Boundary Layer Ozone Dynamics:

Direct Observations over Arctic and Ocean Locations

by

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Boundary Layer Ozone Dynamics: Direct Observations over Arctic and Ocean Locations Thesis directed by Associate Research Professor Detlev Helmig

Abstract

Influences of anthropogenic emissions from the northern hemisphere mid-latitudes can be seen in remote arctic and oceanic regions previously thought to be removed from the effects of pollution. Direct observations of surface layer ozone have been underrepresented above the hydrosphere and cryosphere. With oceans covering two thirds of the Earth's surface, the air-sea exchange plays an important role in the surface energy budget and in the transfer of ozone to the ocean surface. Recent developments of a fast response ozone instrument have allowed for ozone flux measurements over the open ocean. I investigated the quenching effect due to water vapor on the ozone instrument and quantified the corrections required for accurate measurements. А method for removing water vapor while leaving ozone unchanged was described. Mean water vapor concentrations were reduced by 77% and fast fluctuations of the water vapor signal were reduced by 97%. The transport of ozone over the open ocean was examined at island monitoring stations and from ship-board measurements. It has been speculated that ozone ocean uptake is determined by chemical enhancements. Currently, limited concurrent measurements of ozone flux and ocean surface chemistry have occurred. This work examined the use of satellite derived ocean surface chemistry measurements. In-situ and satellite derived measurements of chlorophyll agreed within 1 μ g l⁻¹ when the wind speed was greater than 6 m s⁻¹.

The fast response ozone instrument was deployed during a two month long field campaign to study ozone depletion events in Barrow, Alaska. During the campaign, seven ozone depletion events (ODE) where the ozone would drop below 1.0 ppbv were observed. The longest ODE lasted over 72 hours with residual ozone varying between 0.1 to 0.8 ppbv. Ozone surface deposition rates were relatively low, $\leq 0.02-0.05$ cm s⁻¹ during most times. There was no clear evidence of ozone in interstitial air being influenced by photochemical processes. Concurrent atmospheric turbulence measurements from seven sonic anemometers showed general agreement except when winds were disturbed by the location of a nearby building. A composite boundary layer height was defined during the campaign, based on atmospheric turbulence measurements and validated against over 100 radiosonde observations. Sustained periods of boundary layer heights below 50 m were seen for several days. There was not a clear correlation between ozone depletion events and boundary layer height.

For my beloved grandfather, Richard Boylan, who could always make me smile.

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Chapter 1: Introduction	1
1.1 Overview and Motivation	1
1.2 Research Objectives 1.3 Thesis Focus	8
Chapter 2: Characterization and Mitigation of Water Vapor Effects in the Measurement of Ozone by Chemiluminescence with Nitric Oxide	9
2.1 Introduction and Background	9
2.2 Instrumentation and Methodology 2.3 Results and Discussion	.15 .21
2.3.1 Effects of water vapor on the chemiluminescence ozone signal	.21
2.3.2 The removal of water vapor with a Nahon drying system	.22
2.3.4 Reduction of atmospheric water vapor high frequency signals	.31
2.4 Conclusions	.34
2.5 Acknowledgements 2.6 Appendix	.35
Chapter 3: Transport of Ozone in the Marine Boundary Layer	. 39
3.1 Introduction and Motivation	.39 .41
3.2.1 Land Based Stations	.41
3.2.2 Open Ocean Ozone Data	.42
3.3 Besults	.46
3.3.1 Tudor Hill	.46
3.3.2 Cape Verde	.49
3.3.3 Ragged Point	.52
3.4 Discussion	.59
3.5 Conclusions	.61
3.6 Acknowledgements	.62
4.1 Introduction	. 03
4.1 Introduction	.03
4.3 Results and Discussions	.66
4.4 Conclusions	.70
Chapter 5: Boundary Layer Dynamics during the Ocean-Atmosphere-Sea-Ic	e-
Snow (OASIS) 2009 Experiment at Barrow, AK	. 72
5.1 Introduction & Motivation 5.2 Experimental Setup	$.73 \\ .74$
5.2.1 Study Location 5.2.2 Instrumentation	.74 .76
5.3 Turbulence Observations	.80
5.3.1 Meteorological conditions	.80

