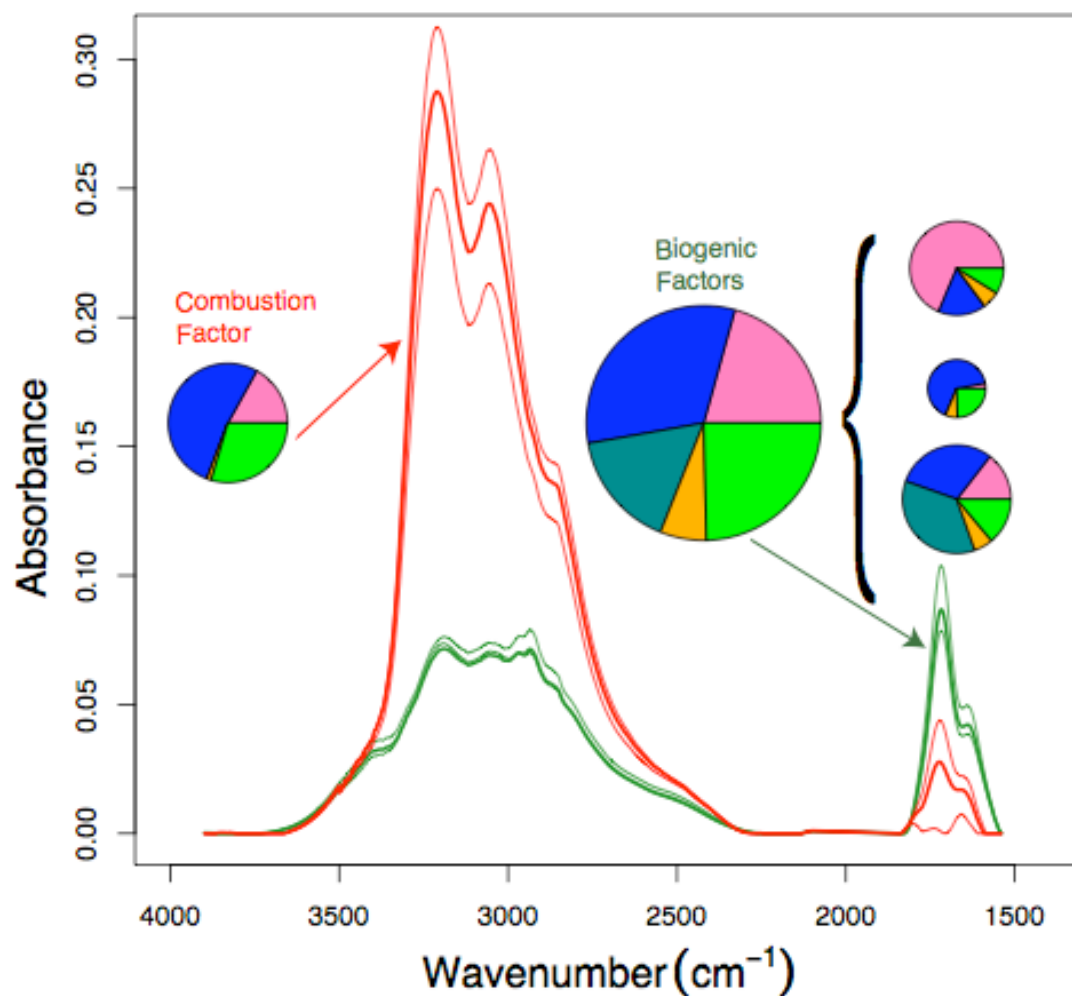
Figure 2.5: FTIR spectra (for FPEAK of $0, 0.2$ (bold), and 0.4) and OFG composition of summed biogenic and combustion PMF source factors. The pie charts show the average OFG composition for each factor, with the colors as given in Fig. 2.3 (organic hydroxyl (pink), alkane (blue), ketone (teal), amine (orange), acid (green)). The summed biogenic factor is made up of the three parts shown, where the composition pie for each part is scaled to its contribution to OM.
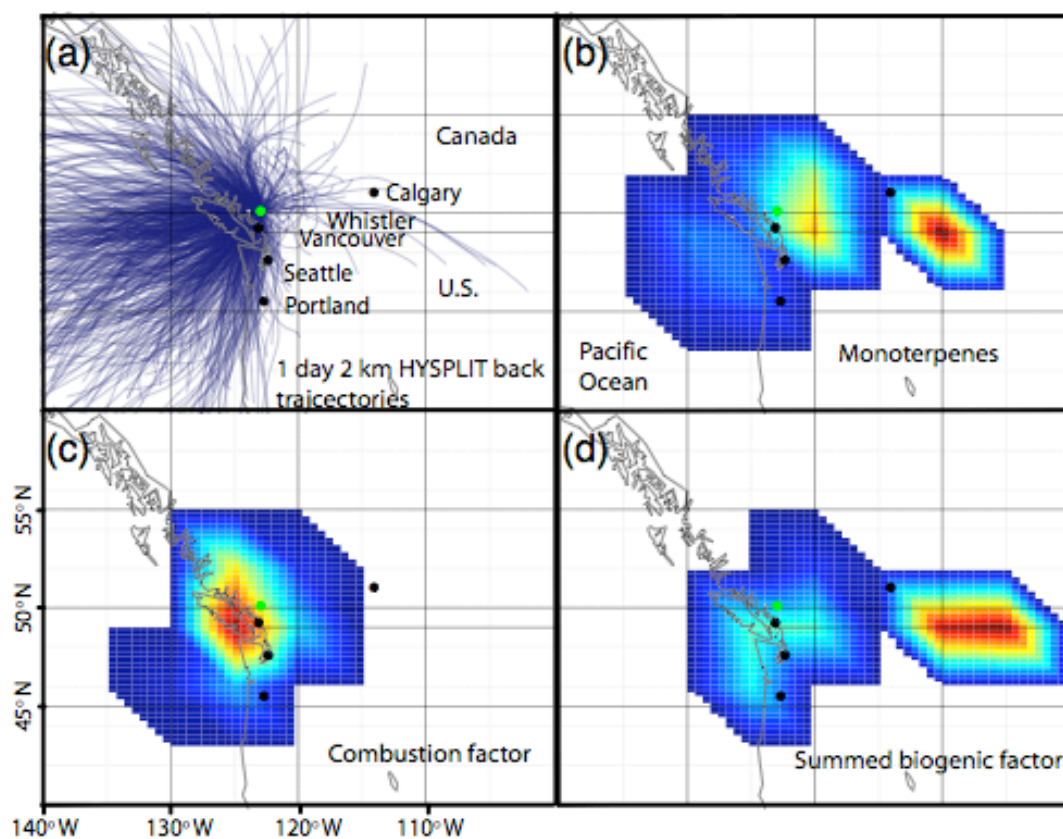
Figure 2.6: Maps of British Columbia and surrounding regions showing (a) one day NOAA HYSPLIT back trajectories and potential sources contribution functions (PSCF) of (b) monoterpenes, (c) the combustion factor, and (d) the summed biogenic factor.
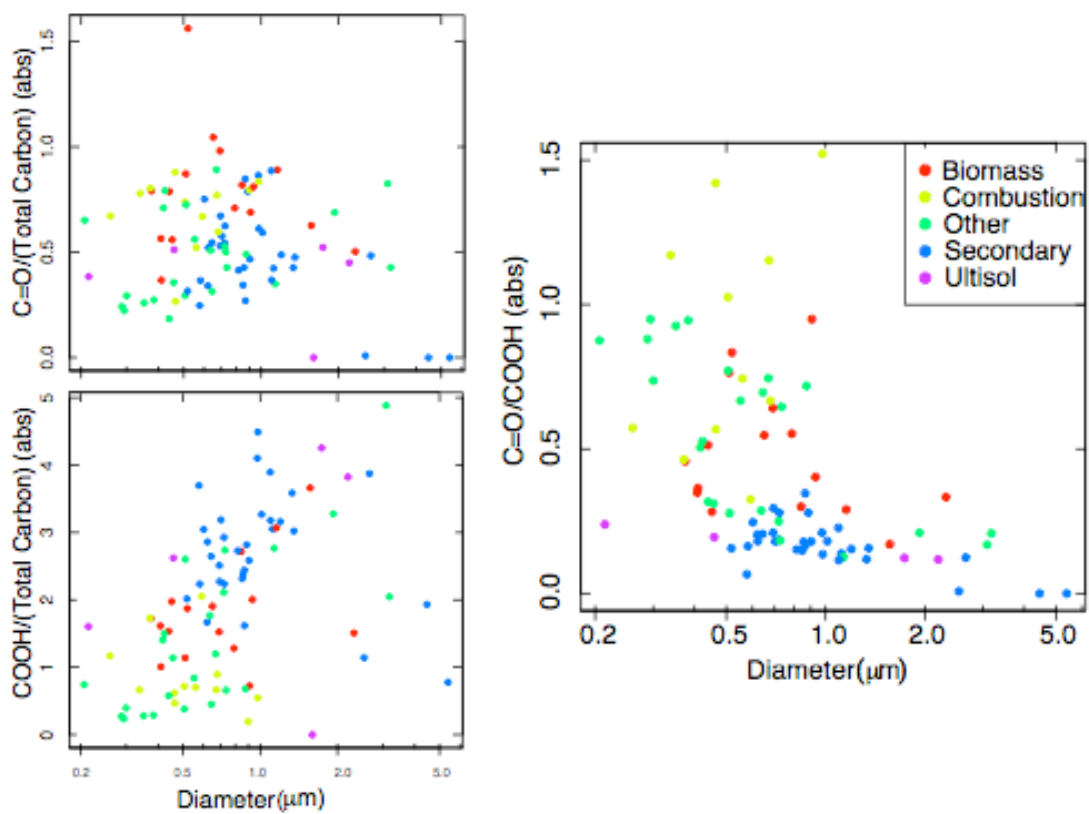
Figure 2.7: Summary of ketone groups and carboxylic acid groups, for individual particles measured by STXM-NEXAFS, as a function of the apparent geometric diameter after impaction on the substrate.

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, doi:10.1021/es703009q, 2008.

Altieri, K. E., Seitzinger, S. P., Carlton, A. G., Turpin, B. J., Klein, G. C., and Marshall, A. G.: Oligomers formed through in-cloud methylglyoxal reactions: Chemical composition, properties, and mechanisms investigated by ultra-high resolution FT-ICR mass spectrometry, Atmos. Environ., 42, 1476–1490, 2008.

Bahadur, R., Uplinger, T., Russell, L.M., Sive, B.C., Cliff, S.S., Millet, D.B., Goldstein, A., and Bates, T.S.: Phenols in Northeastern US Submicron Aerosol Particles from Seawater Sources, Environ. Sci. Technol., in press, 2010.

Böge, O., Miao, Y., Plewka, A., and Herrmann, H.: Formation of secondary organic particle phase compounds from isoprene gas-phase oxidation products: An aerosol chamber and field study, Atmos. Environ., 40, 2501–2509, 2006.