Table of Contents

5.3.2 Comparison of turbulence measurements 5.3.3 What is the effect from the building on tower 1 measurements? 5.3.4 Evaluation of the turbulence measurements	82 87 91
5.4 Boundary Layer Height	94
5.4.1 Calculation of boundary layer height from turbulence 5.4.2 Use of surface turbulence variables to approximate the boundary layer in Barrow during springtime 5.4.3 Comparison of boundary layer height behavior with other polar sites	94 er height 95 105
 5.5 Summary and Conclusions 5.6 Acknowledgements 5.7 Appendix 	106 108 109
Chapter 6: Ozone Dynamics and Snow-Atmosphere Exchanges during Depletion Events at Barrow, AK	Ozone 111
6.1 Introduction 6.2 Experimental Setup	112 114
6.2.1 Study Site 6.2.2 Instrumentation	114 114
 6.2.2.a Ozone in the Snowpack 6.2.2.b Surface Ozone Monitoring 6.2.2.c Surface Ozone Fluxes 6.2.2.d Ozone Vertical Gradient Measurements from a Stationary Tower Tethered Balloon Tower 6.2.2.e Ozonesonde Profiles 6.2.2.f BrO Measurements from Longpath-DOAS 6.2.2.g Meteorological Measurements 	114 115 115 r and 116 117 117 118
6.3 Results and Discussion	118
 6.3.1 Ozone in the snowpack 6.3.2 OASIS Surface Ozone 6.3.3 Ozone during ODE 6.3.4 Ozone Surface Fluxes 6.3.5 Boundary Layer Ozone Dynamics 	118 121 127 134 140
6.4 Summary and Conclusions6.5 Acknowledgements6.6 Appendix	146 148 149
Chapter 7: Conclusions	165
7.1 Summary 7.2 Future work	$165 \\169$
References	

List of Tables

Table 2-1: The comparison of measured ozone signals (mean of 15 minute data) at 30 nmol mol ⁻¹ (in counts s ⁻¹) for Cases 1, 2 and 3, before each correction term30
Table 2-2: Averaged loss of ozone signal at the 3 different ozone levels
Table 3-1: Cruise name, ports and dates. 44
Table 5-1: Sonic anemometer technical details 79
Table 5-2: Absolute uncertainties in sonic calculations after filtering by wind direction.
Table 6-1: Length of Ozone Decline during an ODE Onset, Recovery Time, Overall Duration, and Median Residual Ozone during the Seven ODEs130

List of Figures

Figure 2.5: Fraction of water vapor removed by the Nafion dryer versus water vapor mole fraction upstream from the Nafion dryer. Data are color-coded by ozone level. ...26

Figure 2.8: Flow rate determined with a bubble meter plotted, corrected for ambient pressure and temperature, against water vapor mole fraction, for MFC 3 (Tylan FC-2900) operated at a constant set point. Each point shows the mean flow rate and the error bars represent the standard error with a sample size of 20. The numbers to the left of each point correspond to the water vapor content determined with the LICOR...36

Figure 2.9: Flow rate determined with a bubble meter plotted, corrected for ambient pressure and temperature, against water vapor mole fraction, for MFC 3 (Tylan FC-260) operated at a constant set point. Each point shows the mean flow rate and the error bars represent the standard error with a sample size of 20. The numbers to the left of each point correspond to the water vapor content determined with the LICOR...37

Figure 3.3: Map showing daily back trajectories for the AMMA cruise. The solid red line is the cruise track from Uruguay to South Carolina. The three north Atlantic island ozone monitoring stations are marked by a maroon star. The 144 hour back trajectories are the black, blue and green lines. The three colors and three symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 24 hours. Day of year is labeled next to each trajectory......50

Figure 3.8: Map showing daily back trajectories for the GasEx cruise. The solid red line is the cruise track. The Ushuaia coastal ozone monitoring station is marked by a maroon star. The 144 hour back trajectories are the black, blue and green lines. The Figure 5.5: Time series of 1/L where L is the Monin-Obukhov length. Colors represent individual sonic anemometer calculations. A) Linear y-axis from -0.45 to 1.00. B) Logarithmic y-axis from 0.0001 to 10 to show detail in the nearly neutral stability range.

Figure 5.6: Boxplots showing friction velocity and sensible heat flux median, 25 and 75 percentiles, and 5 to 95% whiskers separated by unstable (z/L < 0.02) and stable $(z/L \ge 0.02)$ regimes. Sonic NC2 does not follow the general pattern of the other sonics. A) Friction velocity during unstable atmospheric conditions. B) Friction velocity during stable atmospheric conditions. C) Sensible heat flux during unstable atmospheric conditions. Mean stable atmospheric conditions. B)

Figure 5.7: Regression analysis of friction velocity using: A) Sonics NC2 vs. EC4. 1:1 line is shown in red. The best fit line is shown by black dashes. Color coded by wind direction. B) Sonics NC1 vs. EC2. C) Sonics EC4 vs. EC2. D) Sonics NC2 vs. NC1. For reference, the inset shows a sketch of the sonic anemometer heights and locations.88

Figure 5.14: Scatter plot of composite BLH and surface ozone, color-coded by wind speed, local wind direction, day of year, and local atmospheric stability......110

Figure 6.2: Time series of ozone mixing ratio (5-min mean data) from three independent measurements. Data from the NCAR tower are labeled for indication of the three tower inlet heights. The INSTAAR data are from a flux tower, approximately 40 m south of the NCAR tower. NOAA data are from the NOAA Barrow observatory. Seven ozone depletion events identified during this campaign are indicated at the top of the figure.