Cahill, T. M., Seaman, V. Y., Charles, M. J., Holzinger, R., and Goldstein, A. H.: Secondary organic aerosols formed from oxidation of biogenic volatile organic compounds in the Sierra Nevada Mountains of California, J. Geophys. Res., 111, D16312, doi:10.1029/2006JD007178, 2006.

Calogirou, A., Larsen B. R., Kotzias, D.: Gas-phase terpene oxidation products: a review, Atmos. Environ., 33, 1423-1439, 1999.

Canagaratna, M. R., Jayne, J. T., Jimenez, J. L., Allan, J. D., Alfarra, M. R., Zhang, Q., Onasch, T. B., Drewnick, F., Coe, H., Middlebrook, A., Delia, A., Williams, L. R., Trimborn, A. M., Northway, M. J., DeCarlo, P. F., Kolb, C. E., Davidovits, P., and Worsnop, D. R.: Chemical and microphysical characterization of ambient aerosol with the Aerodyne aerosol mass spectrometer, Mass. Spectrom. Rev., 26, 185–222, 2007.

Claeys, M., Wang, W., Ion, A. C., Kourtchev, I., Gelencser, A., and Maenhaut, W.: Formation of secondary organic aerosols from isoprene and its gas-phase oxidation products through reaction with hydrogen peroxide, Atmos. Environ., 38, 4093–4098, 2004.

de Gouw J. A., Warneke C., Montzka S.A., Brioude, J., Holloway, J.S., Parrish, D.D., Fehsendfeld, F.C.: How much biogenic SOA is present in the Northeastern US?, Geochim Cosmochim AC., 73, A273-A273, 2009.

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

Edney, E. O., Kleindienst, T. E., Jaoui, M., Lewandowski, M., Offenberg, J. H., Wang, W., and Claeys, M.: Formation of 2-methyltetrols and 2-methylglyceric acid in secondary organic aerosol from laboratory irradiated isoprene/NO_x /SO_2 /air mixtures and their detection in ambient PM2.5 samples collected in the eastern United States, Atmos. Environ., 39, 5281–5289, 2005.

Gilardoni, S., Russell, L. M., Sorooshian, A., Flagan, R. C., Seinfeld, J. H., Bates, T. S., Quinn, P. K., Allan, J. D., Williams, B., Goldstein, A. H., Onasch, T. B., and Worsnop, D. R.: Regional variation of organic functional groups in aerosol particles on four US east coast platforms during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign, J. Geophys. Res.-Atmos., 112, D10S27, doi:10.1029/2006JD007737, 2007.

Goldstein, A. H. and Galbally, I. E.: Known and Unexplored Organic Constituents in the Earth's Atmosphere, Environ. Sci. Technol., 41, 1514–1521, 2007.

Guenther, A., Hewitt, C., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W., Pierce, T., Scholes, R., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, J. Geophys. Res., 100, 8873–8892, 1995.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, proper ties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5235, 2009.

Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates T. S.: Carboxylic Acids, Sulfates, and Organosulfates in Processed Continental Organic Aerosol over the Southeast Pacific Ocean during VOCALS-REx 2008, Geophys. Res. Lett., in press, doi:10.1029/2009JD013276, 2010.

Hawkins, L. N. and L. M. Russell, Oxidation of ketone groups in transported biomass

burning aerosol from the 2008 Northern California Lightning Series fires, in review, available for review at http://aerosols.ucsd.edu/publications.html), 2010.

Iinuma, Y., Müller, C., Berndt, T., Böge, O., Claeys, M., and Herrmann, H.: Evidence for the existence of organosulfates from beta-pinene ozonolysis in ambient secondary organic aerosol, Environ. Sci. Technol., 41, 6678–6683, 2007.

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(D19), 4410, doi:10.1029/2001JD001376, 2002.

Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., and Edney, E. O.: Identification and quantification of aerosol polar oxygenated compounds bearing carboxylic or hydroxyl groups: 2. Organic tracer compounds from monoterpenes, Environ. Sci. Technol., 39, 5661–5673, 2005.

Jayne, J. T., Leard, D. C., Zhang, X., Davidovits, P., Smith, K. A., Kolb, C. E., and Worsnop, D. R.: Development of an aerosol mass spectrometer for size and composition analysis of submicron particles, Aerosol Sci. Tech., 33, 49–70, 2000.

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., Putaud, J. 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.

Kroll, J. H., Ng, N. L., Mur phy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary aerosol formation from isoprene photooxidaation, Environ. Sci. Technol., 40, 1869–1877, 2006.

Kulmala, M., Hämeri, K., Aalto, P. P., Mäkelä, J. M., Pirjola, L., Nilsson, E. D., Buzorius, G., Rannik, U, Dal Maso, M., Seidl, W., Hoffmann, T., Janson, R., Hansson, H.-C., Viisanen, Y., Laakonen, A., and O'Dowd, C. D.: Overview of the international project on Biogenic aerosol formation in the boreal forest (BIOFOR), Tellus 53B, 324–343, 2001.

Leaitch, W. R., Bottenheim, J. W., Biesenthal, T. A., Li, S. M., Liu, P. S. K., Asalian, K., Dryfhout-Clark, H., Hopper, F., and Brechtel, F.: A case study of gas-to-particle conversion in an eastern Canadian forest, J. Geophys. Res., 104, 8095–8111, 1999.

Leaitch, W. R, Macdonald, A. M., Anlauf, K. G., Liu, P. S. K., Toom-Sauntry, D., Li,

S.-M., Liggio, J., Hayden, K., Wasey, M. A., Russell, L. M., Takahama, S., Liu, S., van Donkelaar, A., Duck, T., Martin, R. V., Zhang, Q., Sun, Y., McKendry, I., Shantz, N. C., and Cubison, M.: Evidence for Asian dust effects from aerosol plume measurements during INTEX-B 2006 near Whistler, BC, Atmos. Chem. Phys., 9, 3523-3546, 2009.

Liggio, J., McLaren, R., and Li, S.-M.: Heterogeneous reactions of glyoxal in particulate matter: Identification of acetals and sulfate esters, Environ. Sci. Technol., 39, 1532–1541, 2005a.

Liggio, J., McLaren, R., and Li, S.-M.: Reactive uptake of glyoxal on particulate matter, J. Geophys. Res., 110, D10304, doi:10.1029/2004JD005113, 2005b.

Liu, S., Takahama, S., Russell, L. M., Gilardoni, S., and Baumgardner, D.: Cluster and Positive Matrix Factorization Analysis of Organic Functional Groups in Fine Particles During the MILAGRO 2006 Campaign, Atmos. Chem. Phys., 9, 6849-6863, 2009.

Maria, S. F., Russell, L. M., Turpin, B. J., and Porcja, R. J.: FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean, Atmos. Environ., 36(33), 5185–5196, 2002.

Maria, S. F., Russell, L. M., Gilles, M. K., and Myneni S.C.B.: Organic aerosol growth mechanisms and their climate-forcing implications, Science 306, 1921-1925, doi:10.1126/science.1103491, 2004.

McKendry, I. G., Hacker, J. P., Stull, R., Sakiyama, S., Mignacca, D., and Reid, K.: Long range transport of Asian dust to the Lower Fraser Valley, British Columbia, Canada, J. Geophys. Res., 106(D16), 18 361–18 370, 2001.

Paatero, P. and Tapper, U.: Positive Matrix Factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics, 5, 111–126, 1994.

Paulot, F. and Crounse, J.D. and Kjaergaard, H.G. and Kurten, A. and St Clair, J.M. and Seinfeld, J.H. and Wennberg, P.O.: Unexpected epoxide formation in the gas-phase photooxidation of isoprene, Science, 325, 730-733, doi:10.1126/science.1172910, 2009.

Pekney, N. J., Davidson, C. I., Zhou, L. M., and Hopke, P. K.: Application of PSCF and CPF to PMF-modeled sources of PM2.5 in Pittsburgh, Aerosol Sci. Technol., 40, 952–961, 2006.

Rissanen T., Hyötyläinen T., Kallio M., Kronholm J., Kulmala M., Riekkola M-L.:

Characterization of organic compounds in aerosol particles from a coniferous forest by GC–MS, Chemosphere, 64,1185–1195, 2006.

Russell, L. M., Mensah, A. A., Fischer, E.V., Sive B.C., Varner, R.K., Keene, W.C., Stutz, J., and Pszenny, A.A.P.: Nanoparticle Growth Following Photochemical a- and b-pinene Oxidation at Appledore Island During International Consortium for Research on Transport and Transformation/Chemistry of Halogens at the Isles of Shoals 2004, J. Geophys. Res. Atms. 112, dio: 10.29/2006JD007736, 2007.

Russell, L. M., Bahadur, R., Hawkins, L. N., Allan, J., Baumgardner, D., Quinn, P. K., and Bates, T. S.: Organic Aerosol Characterization by Complementary Measurements of Chemical Bonds and Molecular Fragments, Atmos. Environ., 43, 6100-6105, doi10.1016/j.atmosenv.2009.09.036, 2009a.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated Fraction and Mass of Organic Aerosol from Direct Emission and Atmospheric Processing Collected on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, Journal of Geophysical Research - Atmospheres, 114(D00F05), doi10.1029/2008JD011275, 2009b.

Russell, L. M., Hawkins, L. N., Frossard, A. A., Quinn, P. K., and Bates T. S., Carbohydrate-like composition of submicron atmospheric particles and their production from ocean bubble bursting, Proc. Nat. Acad. Sci. U.S.A., in press, 2010.

Sax, M., Zenobi, R., Baltensperger, U., and Kalberer, M.: Time resolved infrared spectroscopic analysis of aerosol formed by photo-oxidation of 1,3,5-trimethylbenzene and α-pinene, Aerosol Sci. Technol., 39, 822–830, 2005.

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, doi:10.1029/2006JD007076, 2006.

Seinfeld, J. H., and Pandis, S. N., Atmospheric Chemistry and Physics Second Edition, Wiley-Interscience, New York, NY, USA, 43–46, 2006.

Sellegri, K., Hanke, M., Umann, B., Arnold, F., and Kulmala M.: Measurements of organic gases during aerosol formation events in the boreal forest atmosphere during QUEST, Atmos. Chem. Phys., 5, 373-384, 2005.

Simpson, D., Yttri, K., Klimont, Z., Kupiainen, K., Caseiro, A., Gelencsèr, A., Pio, C., and Legrand, M.: Modeling carbonaceous aerosol over Europe. Analysis of the CARBOSOL and EMEP EC/OC campaigns, J. Geophys. Res., 112, D23S14, doi:10.1029/2006JD008158, 2007.

Slowik, J. G., Stainken, K., Davidovits, P., Williams, L. R., Jayne, J. T., Kolb, C. E., Worsnop, D. R., Rudich, Y., DeCarlo, P., and Jimenez, J. L.: Particle Morphology and Density Characterization by Combined Mobility and Aerodynamic Diameter Measurements. Part 2: Application to Combustion Generated Soot Particles as a Function of Fuel Equivalence Ratio, Aerosol Sci. Technol. 38, 1206–1222, 2004.