Figure 6.10: Whisker plot showing the distribution of the ozone deposition velocity as a function of the time of day from March 8 through April 14. Whiskers depict the median result in the center, the 25 and 75 percentile as the box edges, and 5 and 95 percentile as the cross bars on the staggered lines. The time axis scale uses Alaska Standard Time.

Figure 6.16: Record of available vertical profiling observations. The brown lines show the days/times when the tethered balloon was up, green lines show vertical ozone sonde profiles from the tethered balloon, pink labels show available observations from the long sampling line experiment, and grey lines show the NOAA release ozone sonde launches.

Chapter 1

Introduction

1.1 Overview and Motivation

Ozone is one of the most important trace gasses in the Earth's atmosphere due to its effect on the radiation budget of Earth's climate system. Ozone (O_3) in the atmospheric boundary layer has large variations in space and time. Since industrialization, the mean concentration of tropospheric ozone has roughly doubled [Lamarque et al., 2005] and surface ozone continues to increase in many regions [Coyle et al., 2003; Vingarzan 2004; Helmig et al., 2007a]. In the troposphere, ozone acts as a greenhouse gas with a background mole fraction of 35 parts per billion by volume (ppbv). The human-induced increase of ozone in the lower troposphere is estimated to contribute ~13% (0.35 ± 0.2 W m⁻²) to anthropogenic greenhouse gas forcing [*IPCC*, 2007, ranking ozone the third most important greenhouse gas after carbon dioxide (CO_2) and methane (CH_4) . Ozone is the primary precursor of the hydroxyl radical (OH)in the troposphere. Both OH and ozone are fundamental for the oxidizing capacity of the atmosphere and removal of many atmospheric contaminants. Within the stratospheric ozone layer, ozone mole fractions approach 10,000 ppbv. Stratospheric ozone blocks ultraviolet (UV) radiation coming from the sun. Anthropogenic activity has reduced the "good" ozone in the stratosphere and increased the "bad" ozone in the troposphere. Ozone became the topic of discussion during the 1940's with a remarkable increase in air pollution in the Los Angeles basin, known as Los Angeles smog [Middleton et al., 1950]. During the 1950s and 1960s, southern California had the highest ozone concentrations in the world with frequent and reoccurring smog alerts. In the years following, dramatic increases in ozone, often over 100 ppbv, were observed at

large metropolises worldwide. Pre-industrial revolution ground level ozone mole fractions were approximately 10 ppbv. Peak mole fractions now are an order of magnitude higher in urban areas and even background mole fractions far removed from pollution sources are substantially higher.

Projected increases in tropospheric ozone are a concern for life on Earth. Ozone is a toxic gas and breathing surface level ozone can result in a number of health effects. Due to the low solubility in water, ozone passes through the upper respiratory tract and dissolves on the thin layer of the lungs surface. Short term effects include cough, throat irritation and shortness of breath [Brunekreef and Holgate, 2002]. These effects are reversible; however, long term exposure to ozone results in a decrease in lung function, inflammation of breathing airways, and susceptibility to infection. Children and the elderly are more susceptible to the effects of ozone, especially during the summer months when ozone is higher and people spend more time outside. Ozone is absorbed by plant leaves during normal gas exchange and results in the discoloration (chlorosis) or death (necrosis) of the leaves [Ashmore, 2005]. The crop yield lost by ozone can be as high as 15% for dicot species such as soybean, cotton and peanut |Ashmore, 2005|. Monocot species such as wheat, alfalfa and corn, lose between 5-8% crop yield due to ozone [Ashmore, 2005]. The loss of crop yield dramatically increases as the background level of ozone increases. Ozone attacks polymers containing double bonds, including rubber. This ozone cracking was common in older tires but it rarely seen today due to the addition of antiozonants to the rubber before vulcanization.