Slowik J. G., Stroud, C., Bottenheim, J. W., Brickell, P. C. , Chang, R. Y.-W., Liggio, J., Makar, P. A., Martin, R. V., Moran, M. D., Shantz, N. C., Sjostedt, S. J., van Donkelaar, A., Vlasenko, A., Wiebe, H. A., Xia, A. G., Zhang, J., Leaitch, W. R., and Abbatt, J. P. D.: Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests, Atmos. Chem. Phys. Discuss., 9, 18113-18158, 2009.

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

Surratt. J.D., Murphy, S. M., Kroll, J. H., Ng, N. L., Hildebrandt, L., Sorooshian, A., Szmigielski, R., Vermeylen, R., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Chemical Composition of Secondary Organic Aerosol Formed from the Photooxidation of Isoprene, J. Phys. Chem. A, 110, 9665-9690, DOI:10.1021/jp061734m, 2006.

Surratt, J. D., Kroll, J. H., Kleindienst, T. E., Edney, E. O., Claeys, M., Sorooshian, A., Ng, N. L., Offenberg, J. H., Lewandowski, M., Jaoui, M., Flagan, R. C., and Seinfeld, J. H.: Evidence for organosulfates in secondary organic aerosol, Environ. Sci. Technol., 41, 517–527, 2007.

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate formation in biogenic secondary organic aerosol, J. Phys. Chem, A., 112, 8345–8378, 2008.

Surratt, J. D., Chan, A.W.H., Eddingsaas, N.C., Chan, M.N., Loza, C.L., Kwan, A.J., Hersey, S.P., Flagan, R.C., Wennberg, P.O., Seinfeld, J.H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, Proc. Natl. Acad. Sci. in press, doi:10.1073/pnas.0911114107, 2009.

Szidat, S., Jenk, T. M., Synal, H.-A., Kalberer, M., Wacker, L., Hajdas, I., Kasper-Giebl, A., and Baltensperger, U.: Contributions of fossil fuel, biomass burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by 14 C, J. Geophys. Res., 111, D07206, doi:10.1029/2005JD006590, 2006.

Szmigielski, R., Surratt, J. D., Vermeylen, R., Szmigielska, K., Kroll, J. H., Ng, N. L., Murphy, S. M., Sorooshian, A., Seinfeld, J. H., and Claeys, M.: Characterization of 2-methylglyceric acid oligomers in secondary organic aerosol from the photooxidation of isoprene using trimethylsilylation and gas chromatography/ion trap mass spectrometry, J. Mass Spectrom., 42, 101– 116, 2007a.

Szmigielski, R., Surratt, J. D., Gómez-González, Y., Van der Veken, P., Kourtchev, I., Vermeylen, R., Blockhuys, F., Jaoui, M., Kleindienst, T. E., Lewandowski, M., Offenberg, J. H., Edney, E. O., Seinfeld, J. H., Maenhaut, W., and Claeys, M.: 3-methyl-1,2,3-butanetricarboxylic acid: An atmospheric tracer for terpene secondary organic aerosol, Geophys. Res. Lett., 34, L24811, doi:10.1029/2007GL031338, 2007b.

Takahama, S., Gilardoni, S., Russell, L. M., et al.: Classification of multiple types of organic carbon composition in atmospheric particles by scanning transmission X-ray microscopy analysis, Atmos. Environ., 41, 9435-9451, doi:10.1016/j.atmosenv.2007.08.051, 2007.

Takahama, S., Liu, S., and Russell L. M.: Coatings and clusters of carboxylic acids in carbon-containing atmospheric particles from spectromicroscopy and their implications for cloud-nucleating and optical properties . Geophys. Res., 115, D1, doi:10.1029/2009JD012622, 2010.

Tsigaridis, K. and Kanakidou, M.: Secondary organic aerosol importance in the future atmosphere, Atmos. Environ., 41, 4682–4692, doi:10.1016/j.atmosenv.2007.03.045, 2007.

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.

Vereecken, L. and Peeters, J.: Theoretical study of the formation of acetone in the OH initiated atmospheric oxidation of α±-pinene, J. Phys. Chem. A, 104, 11140-11146, 2000.

Vlasenko, A., Slowik, J. G., Bottenheim, J. W., Brickell, P. C., Chang, R. Y.-W., Macdonald, A. M., Shantz, N. C., Sjostedt, S. J., Wiebe, H. A., Leaitch, W. R.,

and Abbatt, J. P. D.: Measurements of VOCs by proton transfer reaction mass spectrometry at a rural Ontario site: Sources and correlation to aerosol composition, J. Geophys. Res., 114, D21305, doi:10.1029/2009JD012025, 2009.

Williams, B. J., Goldstein, A. H., Millet, D. B., Holzinger, R., Kreisberg, N. M., Hering, S. V., Allan, J. D., Worsnop, D. R., Jimenez, J. L., and White, A. B.: Chemical speciation of organic aerosol during ICARTT 2004: results from in-situ measurements, J. Geophys. Res., 112, D10S26, doi:10.1029/2006JD007601, 2007.

Chapter 3

Oxidized Organic Functional Groups in Aerosol Particles from Burning and Non-burning Forest Emissions at a High-Elevation Mountain Site

3.1 Abstract

Ambient particles collected at Whistler, British Columbia, at a high-elevation mountain peak site (2182 masl) during March to September 2009 on Teflon filters were measured by Fourier transform infrared (FTIR) spectroscopy for organic functional groups (OFG). The OM project mean and standard deviation for all samples was 3.2 ± 3.3 µg m^{-3}. The mean OM and maximum concentrations during the second period, May to September, (maximum of 13.6 µg m^{-3}) were significantly higher than during the first month (maximum of 1.2 µg m^{-3}). The OM concentrations measured during spring 2008 in the Whistler valley, at a site over a km lower than the peak location, were lower than the concentrations observed during a similar time period in 2009 at the peak. On average, organic hydroxyl, alkane, carboxylic acid, ketone, and amine, groups represented $31\% \pm 11\%$, $34\% \pm 9\%$, $23\% \pm 6\%$, $6\% \pm 7\%$, and $6\% \pm 3\%$ of OM, respectively. Ketone groups were not measured in the first month but contributed up to 27% of the average organic aerosol composition in the second period from 23 May 2009 to 10 September 2009. Positive matrix factorization (PMF) analysis was used to separate combustion and forest sources of the measured organic aerosol. The forest source was made-up of secondary organic aerosol (SOA) from burning and non-burning forest-derived volatile organic compounds (VOCs).

3.2 Introduction

There is strong evidence that burning and non-burning forest emissions are important contributors to primary and secondary organic mass (OM) (Bond et al., 2004; Hallquist et al., 2009). Bond et al. (2004) name biomass burning (BB) as the largest (42%) combustion source of primary organic carbon, outweighing both fossil fuel (38%) and biofuel (20%) combustion. Bond and colleagues estimate BB emissions account for 31-45 Tg Cyr^{-1} of global primary organic aerosol (POA). Gas phase compounds also result in significant aerosol formation (secondary organic aerosol, SOA). Globally, biogenic volatile organic compounds (BVOC) emissions may be 10 times greater than anthropogenic VOC emissions (Seinfeld and Pandis, 2006). Oxidation of BVOCs yields a large biogenic contribution to SOA, with estimates ranging from 12 to 70 Tg Cyr^{-1} (Hallquist et al., 2009).

These significant forest-related emissions present a complex issue for climate science and climate prediction due to a number of possible feedbacks. Large uncontrollable fires are expected to increase with climate change (IPCC, 2007) due to reduced rainfall and increased temperatures. Bowman et al. (2009) discuss how fires in turn influence climate due to their large greenhouse gas (CO_2 emissions equal to 50% of those from fossil fuel combustion) and aerosol particle (40% of black carbon, along with large POA emissions discussed) emissions. Bowman and colleagues urge future IPCC assessments to include specific analyses of the role of forest fires because of their large emissions and potential for positive feedbacks. Similarly, Kulmala et al. (2004) explores feedbacks between climate and non-burning forest emissions. They

present evidence that increased temperatures and CO_2 concentrations will act to fertilize forests, which will in turn create a large BVOC source and ultimately result in a cooling effect from the increased biogenic aerosol.

The radiative impacts of aerosol particles are altitude-dependent (Penner et al., 2003). Chuang et al. (2002) estimated the first indirect forcing associated with organic aerosol from BB to be - 1.16 Wm^{-2}. Yet, injection of aerosol particles higher in the atmosphere increases particle lifetime and thus ability to influence climate. Higher-altitude injections of organic BB aerosol may in general enhance the negative longwave forcing (Penner et al., 2003). Additionally, global chemical transport models under-predicted organic aerosol in the free troposphere by up to 100 times when compared to ambient measurements (Heald et al., 2005).

Here, we use ambient measurements and statistical techniques to present evidence for organic functional groups (OFG) associated with both burning and non-burning forest emissions. At a lower free troposphere, high-elevation mountain site in Whistler, British Columbia, in spring and summer 2009 FTIR spectroscopy measurements were used to identify the sources and composition of the OM. Separate day, night, total, and submicron samples allow for several comparisons. The ambient conditions provide an opportunity to examine burning and non-burning forest emissions together. We also discuss possible separation of these sources.

3.3 Methods

Environment Canada (EC) maintains a measurement platform at Whistler Peak in the lower free troposphere (2182 masl) established in spring 2002 (Macdonald et al., 2006). One of the many objectives of the site is to monitor changes in the composition and concentration of particulate pollutants entering North America from Asia. Atmospheric particles were sampled and measured by Fourier transform infrared (FTIR) spectroscopy and X-ray fluorescence (XRF) techniques for organic functional groups (OFG) and elemental composition in Whistler, BC, at the high-elevation Whistler Peak site during April, May, June, and July of 2009.

FTIR spectroscopy provides OFG concentrations, including alkane, carboxylic acid, organic hydroxyl, amine, ketone, alkene, and aromatic groups, through chemical bond-based measurements (Russell et al., 2009). Over a sampling period of approximately three days, five filter samples were collected, with three measurements collected simultaneously on 37 mm Teflon filters (Pall Inc.). The filter collection was divided by size into total and submicron filters, and by day and night samples with an automated switch occurring at 6:30 am and 6:30 pm PST daily. The total samples were collected from an inlet with no size-selection. Total samples can be considered to include collection of particles up to 10 μm with the absolute upper limit dependent on ambient conditions, such as wind speed and precipitation. Submicron samples were collected downstream of a 1μm impactor (Brechtel Manufacturing, Inc., Hayward, CA). Aerosol particles were collected on one filter during both day and night and on May 29, 2009 this filter was changed from submicron to total size. During sampling

all filters were kept in a freezer to reduce losses over the multiple day exposure period. Samples were kept frozen before analysis by FTIR spectroscopy and allowed to equilibrate in a temperature and humidity controlled cleanroom environment for 24 hours before FTIR spectroscopic analysis. As described in Chapter 2, FTIR sample spectra were measured with a Tensor 27 spectrometer (Bruker, Billerica, MA), and baselined and fitted with peaks to identify OFG using the method described by Russell et al. (2009). Alkene, aromatic, and organonitrate groups were below detection limit for all samples. Organosuflate groups were above detection limit during only one three day-long sampling period.