The Air Pollution Control Act of 1955 was the first federal legislation involving air pollution which funded air pollution research. These findings led to the Clean Air Act of 1963 which was the first federal legislation regarding the regulation of air pollution. Extensive ambient monitoring studies were conducted under the 1967 Air Quality Act, which investigated areas prone to interstate transport of air pollution. A major increase in the federal government's role in air pollution control was due to the

Clean Air Act of 1970. This authorized state and federal government regulations on emissions from industrial and automotive sources. As a result, the National Ambient Air Quality Standards (NAAQS) was initiated along with the creation of the Environmental Protection Agency (EPA). The NAAQS sets levels of pollutants considered harmful to the public health and environment. An amendment to the Clean Air Act in in 1977 addressed requirements for pollution sources in non-attainment areas and initiated a permit process to ensure future attainment of the NAAQS. An amendment in 1990 dramatically increased the authority of the federal government in attaining NAAQS levels. A program was established to phase out the use of chlorofluorocarbons (CFC) that deplete the stratospheric ozone layer. The amount of ozone in the atmosphere to reach nonattainment status has been reduced over the years. In 1979, non-attainment was reached when the 1 hour mole fraction of ozone was 120 The EPA changed the requirement in 1997 to levels of ozone over 80 ppbv over ppbv. an 8-hour period. Non-attainment is when the annual fourth-highest daily maximum 8hour mole fraction was over the threshold. The non-attainment level was reduced again in 2008 to 75 ppby. Currently there are over 4,000 state and local ozone monitoring stations. Current 8-hour ozone nonattainment areas are concentrated at urban centers across the Midwest, the eastern seaboard stretching from Washington D.C. to Connecticut, and most of central and southern California. Recent field studies have looked at the wintertime ozone exceedances over 160 ppbv in the rural Green River Valley in Wyoming and Uintah Basin in Utah.

Contributions to background surface level ozone concentrations include entrainment of ozone from the stratosphere and ozone formation due to photochemical reactions of locally emitted natural precursors. Background ozone is created through photochemical reactions of volatile organic compounds (VOCs) emitted from plants and nitrogen oxides (NO_x) produced by soil microbes. Increased levels of VOCs and NO_x due to anthropogenic activity significantly increase the amount of ozone produced. The



Figure 1.1: Ozone cycle with nitrogen oxides. (Figure from Amos, 2012).

 $ozone/NO_x$ cycle is shown in Figure 1.1 [*Amos*, 2012]. Sunlight seperates an oxygen atom from nitrogen dioxide resulting in nitric oxide. The oxygen atom combines with molecular ozone to form ozone. This leads to the production of ozone during daylight hours. The reaction of ozone and nitric oxide, which forms nitrogen dioxide, is a slower process. Excess nitrogen dioxide builds up during the night and photochemically reacts to form ozone the following morning. Lower concentrations of ozone are present in the non-polluted troposphere; however, transport of ozone or ozone precursors from polluted areas can lead to an enhancement of ozone in remote locations, such as over the open ocean and in the Arctic.

Although minimal mixing normally occurs between the troposphere and the stratosphere, intrusions of ozone from the stratosphere can cause regional tropospheric ozone increases. These intrusions tend to occur in the springtime and are not the cause of nonattainment of the NAAQS, which usually happen during the summer months. Creation and destruction reactions lead to a steady state of ozone in the stratosphere through the Chapman cycle. Molecular oxygen is destroyed by UV light ($\lambda < 242$ nm) to form atomic oxygen which can either react with molecular oxygen to form ozone or react with ozone to create molecular oxygen.

The tropospheric ozone budget is determined by transport from the stratosphere, surface deposition, and chemical production and depletion. Total global chemical production of ozone in the troposphere is 5060 Tg yr⁻¹. The yearly entrainment of tropospheric ozone from the stratosphere is 520 Tg yr⁻¹, roughly 10% of the total tropospheric ozone. In situ chemical loss accounts for 4560 Tg yr⁻¹ loss of ozone while 1010 Tg yr⁻¹ of ozone is lost to the Earth's surface through dry deposition [*Stevenson et al.*, 2006]. With the oceans covering 2/3 of the Earth surface, the air-sea exchange plays an important role in the surface energy budget and in the transfer of climate relevant compounds. It is estimated that oceanic ozone dry deposition accounts for approximately 1/3 of the global ozone deposition sink [*Ganzeveld et al.*, 2009].