XRF analysis provides quantitative measurements of elemental composition. 90 of the same filter samples used for FTIR, the majority of which are submicron samples, were sent to Chester LabNet (Tigard, Oregon) for elemental analysis of elements Na and heavier (Maria et al., 2003).

The sampling campaign was nearly continuous for 4.5 months during two sampling periods separated by a month when the sampling site was inaccessible. 26 March 2009 to 27 April 2009 and 23 May 2009 to 10 September 2009 are referred to as the first and second sampling periods, respectively.

3.4 Results and Discussion

3.4.1 OFG composition

The OM was composed of alkane, carboxylic acid, ketone, organic hydroxyl, and amine groups and was highly variable throughout the project for all sample types

as shown in Fig. 3.1. The OM project mean and standard deviation for submicron samples, total samples, and both submicron and total samples together, are 3.1 ± 3.2 $\mu g\ m^{-3}$, $3.3 \pm 3.2\ \mu g\ m^{-3}$, and $3.2 \pm 3.3\ \mu g\ m^{-3}$, respectively. The mean OM of 4.1 ± 3.5 $\mu g\ m^{-3}$ during the second period is significantly higher than the $0.6 \pm 0.3\ \mu g\ m^{-3}$ mean concentration measured during the first month. This difference in the periods is emphasized by a comparison of the maximum concentrations of $1.2\ \mu g\ m^{-3}$ and 13.6 $\mu g\ m^{-3}$ during the first and second periods, respectively. As seen in Fig 3.1, the largest OM concentrations for all sample types occurred during three samples from 28 July 2009 to 8 August 8 2009. In general, the variability in OM during the project is similar across the sample types. Organosulfate groups were above detection limit during only three samples in one sampling period (marked in Fig 3.1) and represented 2 to 9% of OM when present. Two periods during which total OM was significantly larger than submicron OM are marked by a red bar in Fig 3.1 and will be discussed further in Section 3.4.2.

The OFG composition as OM fraction is shown in Fig 3.2. On average, organic hydroxyl, alkane, carboxylic acid, ketone, and amine, groups represented $31\% \pm 11\%$, $34\% \pm 9\%$, $23\% \pm 6\%$, $6 \pm 7\%$, and $6\% \pm 3\%$ of OM, respectively. Acid group fraction and alkane group fraction are strongly correlated to each other ($r = 0.82$) and mildly anti-correlated to organic hydroxyl group fraction ($r = -0.74$). Ketone groups were observed in the second time period only. In samples during the second period that had ketone groups above detection limit, ketone groups composed up to 27% of OM with an average of 14% of OM, indicating that the conditions favoring ketone

group formation were significantly different from those that did not. Overall, the OFG composition is similar for corresponding day and night, and total and submicron samples.

3.4.2 Size and diurnal comparison

Simultaneous total and submicron aerosol collection and analysis for OFG composition allows for a calculation of supermicron organic particles (supermicron = total-submicron). The comparisons between the submicron and total OM and OFGs for both day and night are shown in Fig. 3.3. In all but a few samples, the total and submicron OM measurements compare very well and within the uncertainties of the measurements. The average total to submicron OM ratio is 0.99 with a correlation coefficient (r) equal to 0.97. Total and submicron OM are indistinguishable during most samples, suggesting that little organic mass is present in supermicron particles. No clear differences exist between day and night samples. As shown in Fig. 3.4, the concentrations of each OFG are similar through day and night samples and there is no consistent trend across OFG. That is, we do not see one OFG dominating in day or night samples as would be expected if local photochemical reactions were controlling particle composition.

During two periods, 17 August to 21 August (night only) and 24 August to 31 August, a difference between total and submicron OM measurements was observed, indicating OM was present in supermicron particles. The composition of the supermicron aerosol was calculated by subtracting the integrated submicron OFG

measurements from the total OFG measurements. A comparison between the submicron and supermicron OFG concentrations is shown in Fig. 3.5. In these three samples, the submicron OM concentrations are greater than the supermicron concentrations. Supermicron and submicron OFG composition is similar in all but the 17 August to 21 August night sample. Although these periods are close in time, supermicron aerosol was not observed during the sample separating them. It is interesting to note that the 21 August to 24 August three-day sample was the only period for which organosulfate groups were above detection limit. The combination of organosulfate groups and supermicron organic particles suggests that air masses sampled from 17 August to 31 August may have been influenced by different sources than those controlling the particle composition during most of the project.

The total and submicron OM are indistinguishable during all samples with few exceptions suggesting supermicron particles contain little organic mass. This observation is consistent with non-local sources. Similarly, a lack of diurnal variation suggests that the measured aerosol is non-local as temporal variation in source is expected to be lost in aged air masses. Vertical motion needed to bring regional aerosols to the peak altitude may act similar to long range transport processes during which supermicron particles are not as efficiently transported and diurnal variations in sources are smeared. Non-local aerosol sources are consistent with previous studies at the Whistler Peak location and are expected for this high-altitude, relatively remote site (Sun et al., 2009; Leaitch et al., 2009).

3.4.3 Influence of regional wildfires

A prominent feature of many Whistler 2009 FTIR spectra was a pair of sharp peaks at 2920 cm^{-1} and 2850 cm^{-1}. These peaks have been observed and briefly described by Hawkins and Russell (2010) (HR2010). The authors observed this same spectral feature in certain samples collected at the Scripps pier during summer 2008 and in the identified biomass burning Positive Matrix Factorization (PMF) factor. The sharpness of the peaks, which are located at the sp^3 C-H stretching absorption from methylene groups, is due to the absorption of repeating methylene units. HR2010 attribute these sharp methylene peaks to long-chain plant cuticle wax detritus, which are lofted in large wildfires. The authors suggest a prominence of this spectral feature can separate wildfire biomass burning from smaller fires and other types of burning that are not expected to contain the plant waxes.

The BC 2009 wildfire season was exceptionally severe in its length, number of fires, and area burned. Figure 3.6 shows the forest fire hotspot map for the 2009 forest fire season compiled by Natural Resources Canada (www.nrcan.gc.ca) from advanced Very High Resolution Radiometer (AVHRR) imagery, Moderate Resolution Imaging Spectroradiometer (MODIS) imagery, and Along Track Scanning Radiometer (ATSR) World Fire Atlas and the large active fires on July 31, 2009 in the Western US as reported by National Interagency Fire Center. According to the BC Wildfire Management branch, the 2009 fire season had one the highest number of fires on record, with a total of 3,040 fires due to "exceptional weather and fire behavior conditions". During several time periods in the 2009 project smoke was visible at the

sampling site. Two separate fires occurred on Blackcomb mountain (less than 20 km from Whistler Peak) during 30 July to 8 August, one of which caused an evacuation of Whistler Village. During this fire period, the OM concentrations were at a maximum and the sharp methylene peaks were prominent in all ambient spectra.

3.4.4 Positive Matrix Factorization of FTIR organic spectra

The aerosol composition of any given sample is a complex mixture of components from multiple sources. General aerosol source types were identified by application of Positive Matrix Factorization (PMF, using PMF2 software purchased from P. Paatero, Helsinki University, based on Paatero and Tapper (1994)) to the FTIR submicron spectra. This method has been used previously on FTIR spectra to identify and separate varying sources (Russell et al., 2009; Hawkins and Russell, 2010; Schwartz et al., 2010). Rotation parameter FPEAK of –1.2 to 1.2 by 0.4 and two, three, four, and five factor solutions were examined. A lack of differences between the source spectra for different rotations suggest that the PMF solutions are robust and independent of rotation; FPEAK = 0 was selected for further analysis. The source factor composition and factor contribution to the submicron aerosols for a two factor PMF solution are shown in Fig. 3.7.

The PMF analysis of organic spectra allows for identification and quantification of multiple types of organic aerosol, indicating multiple types of sources influencing the measured aerosol at the peak location. Factor 1, shown in red in Fig. 3.7, is identified as a fossil fuel combustion factor. Spectrally it resembles the

combustion factor identified at the Whistler mid-mountain site (Schwartz et al., 2010), as shown in Fig. 3.8, and other combustion factors identified in several other field projects from diverse locations (Russell et al., 2009, Liu et al., 2009; Hawkins and Russell, 2010). This spectrum has the characteristic ammonium absorbance that is observed throughout the combustion factors identified by PMF on FTIR spectra. Factor 1 is correlated mildly ($0.5 < r < 0.75$) with XRF S and consists mostly of alkane and acid, with no ketonic constituent. The combustion source likely includes regional emissions from Northwest cities such as Vancouver and pollutants from long range transport of Asian emissions, consistent with measurements of sulfate at Whistler Peak by Sun et al. (2009).

Factor 2 has large alcohol and ketone group fractions and the spectrum includes the sharp methylene peaks previously discussed. These peaks suggest that this factor may represent a BB source. The presence of ketone is supportive of BVOC oxidation. Schwartz et al. (2010) in Table 2 summarizes several laboratory chamber studies in which monoterpene and isoprene oxidation products contain ketone groups. HR2010 also observed a significant fraction of ketone in their BB fraction. As seen in Fig. 3.7, the contrast between the fractional contribution of Factors 1 and 2 to the measured OM is drastically different during the first and second periods. While Factor 1 is highly prominent in the low OM March and April period, Factor 2 is the main source of the high OM May to September period characterized by higher temperatures and sporadic fires. For these reasons Factor 2 is labeled as "forest".

For a number of reasons it appears that the forest factor may have both burning and non-burning sources. A large fractional contribution of ketone has not been observed in combustion or marine FTIR PMF components, but has been observed in both BB and biogenic sources (Hawkins and Russell, 2010; Schwartz et al. 2010; Bahadur et al., 2010). While the contribution of the forest factor is small in the first period, before the fire season began, its presence during this period suggests the forest factor may have a non-burning component. Although it is very likely that the wildfire emissions dominate the measured organic aerosol during the second sampling period, non-burning emissions are also a likely contributor. The high temperatures that contributed to the large number of forest fires are also likely to increase the biogenic emissions (Helmig et al., 2006). To investigate a possible separation of burning and non-burning forest emissions we expand the two-factor solution to three factors.

In the three-factor solution the forest factor splits into two factors (referred to as "parts") while the combustion factor remains largely unchanged. This suggests that there was higher variability among components in the forest factor than in the combustion factor. In addition, the similarity of the two combustion factors both in composition and in temporal contribution to OM over the whole campaign as shown in Fig. 3.7 is noteworthy. This robustness in the combustion factor suggests combustion is a consistent source of organic aerosol to Whistler Peak and is not as highly dependent on season as other sources may be. The two and three factor source spectra for this project and relevant previously reported factor spectra are shown together in Fig 3.8.

The spectrum of one of the two forest factor parts closely resembles the BB source spectra reported by HR2010 as seen in Fig 3.8c and for this reason it is referred to as Factor 2BB. The Factor 2BB spectra retains the sharp methylene double peaks noted in the forest factor, and the relative contribution of these peaks to other OFG absorbing regions increases relative to in the forest factor. The ketone group contribution of Factor 2BB also increases and is similar to the ketone fraction reported by HR2010 (25%). Both Factor 2BB and the forest factor are highly correlated to Br, a tracer for BB (Andreae et al., 1996).

The other forest factor part, which should represent the non-burning forest emissions if the PMF three-factor solution was able to separate the forest parts successfully, is referred to as Factor 2Bio. As expected, the contribution of this factor to the first period when there was no fires is higher relative to Factor 2BB. Supporting the idea that this factor represents a non-burning biogenic source, the Factor 2Bio spectrum resembles the high alcohol "Biogenic Part 1" identified at the mid-mountain Whistler site by Schwartz et al. (2010). Biogenic Part 1 was correlated to monoterpenes and dust. Factor 2Bio has a ketone contribution unlike Biogenic Part 1, but similar to the combined Whistler 2008 biogenic factor. The methylene peaks remain in Factor 2Bio. As HR2010 attribute these peaks to plant waxes it would not be inconsistent to observe plant waxes is non-burning forest emissions. Yet, these peaks were not identified previously in the Whistler mid-valley location and are probably more consistent with a POA component of Factor 2Bio. Factor 2Bio is mildly correlated with Br.

Factor 2BB and Factor 2Bio are strongly correlated (r = 0.88). Because high temperature is critical to both burning and non-burning forest emissions, the two factors appear to be mostly co-emitted. Due to this correlated relationship between burning and non-burning emissions, separation by PMF analysis may be difficult. Some observations suggest that Factor 2Bio and Factor 2BB may not represent separation. During the large local fire period of 30 July to 8 August the relative contribution of Factor 2Bio increases rather than Factor 2BB. Factor 2BB, in small contributions, is observed during time periods of no to little wildfires such as the first period and early July. The methylene peaks in Factor 2Bio may represent either poor separation or the presence of non-burning POA. Since the forest parts are correlated to each other drawing conclusions from correlations of trace metals also may not be completely clear.

3.4.5 Mid-mountain and peak comparison

Through a comparison between the Whistler mid-valley 2008 (1020 masl) and a period of Whistler Peak 2009 measurements the impact of elevation (and geography) on measured OFG concentrations and on aerosol influences can be examined. Whistler 2008 submicron ~ 12 hr measurements were collected for a month from 16 May to 16 June 2008. The 2008 submicron OM at the valley site ranged from less than 0.5 to 3.1 μg m^{-3}, with a project mean and standard deviation of 1.3 ± 1.0 μg m^{-3}. The 2009 measurements from 23 May to 17 June (the most comparable time period) ranged from less than 1.3 to 5.1 μg m^{-3}, with a project mean and standard deviation of 3.6 ±

1.6 μg m^{-3}. The 2009 peak OM concentrations were significantly higher than those measured at the mid-valley site in 2008. The OFG composition for 2008 and the 2009 period were respectively 34% and 23% organic hydroxyl, 33% and 37% alkane, 23% and 26% carboxylic acid, 6% and 9% ketone, and 5% and 5% amine groups. One notable difference between the sites is that trees surround the 2008 mid-mountain site while the Whistler Peak site is above the tree line. In addition to the elevation difference, differences between the 2008 and 2009 measurements may be a result of the early 2009 fire season. In contrast to 2009, the 2008 fire season started slowly due to cool spring temperatures and Schwartz et al. (2010) did not observe a BB influence for the Whistler 2008 study.

3.5 Conclusions

The ambient OM concentrations measured at Whistler Peak during spring and summer 2009 varied from 0.06 to 13.6 μg m^{-3} with a project mean and standard deviation of 3.2 ± 3.3 μg m^{-3}. The OM concentrations, which reached 1.2 μg m^{-3} during the first period of sampling from March to April, were consistently lower than the concentrations from May to September. Ketone groups were not measured in the first period but contributed up to 27% of the average organic aerosol composition in the second period. The 2009 forest fire season in BC set a record for most recorded fires while the total area burned was well above average. The fire season was also longer than usual with notable fires in September and multiple fires burning as early as May due to abnormally high temperatures and low precipitation.

HR2010 suggest the sharp methylene peaks observed in FTIR spectra may be used as an indicator of the influence of large wildfires on the chemical composition of the measured aerosol. This hypothesis is further supported by the presence of these peaks and the large number of wildfires during the 2009 project. However, the presence of methylene peaks in two PMF factors (Factor 2BB and 2Bio) suggest either co-emission or co-production of the two components, or chemical similarity with regard to the hydrocarbon bonding in the emitted compounds from the two proposed sources.