1.2 Research Objectives

This thesis identifies several topics regarding surface layer ozone dynamics that require attention. Global climate models and global chemistry models are currently using a fixed value for ozone deposition to the ocean surface. This is primarily due to the lack of direct observations of ozone deposition to the open ocean. Typically applied values for the oceanic deposition velocity (v_d , the ozone deposition flux divided by the surface layer ozone concentration times -1) in atmospheric models are on the order of $\tilde{}$ 0.013 to 0.05 cm s⁻¹. This consideration is based upon data reported in the literature, which range from $v_{\rm d}$ $\tilde{}~0.01$ to 0.15 cm s^-1 for ocean water, and 0.01 - 0.1 cm s^-1 for fresh water [Ganzeveld et al., 2009]. The previous literature data resulted from different types of experimental approaches; observing ozone decay in the headspace of ocean water enclosure experiments [Aldaz, 1969], wind tunnel experiments [Garland & *Penkett*, 1976, and eddy covariance (EC) measurements. Reported EC flux experiments were either measured onboard an aircraft [Kawa & Pearson, 1989] [Lenschow et al., 1981] or took place on stationary platforms in coastal areas, i.e. from lighthouses and flux towers [McFiggans et al., 2010; Whitehead et al., 2010]. The airborne ozone flux observations only covered short time periods in locations near the North American Continent. The coastal flux observations are expected to mainly reflect the ozone air-ocean exchange regime of the coastal zone with rather different physical and biogeochemical properties compared to the open ocean [Ganzeveld et al., 2009]. It has been suggested that oceanic ozone deposition depends on a number of environmental factors, including wind speed, surface roughness, sea surface temperature, salinity, air temperature, humidity and ocean biogeochemistry. However, previous work on this topic has not yet produced a clear description and parameterization of these dependencies. This deficiency is largely due to the fact that suitable ship-borne open ocean ozone flux measurements with concurrent characterization of the oceanic physical, chemical, and biological conditions had not been accomplished. This thesis will look at

feasibility of using archived remote sensing data of chemical and physical parameters of the ocean in place of in-situ measurements.

The western United States is a nonattainment area for one or more species defined by the NAAQS. The primary source of pollution is from local sources, and combined with local topography this pollution tends to remain stationary. It has been argued that a secondary source of air pollution is the transport of ozone and ozone precursors from eastern Asia to the western US. This thesis will look at the ability of ozone to be transported across the open ocean and will compare island ozone monitoring stations with ozone measured aboard several research cruises. The ship-borne instrument used in this study has a known sensitivity to water vapor. The effects of water vapor need to be parameterized for this instrument. Methods have previously been proposed to reduce the amount of water vapor in the sample without effecting ozone mole fractions. An ozone measurement with less uncertainty due to water vapor can help guide estimations of the ozone budget in global chemistry models.

Even 30 years after the first observations of ozone depletion events (ODE) in the Arctic, several questions remain unanswered regarding the formation of these events. A multi-institute campaign at Barrow, AK was directed at answering the questions regarding the formation of ODEs. One overlying question was the influence of local chemistry compared to meteorology: is the ozone being depleted locally or at a remote location and then transported to the study site? To help answer this question, the boundary layer dynamics at the site needs to be investigated. If the primary formation of ODEs are the transport of an ozone depleted air mass then there could be a response in the boundary layer, which could help guide future Arctic campaigns towards determining the source of ODEs.

Even though the open ocean and the arctic greatly vary in meteorology and chemical constituents, a similar analytical approach will be taken for each environment. Within the marine and arctic boundary layers, specific focus will be on the role of the planetary boundary layer on ozone mole fractions and the transport of ozone in these environments.

1.3 Thesis Focus

The intent of this work is to better explain the ozone dynamics in regions previously thought to be removed from urban pollution and the role it plays in tropospheric chemistry. Direct observations of ozone over the open ocean are crucial in determining the transport and disposition to the ocean surface; however, water vapor interferes with the ozone measurement. Each chapter has an introduction describing the motivation for the research presented. Chapter 2 looks at the effects of water vapor on a chemiluminescence ozone signal in a controlled laboratory setting. A drying system for reducing the effects of water vapor is introduced along with several experiments validating its use for ocean work. The transport of ozone from continental outflow over the ocean is investigated in Chapter 3. With no source of ozone or ozone precursors over the ocean, ozone enriched air masses can travel for several thousand kilometers over the ocean. Ozone deposition to the ocean surface is strongly influenced by the surface layer chemistry. Unfortunately, several prior research expeditions on the ocean were lacking surface microlayer chemical measurements. The ability to use satellite derived chemical measurements is discussed in Chapter 4. Focus is switched to the boundary layer dynamics of the Arctic. Chapter 5 investigates the concordance of turbulence measurements in Arctic, providing an in-depth field comparison of seven sonic anemometers. Two estimations of boundary layer height are examined, providing a link between surface meteorology and chemistry. The behavior of ozone from within the snowpack and from the surface to 150m is explored in Chapter 6. This work identifies that transport, not local chemistry, defines ozone behavior at this Arctic coastal site. Concluding remarks and a general summary are found in Chapter 7. The ozone budget for ocean and snowy Arctic environments are compared and contrasted.