The OM concentrations measured during spring 2008 in the Whistler valley, at a site over a km lower than the peak location, were lower than the concentrations observed during a similar time period at the peak in 2009. The average OFG composition of the submicron aerosol was in general similar between the two sites. Most notably, 11% by mass less organic hydroxyl groups were observed in the peak measurements. Both the OM concentrations and composition may have been influence by the early 2009 fire season.
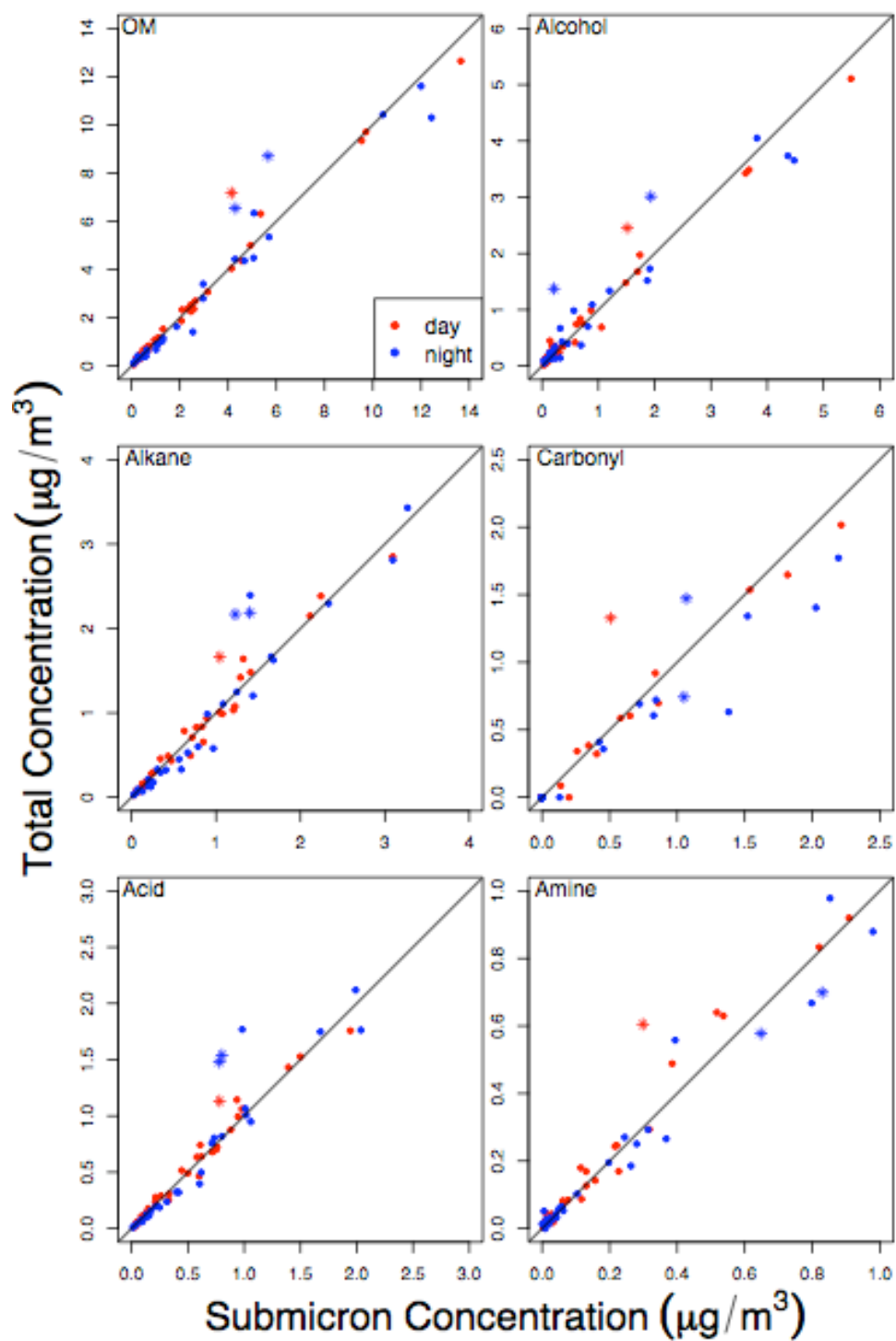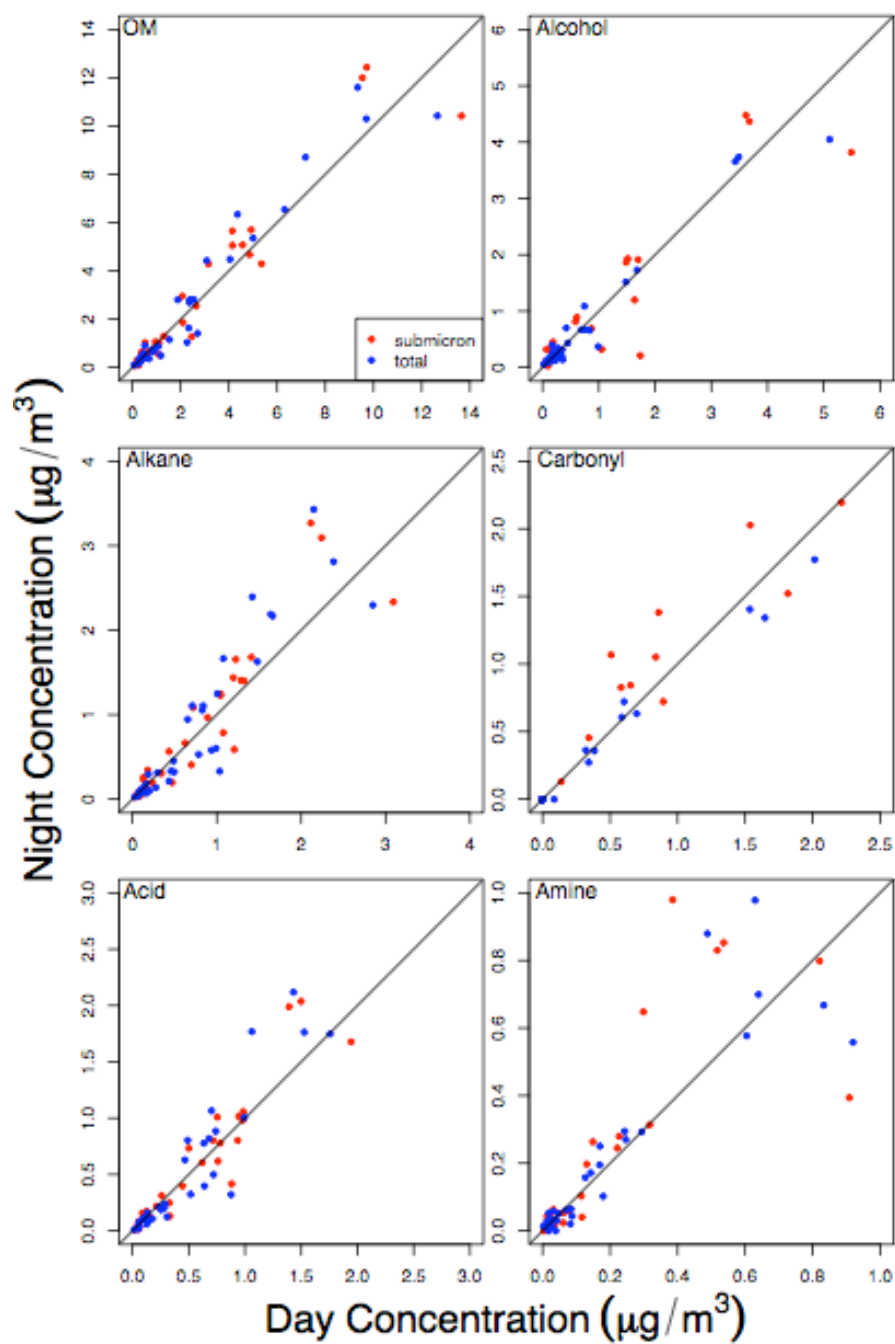
Figures
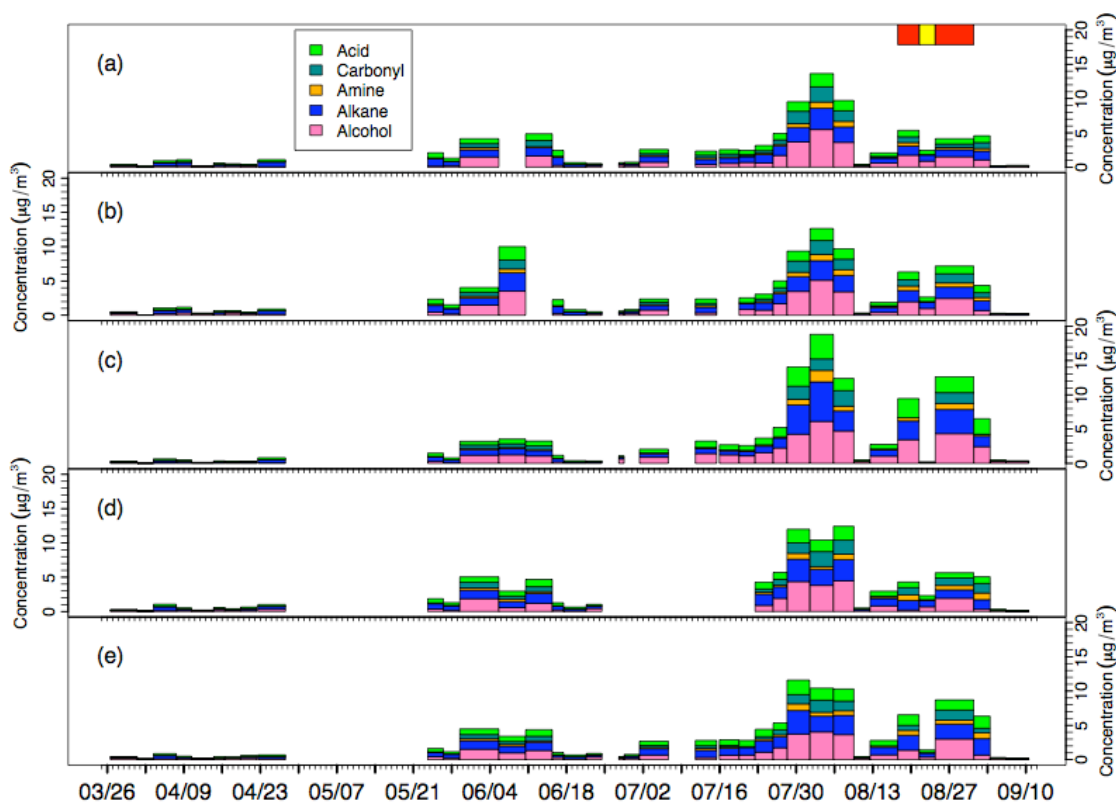
Figure 3.1: Time series of OM and OFG as stacked bars: organic hydroxyl (pink), alkane (blue), ketone (teal), amine (orange), acid (green) in a) day submicron, b) day total, c) day and night (submicron before May 29, 2009, and total post that date), d) night submicron and, e) night total aerosol during the 2009 sampling period. The color bar on top shows periods when supermicron aerosol was measured (red) and organosulfate groups were above detection limit (yellow).
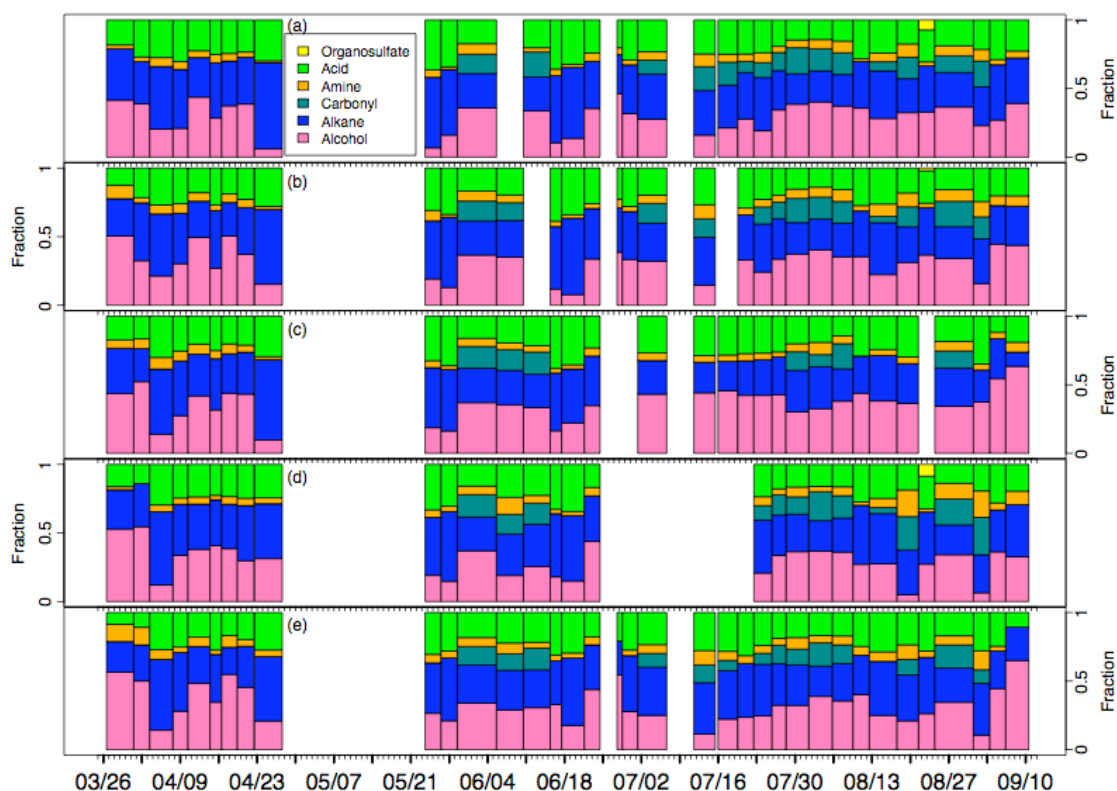
Figure 3.2: Time series of OFG fraction as stacked bars with colors as in Fig. 3.1 (organic hydroxyl (pink), alkane (blue), ketone (teal), amine (orange), acid (green), organosulfate (yellow)) in a) day submicron, b) day total, c) day and night (submicron before May 29, 2009, and total post that date), d) night submicron and, e) night total aerosol for OM above detection limit samples.
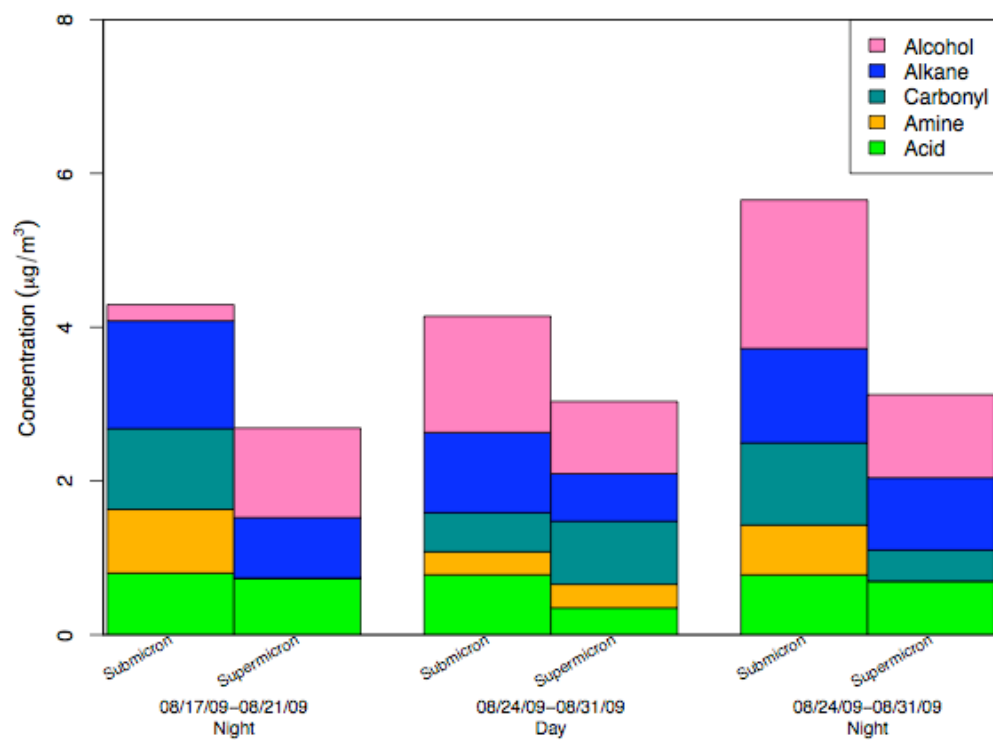
Figure 3.3: Comparison between total and submicron sample types by OFG including both day (red) and night (blue) samples. Asterisks label samples with detectable supermicron organic aerosol included in Fig. 3.5.
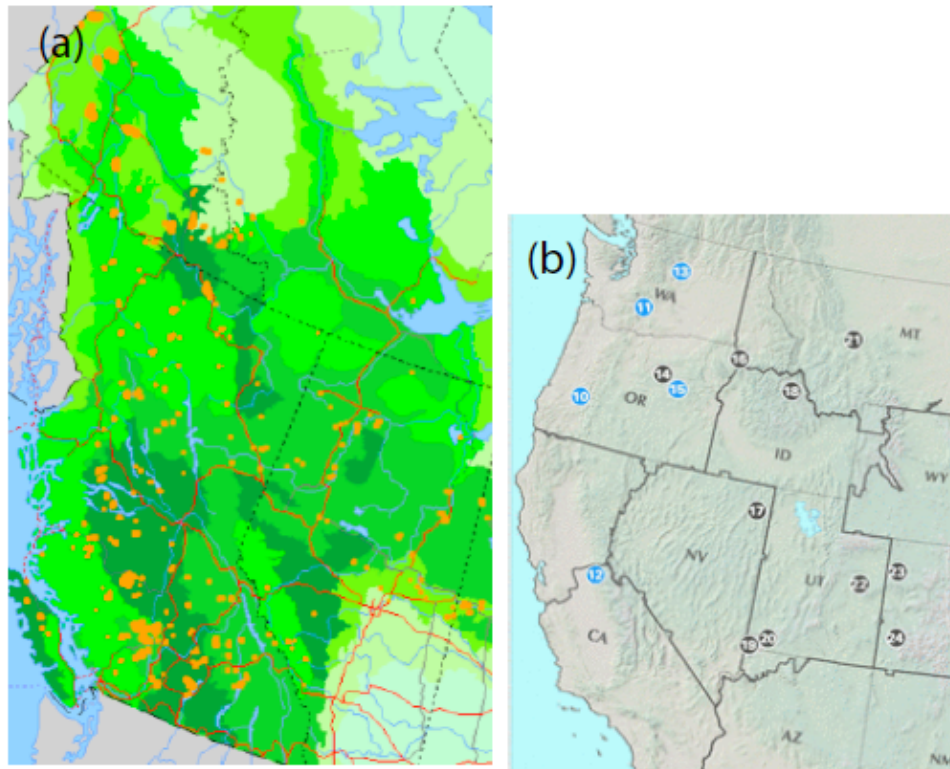
Figure 3.4: Comparison between day (6:30 AM PST to 6:30 PM PST) and night sample types by OFG including both submicron (red) and total (blue) samples.