Chapter 2

Characterization and Mitigation of Water Vapor Effects in the Measurement of Ozone by Chemiluminescence with Nitric Oxide

Laboratory experiments were conducted with a chemiluminescence instrument to determine the effects of water vapor on the reaction of nitric oxide used for fast response and high sensitivity detection of atmospheric ozone. Water vapor was introduced into a constant ozone standard and both ozone and water vapor signals were recorded at 10 Hz. The presence of water vapor was found to reduce, i.e. quench the ozone signal. A correction factor was determined to be $4.15 \pm 0.14 \times 10^3$, which corresponds to a 4.15%increase in the measured ozone signal per 10 mmol mol⁻¹ co-sampled water vapor. An ozone-inert water vapor permeable membrane (Nafion dryer) was installed in the sampling line and was shown to remove the bulk of the water vapor mole fraction in the sample air. At water vapor mole fractions above 25 mmol mol⁻¹, the Nafion dryer removed over 75% of the water vapor in the sample. This reduced the ozone signal correction needed from over 11% to less than 2.5%. The Nafion dryer was highly effective at reducing the fast fluctuations of the water vapor signal (more than 97%) while leaving the ozone signal unaffected, which is a crucial improvement for minimizing the interference of water vapor fluxes on the ozone flux determination by the eddy covariance technique.

2.1 Introduction and Background

Recent developments in instrumentation for ambient air ozone measurements have enabled direct observations of open ocean ozone concentrations and fluxes. The measurement of ozone is based on the chemiluminescence reaction of ozone (O_3) and nitric oxide (NO) (Reaction 2-R1), which emits light between 600 nm $< \lambda < 2800$ nm that is detected with a photomultiplier tube (PMT):

$$NO + O_3 \xrightarrow{k_1} NO_2^* + O_2$$
 (2-R1)

$$NO_2^* \xrightarrow{\kappa_2} NO_2 + hv \tag{2-R2}$$

$$NO_2^* + M \xrightarrow{k_3} NO_2 + M \tag{2-R3}$$

The electronically excited nitrogen dioxide reaches equilibrium through photoemission (Reaction 2-R2). Excited state NO_2^* can also react with a molecule through collisional energy transfer, reducing it to the ground state and effectively quenching the signal (Reaction 2-R3). The chemiluminescence signal resulting from the reaction of nitric oxide and ozone is sensitive to several other atmospheric molecules such as H₂, CO₂, and H_2O [Matthews et al., 1977]. An earlier study did not find an effect of water vapor at 75% saturation when compared to 0% saturation on the $\rm O_3\text{-}NO$ chemiluminescence reaction [Fontijn et al., 1970]. Matthews et al. [1977] found that water vapor is more than ten times more effective at quenching the chemiluminescence signal than molecular hydrogen and more than three times more effective than carbon dioxide, which makes water the primary interferent of this ozone measurement under ambient air conditions. In contrast to the O_3 -NO chemiluminescence measurement, instruments based on the reaction of ozone and ethylene reported an increase in ozone signal with water vapor [Kleindienst et al., 1993]. This was determined to be due to a second compound being formed in the presence of water vapor that generates chemiluminescence.

Instead of correcting for the quenching effect of water vapor, some instruments were configured to supply a flow of water vapor to the reaction chamber to keep the effect of water vapor constant, complicating the operation of the system [*Ridley and Grahek*, 1990]. Another proposed method to account for the quenching effect of water

was to approximate the reduction in the ozone signal as a function of the water vapor mole fraction and apply a correction factor [Lenschow et al., 1981; Ridley et al., 1992]:

$$O_3 = O_{3m}(1 + \alpha r) \tag{2-1}$$

where O_3 is the corrected ozone mole fraction, O_{3m} is the measured ozone volumetric mole fraction in nmol mol⁻¹, α is the correction factor, and r is the water vapor mole fraction (expressed as the ratio of moles of water vapor to moles of dry air in mmol mol⁻ ¹, which is equivalent to parts per thousand). Lenschow et al. [1981] found the α correction factor as 5 x $10^{-3} \pm 1 x 10^{-3}$ and the work of Ridley et al. [1992] further refined the value to 4.3 x $10^{-3} \pm 0.3$ x 10^{-3} . For example, for a typical equatorial region open ocean atmospheric water vapor mole fraction of 30 mmol mol⁻¹ the correction accounts to 15% when using the correction factor of 5 x 10^{-3} . A correction of this magnitude was applied by Williams et al. [2006] in their chemiluminescence measurement of ozone. Previous work has not detailed if and how much the correction factor is dependent on instrument configuration and operational conditions, or if this correction is universally applicable. Prior to the experiments described here, the correction factor had not been determined for our particular custom-built fast-response ozone instrument (FROI). Previous work with this instrument had therefore selected α = 5 x $10^{\text{-3}}$ according to Lenschow et al. [1981], which resulted in up to a 25% correction for determining the atmospheric ozone mole fraction [Lang, 2008; Bariteau et al., 2010; Helmig et al., 2012b].

A benefit of the fast response time and high sampling frequency of a chemiluminescence ozone instrument is the ability to define surface fluxes in combination with a sonic anemometer by the eddy covariance technique. Applying a correction to the ozone signal to account for the water vapor influences is particularly critical for these eddy covariance calculations as these are susceptible to interferences from the total atmospheric water vapor mole fraction <u>and</u> the water vapor flux. Our FROI has been deployed for ozone flux determination to locations vastly ranging in water vapor content, from the dry arctic to the equatorial ocean [*Bariteau et al.*, 2010; *Helmig et al.*, 2012a; *Helmig et al.*, 2012b]. Reynolds averaging of the corrected ozone signal in Eq. (2-1) and the vertical component of the wind vector results in the following equation for the water vapor corrected ozone flux:

$$F_{O_3} = (1 + \alpha \bar{r}) F_{O_3 m} + \alpha \overline{O_{3m}} \overline{w'r'}$$
(2-2)

where F_{03} is the corrected ozone flux, α is the correction factor, \bar{r} is the mean water vapor mole fraction, F_{O3m} is the calculated ozone flux from the measured ozone signal, and $\overline{w'r'}$ is the average water vapor flux. There are three cases for the interaction between the water vapor flux and the ozone flux: 1) no water vapor flux - no correction for the ozone flux is needed; 2) downward water vapor flux and downward ozone flux – the uncorrected measured ozone fluxes are greater than actual ozone fluxes due to the effect of water vapor; and 3) upward water vapor flux and downward ozone flux – the uncorrected measured ozone fluxes are less than actual ozone fluxes due to the effect of water vapor fluctuations. The magnitude of ozone fluxes vary significantly based on surface properties. Relatively large ozone fluxes, up to 0.4 nmol mol⁻¹ m s⁻¹, have been observed over vegetated land, such as over soybean fields [Wesely and Hicks, 2000] and over tropical forests [Cros et al., 2000]. Much smaller ozone fluxes are observed over snow, ice, and water, typically ranging from 0.01 to 0.08 nmol mol⁻¹ m s⁻¹ [Ganzeveld et al., 2009; Helmig et al., 2009; Helmig et al., 2012a; Helmig et al., 2012b]. Interestingly, upward ozone fluxes up to 0.1 nmol mol⁻¹ m s⁻¹ have been observed in subalpine forests during the winter [Zeller, 2000]. To illustrate the sensitivity of the ozone flux to the water vapor flux, the relative correction to be applied to the ozone flux calculation as a function of the water vapor flux is illustrated in Figure 2.1. For this simulation, typical oceanic values for ambient air water vapor and ozone were chosen. The water vapor flux was varied between $\pm 4.5 \times 10^{-5}$ g kg⁻¹ m s⁻¹ [*Edwards*, 2007], ozone was set at 40 nmol mol⁻¹ and the water vapor content was 18 mmol mol⁻¹ [*Bariteau et al.*, 2010].

The green shaded regions illustrate conditions when the fluxes are in opposite This results in a negative error of the measured ozone flux. Blue regions directions. represent conditions where the ozone and water vapor fluxes are in the same direction, which results in a positive error of the measured ozone flux. For example, an ozone flux of -0.05 nmol mol⁻¹ m s⁻¹ and water vapor flux of 0.05 g kg⁻¹ m s⁻¹ results in a corrected ozone flux of -0.0445 nmol mol⁻¹ m s⁻¹, a difference of 11%. If the water vapor flux is in the same direction as the ozone flux (-0.05 g kg^-1 m s^-1) the corrected flux is -0.0645 nmol mol⁻¹, a difference of 29%. During several open ocean research cruises, Bariteau et al. [2010] calculated corrections of up to 25% to the ozone flux due to the water vapor The FROI measures the mole fraction of ozone relative to air with varying flux. amounts of water vapor. When computing ozone fluxes in the presence of water vapor, density corrections must also be applied to the ozone flux [Webb et al., 1980]. The dilution correction is similar to Eq. (2-1) with an α -value of 1.61, which is the ratio of the molecular weight of dry air to the molecular weight of water vapor [Bariteau et al., 2010. Dilution corrections are applied before the water corrections. The density correction for ozone fluxes observed in the Gulf of Mexico was an additional 8% on average [Bariteau et al., 2010].