Figure 3.5: A comparison between the submicron (left) and supermicron (right) OM and OFG for the periods in which there was a detectable difference between total and submicron samples.

Figure 3.6: Maps of fires a) in Western Canada showing fire hotspots from 2009 fire season. The hotspots are determined by infrared satellite images and are mapped as part of the Fire Monitoring, Mapping and Modeling System (Fire M3) (Natural Resources Canada, www.nrcan-rncan.gc.ca) b) Map of Western US showing the large wildfires active on July 31, 2009 (National Climate Data Center, www.ncdc.noaa.gov).
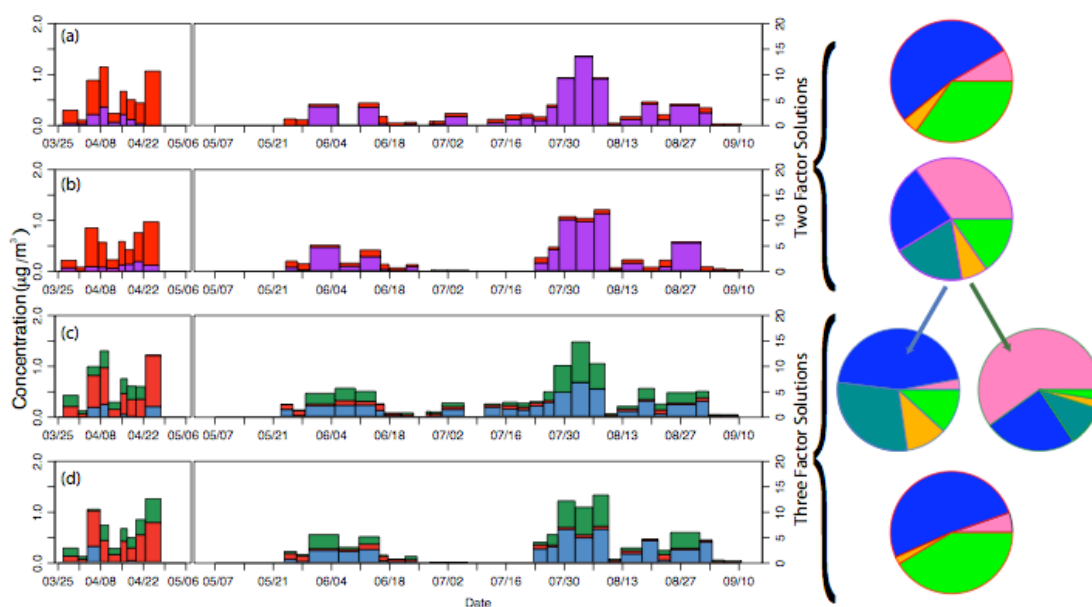
Figure 3.7: Time series of submicron OM reconstructed from a) day samples and b) night samples for two-factor PMF with Factor 1 (red) and Factor 2 (purple). Three-factor PMF is shown for c) day samples and d) night samples with Factor 1 (red), Factor 2Bio (dark green), and Factor 2BB (blue). In the right panel the OFG composition of the factors are represented with organic hydroxyl (pink), alkane (blue), ketone (teal), amine (orange), and acid (green). Factor 2 splits into Factor 2BB (left pie) and Factor 2Bio (right pie). Each pie outline color corresponds to the PMF factor in the bar plot. Note the different scale axis for the first and second periods.
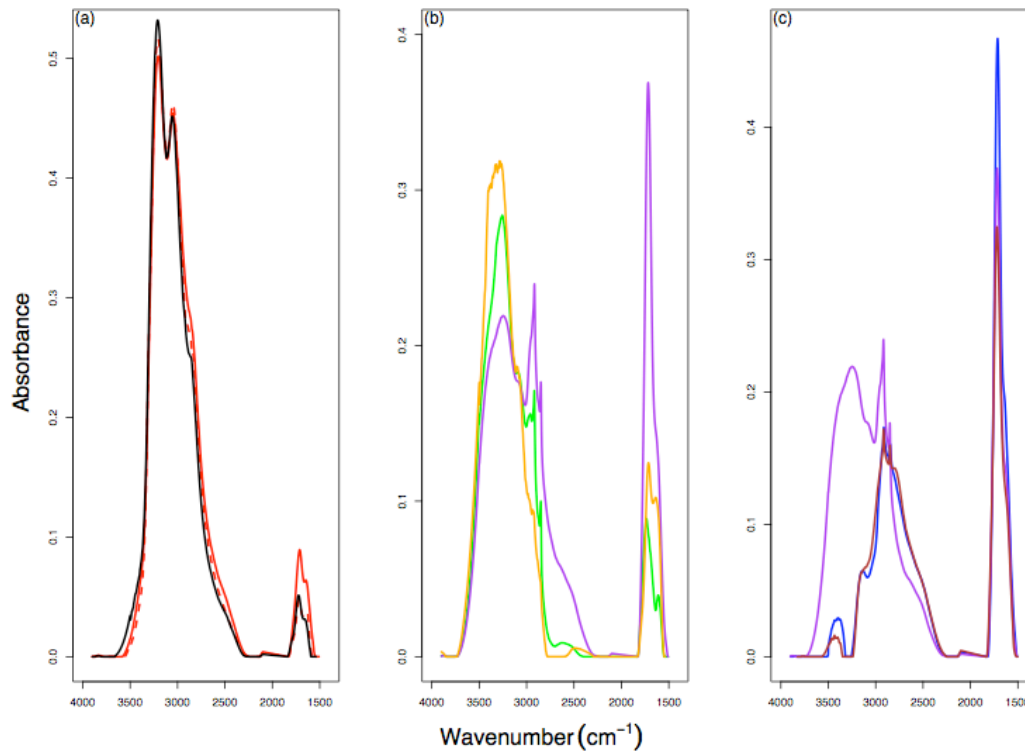
Figure 3.8: Comparison of two factor solution, three factor solution, and previously reported PMF source factor spectra separated by factor types. a) Combustion factors including three factor (dash line) and two factor spectra in red and Whistler mid-mountain combustion factor from Schwartz et al. 2010 (black). b) Biogenic factors including Factor 2Bio (green), Factor 2 Forest factor (purple), and Biogenic Part 1 from Schwartz et al. (2010). c) BB factors including Factor 2BB (blue), Factor 2 Forest factor (purple), and BB factor (brown) from Hawkins and Russell (2010).

References

Bahadur, R., Uplinger, T., Russell, L.M., Sive, B.C., Cliff, S.S., Millet, D.B., Goldstein, A., and Bates, T.S.: Phenols in Northeastern US Submicron Aerosol Particles from Seawater Sources, Environ. Sci. Technol., in press, 2010.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research–Atmospheres 109 (D14), 14203–14203, 2004.

Bowman, D.M.J.S., Balch, J.K., Artaxo, P., Bond, W.J., Carlson, J.M., Cochrane, M.A., D'Antonio, C.M., DeFries, R.S., Doyle, J.C., Harrison, S.P. and others: Fire in the Earth system, Science, 324, 5926, 481, 2009.

BC Wildfire Management branch, Summary of 2009 BC Fire Season, (http://bcwildfire.ca/History/Summary.htm).

Chuang, C. C., J. E. Penner, J. M. Prospero, K. E. Grant, G. H. Rau, and K. Kawamoto, Cloud susceptibility and the first aerosol indirect forcing: Sensitivity to black carbon and aerosol concentrations, J. Geophys. Res., 107(D21), 4564, doi:10.1029/2000JD000215, 2002.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, proper ties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5235, 2009.

Heald, C. L., Jacob, D. J., Park, R. J., Russell, L. M., Huebert, B. J., Seinfeld, J. H., Liao, H., and Weber, R. J.: A large organic aerosol source in the free troposphere missing from current models, Geophys. Res. Lett., 32, L18809, doi: 10.1029/2005GL023831, 2005.

Hawkins, L. N., Russell, L. M., Covert, D. S., Quinn, P. K., and Bates T. S.: Carboxylic Acids, Sulfates, and Organosulfates in Processed Continental Organic Aerosol over the Southeast Pacific Ocean during VOCALS-REx 2008, Geophys. Res. Lett., in press, doi:10.1029/2009JD013276, 2010.

Hawkins, L. N. and Russell L. M.: Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires, in review, available for review at http://aerosols.ucsd.edu/publications.html), 2010.

Helmig, D, Ortega, J., Duhl, T., Tanner, D., Guenther, A., Harley, P., Wiedinmyer, C., Milford, J. and Sakulyanontvittaya, T.: Sesquiterpene emissions from loblolly pine and their potential contribution to biogenic aerosol formation in the Southeastern US Atmospheric Environment, 40, 22, 4150-4157, 2006.

IPCC: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.

Kulmala, M., Suni, T., Lehtinen, K. E. J., Dal Maso, M., Boy, M., Reissell, A., Rannik, U., Aalto, P., Keronen, P., Hakola, H., Back, J., Hoffmann, T., Vesala, T., and Hari, P.: A new feedback mechanism linking forests, aerosols, and climate, Atmos. Chem. Phys., 4, 557–562, 2004.

Leaitch, W. R, Macdonald, A. M., Anlauf, K. G., Liu, P. S. K., Toom-Sauntry, D., Li, S.-M., Liggio, J., Hayden, K., Wasey, M. A., Russell, L. M., Takahama, S., Liu, S., van Donkelaar, A., Duck, T., Martin, R. V., Zhang, Q., Sun, Y., McKendry, I., Shantz, N. C., and CubisonM.,: Evidence for Asian dust effects from aerosol plume measurements during INTEX-B 2006 near Whistler, BC, Atmos. Chem. Phys., 9, 3523-3546, 2009.

Liu, S., Takahama, S., Russell, L. M., Gilardoni, S., and Baumgardner, D.: Cluster and Positive Matrix Factorization Analysis of Organic Functional Groups in Fine Particles During the MILAGRO 2006 Campaign, Atmos. Chem. Phys., 9, 6849-6863, 2009.

Macdonald, A. M., Anlauf, K. G., Leaitch, W. R., and Liu, P. S. K.: Multi-year chemistry of particles and selected traces gases at the Whistler High Elevation Site, EOS Trans., 87(52), AEB-0719, 2006.

Maria, S. F., Russell, L. M., Turpin, B. J., Porcja, R. J., Campos, T. L., Weber, R. J., Huebert, B. J.: Source signatures of carbon monoxide and organic functional groups in Asian Pacific Regional Aerosol Characterization Experiment (ACE-Asia) submicron aerosol types. Journal of Geophysical Research–Atmospheres 108, 8637, 2003.

National Oceanic and Atmospheric Administration, National Climate Data Center, State of Climate, U.S. Wildfire, http://www.ncdc.noaa.gov/sotc/index.php.

Paatero, P. and Tapper, U.: Positive Matrix Factorization: A non-negative factor model with optimal utilization of error estimates of data values, Environmetrics,

5, 111–126, 1994.

Penner, J. E., Zhang, S. Y., and Chuang, C. C.: Soot and smoke aerosol may not warm climate, J. Geophys. Res., 108(D21), 4657, doi:10.1029/2003JD003409, 2003.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated Fraction and Mass of Organic Aerosol from Direct Emission and Atmospheric Processing Collected on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, Journal of Geophysical Research - Atmospheres, 114(D00F05), doi10.1029/2008JD011275, 2009.

Schwartz, R. E., Russell, L. M., Sjostedt, S. J., Vlasenko, A., Slowik, J. G., Abbatt, J. P. D., Macdonald, A.M., Li, S-M., Liggio, J., Toom-Sauntry, D., and Leaitch, W. R.: Biogenic Oxidized Organic Functional Groups in Aerosol Particles from a Mountain Forest Site and their Similarities to Laboratory Chamber Products, Atmos. Chem. Phys. Discuss., 10, 1–34, 2010.

Seinfeld, J. H., and Pandis, S. N., Atmospheric Chemistry and Physics Second Edition, Wiley- Interscience, New York, NY, USA, 43-46, 2006.

Sun, Y., Zhang, Q., Macdonald, A.M., Hayden, K., Li, S-M., Liggio, J., Liu, PSK., Anlauf, K.G., Leaitch, W.R., Steffen, A.. Cubison, M., Worsnop, D. R., van Donkelaar, A., and R. V. Martin, R.V.: Size-resolved aerosol chemistry on Whistler Mountain, Canada with a high-resolution aerosol mass spectrometer during INTEX-B Atmos. Chem. Phys., 9, 3095–3111, 2009.

Chapter 4

Conclusion

Aerosol particles can adversely affect human health and drive many key aspects of the atmospheric and climate systems. Aerosols contribute to the largest uncertainty in climate prediction and the mechanisms that lead to adverse health effects from aerosols have not been resolved (IPCC, 2007; Pöschl, 2005). Organic compounds constitute a large portion of aerosol mass, yet this fraction is poorly characterized. Burning and non-burning forest emissions are important contributors to global primary and secondary organic mass (OM) (Bond et al., 2004; Hallquist et al., 2009). In an effort to address the complexity of organic aerosols and in particular the impact of forest emissions, aerosol particles were collected in Whistler, British Columbia, at a mid-mountain site in spring 2008 and a peak site in spring and summer 2009.

The organic functional group composition of the collected aerosol was measured by Fourier transform infrared (FTIR) spectroscopy. Classifying organic composition by functional group is a useful approach to tackle the complexity of organic compounds since degree of oxidation and bond types relate to solubility. FTIR spectroscopy allows for identification and quantification of carbonyl groups, a functional group of interest for burning and non-burning forest aerosols. As described in Chapters 2 and 3, ambient submicron particles were collected on 37 mm Teflon filters (Pall Inc.). Additionally, larger particles (up to 10 μm) were collected at the peak site. FTIR spectra were measured with a Tensor 27 spectrometer (Bruker,

Billerica, MA) and fit with polynomial baselines and peaks associated with each organic functional group, including alkane, carboxylic acid, organic hydroxyl, amine, organosulfate, and non-acidic carbonyl (ester or ketone) group concentrations (Maria et al., 2002; Gilardoni et al., 2007; Russell et al., 2009).

The mid-mountain (1020 masl) 16 May to 16 June 2008 project and the composition of the non-burning biogenic secondary organic aerosol (SOA) were investigated. In addition to FTIR measurements, atmospheric particles and gases were sampled by a suite of co-located instruments including high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), proton-transfer reaction mass spectrometry (PTR-MS), X-ray fluorescence (XRF), single particle soot photometer (SP2), Scanning Transmission X-Ray Microscopy with Near-Edge Absorption Fine Structure (STXM-NEXAFS), and gas phase (CO, O_3, NO_x). During this project OM ranged from less than 0.5 to 3.1 μg m^{-3}, with a project mean of 1.3 $\pm$ 1.0 μg m^{-3} and 0.21 $\pm$ 0.16 μg m^{-3} for OM and sulfate, respectively. On average, organic hydroxyl, alkane, and carboxylic acid groups represented 34%, 33%, and 23% of OM, respectively.

About 65% of OM during the month-long study and over 80% during identified periods of high monoterpene and isoprene concentrations was associated with secondary biogenic OM. The biogenic factor consisted of 32% alkane, 25% carboxylic acid, 21% organic hydroxyl, 16% ketone, and 6% amine groups. This composition is similar to that of SOA reported from the oxidation of biogenic volatile organic compound (BVOCs) in laboratory chamber studies, providing evidence that

the magnitude and chemical composition of biogenic SOA simulated in the laboratory is similar to that found in actual atmospheric conditions. These findings provide one of the most unambiguous data sets for characterizing the functional group composition of ambient biogenic SOA. The presence of alkane, carboxylic acid, ketone, and organic hydroxyl groups in biogenic SOA is qualitatively consistent with both chamber results and with other biogenic organic functional group measurements (Hallquist et al., 2009; Bahadur et al., 2010).

At the high-elevation mountain peak site (2182 masl) supermicron and submicron aerosol were collected from March and September 2009. The identified forest source, made-up of SOA from burning and non-burning forest-derived volatile organic compounds (VOCs) was investigated. The OM project mean for submicron samples, total samples (including particles up to 10 μm), and both submicron and total samples together, are 3.1 ± 3.2 μg m^{-3}, 3.3 ± 3.2 μg m^{-3}, and 3.2 ± 3.3 μg m^{-3}, respectively. The mean OM of 4.1 ± 3.5 μg m^{-3} during May to September is significantly higher than the 0.6 ± 0.3 μg m^{-3} mean concentration measured during the first month. The OM reached a maximum of 13.6 μg m^{-3} during severe wildfires in early August.

Ketone groups were not measured in the first period (March to April) but contributed up to 27% of the average organic aerosol composition in the second period (May to September). Both burning and non-burning forest emissions contributed to the significant ketone groups measured. These measurements support the hypothesis by Hawkins and Russell (2010) that sharp methylene peaks in the FTIR spectra may be

used as an indicator of the influence of large wildfires on the chemical composition of the measured aerosol. However, the presence of methylene peaks in two Positive Matrix Factorization (PMF) factors (Factor 2BB and 2Bio) suggest either co-emission or co-production of the two components, or chemical similarity with regard to the hydrocarbon bonding in the emitted compounds from the two proposed sources.

The OM concentrations measured during spring 2008 in the mid-mountain site, were lower than the concentrations observed during a similar time period at the peak in 2009. The average organic functional group composition of the submicron aerosol was in general similar between the two sites. Most notably, 11% (by mass) less organic hydroxyl groups were observed in the peak measurements. Both the OM concentrations and composition may have been influence by the early 2009 fire season. Measuring over two seasons and across multiple years provided a more complete picture of the biogenic aerosol during wide variety of conditions including periods of high temperature and nearby forest fires.

References

Bahadur, R., Uplinger, T., Russell, L.M., Sive, B.C., Cliff, S.S., Millet, D.B., Goldstein, A., and Bates, T.S.: Phenols in Northeastern US Submicron Aerosol Particles from Seawater Sources, Environ. Sci. Technol., in press, 2010.

Bond, T. C., Streets, D. G., Yarber, K. F., Nelson, S. M., Woo, J. H., Klimont, Z.: A technology-based global inventory of black and organic carbon emissions from combustion. Journal of Geophysical Research–Atmospheres 109 (D14), 14203–14203, 2004.

Gilardoni, S., Russell, L. M., Sorooshian, A., Flagan, R. C., Seinfeld, J. H., Bates, T. S., Quinn, P. K., Allan, J. D., Williams, B., Goldstein, A. H., Onasch, T. B., and Worsnop, D. R.: Regional variation of organic functional groups in aerosol particles on four US east coast platforms during the International Consortium for Atmospheric Research on Transport and Transformation 2004 campaign, J. Geophys. Res.-Atmos., 112, D10S27, doi:10.1029/2006JD007737, 2007.

Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, Th. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, proper ties and impact of secondary organic aerosol: current and emerging issues, Atmos. Chem. Phys., 9, 5155–5235, 2009.

Hawkins, L. N. and Russell L. M.: Oxidation of ketone groups in transported biomass burning aerosol from the 2008 Northern California Lightning Series fires, in review, available for review at http://aerosols.ucsd.edu/publications.html), 2010.

IPCC: Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, edited by: Solomon, S., Qin, D., Manning, M., Chen, Z., Marquis, M., Averyt, K. B., Tignor, M., and Miller, H. L., Cambridge University Press, Cambridge, UK and New York, NY, USA, 2007.

Maria, S. F., Russell, L. M., Turpin, B. J., and Porcja, R. J.: FTIR measurements of functional groups and organic mass in aerosol samples over the Caribbean, Atmos. Environ., 36(33), 5185–5196, 2002.

Pöschl, U.: Atmospheric Aerosols : Composition, Transformation, Climate and Health Effects. Angew. Chem. Int. Ed., 44, 7520 – 7540, doi: 10.1002/anie.200501122, 2005.

Russell, L. M., Takahama, S., Liu, S., Hawkins, L. N., Covert, D. S., Quinn, P. K., and Bates, T. S.: Oxygenated Fraction and Mass of Organic Aerosol from Direct Emission and Atmospheric Processing Collected on the R/V Ronald Brown during TEXAQS/GoMACCS 2006, Journal of Geophysical Research - Atmospheres, 114(D00F05), doi10.1029/2008JD011275, 2009.