Applying a large correction to the ozone signal is undesirable as it leads to a greater uncertainty in the flux determination. An alternative is to selectively remove water from the sample. To achieve this goal a Nafion drying membrane has been implemented in both chemiluminescence and UV absorption ozone instruments [*Wilson and Birks*, 2006; *Lang*, 2008; *Bariteau et al.*, 2010; *Spicer et al.*, 2010; *Helmig et al.*,



Figure 2.1: Isopleths of the correction to be applied to the measured ozone flux as a function of water vapor flux. When the ozone fluxes and water vapor fluxes are in the same direction, the measured ozone flux has a positive error, as seen in the negative correction factor to be applied for quadrants 1 and 3. When the ozone flux and water vapor flux are in opposite directions, there is a negative error with the measured ozone flux, as seen in quadrants 2 and 4.

2012b]. The hydrophilic properties of the membrane make it permeable to water vapor without affecting the ozone signal [*Wilson and Birks*, 2006]. The drying performance of the Nafion dryer is not uniform and depends on the type of Nafion dryer, length, sample and drying flows, and drying gas used. The amount of water vapor removed by the Nafion dryer has been found to vary from ~25% to over 70% [*Lang*, 2008; *Bariteau et al.*, 2010; *Spicer et al.*, 2010]. Analytical tests have shown that ozone is not removed by the Nafion membrane [*Wilson and Birks*, 2006; *Spicer et al.*, 2010].

Preliminary observations from our system indicated that the use of a Nafion drying system diminished the high frequency water vapor fluctuations, which reduced the water vapor flux by 98% and eliminated the need for density and quenching corrections [*Bariteau et al.*, 2010]. The effects of the Nafion dryer on high frequency ozone signals were not investigated in detail in that study; however, Bariteau et al. [2010] reported no apparent reductions in the ozone flux. In this paper, the effects of water vapor and the installation of a Nafion drying system on a chemiluminescence ozone instrument were studied in more depth, with a critical examination of the applicability of the correction factors determined in the earlier work of Lenschow et al. [1981] and Ridley et al. [1992].

2.2 Instrumentation and Methodology

Ozone was measured by a custom-built FROI with a precision sufficient to resolve small changes in ozone mole fractions at a high temporal resolution. The FROI has a sensitivity of ~2000 counts s⁻¹ ppbv⁻¹ and a background noise of 900 counts s⁻¹. Details and a schematic of the FROI have been published by Bariteau et al. [2010] (see Figure 1 in this reference for a schematic of the FROI). Sample air was pulled through a Teflon® (PFA, perfluoroalkoxy copolymer) line controlled to 1.5 L min⁻¹ by a mass flow controller (MFC). All ozone sample tubing was 0.64 cm outer diameter Teflon® tubing. Nitric oxide reactant gas flowed through stainless steel tubing and was controlled at 3 ml min⁻¹. The sample and NO were mixed in a 44 cm³ gold-plated reaction chamber. The reaction chamber temperature was maintained at 30°C by a heater and temperature controller. An integrated PMT housing Peltier cooler maintained the PMT temperature at -30°C (Hamamatsu, Model C10372, Japan), essential to reach low noise and high sensitivity levels. The reaction chamber pressure was controlled to 18 Torr by a pressure controller (UPC 1300, Coastal Instruments) downstream of the reaction chamber, which asserted that the instrument response was insensitive to fluctuations in the sample delivery flow rate. Photons were counted by a PMT (Hamamatsu Photonics K. K., Shizuoka, Japan) with a cutoff filter (RG-610, Newport Industrial Glass, Stanton, CA) removing radiation with wavelengths less than 600 nm. The FROI was calibrated against a commercial UV absorption instrument (Model TEI 49i, Thermo Scientific, Franklyn, MA, USA). This UV-instrument was referenced against the ozone standard at the Global Monitoring Division (GMD), National Oceanic and Atmospheric Administration (NOAA), Boulder, Colorado.

A detailed schematic of the experimental setup is shown in Figure 2.2. Water vapor measurements were achieved with a high precision closed path infrared hygrometer (LI-COR LI-7000, LI-COR Inc., Lincoln, NE, USA). The sample flow for the LI-COR was controlled at 1.5 L min⁻¹ using a MFC. The LI-7000 recorded water vapor data as mmol mol⁻¹. A water removal system was designed around a 2.44 m Nafion dryer (MD-110-96F, Perma Pure LLC, Toms River, NJ, USA). The pressure in the dryer outer annual space was maintained at a lower pressure to prevent the collapse of the inner membrane. The sample flow and dryer flow ran in opposite directions. The Nafion dryer system included a rotameter and needle valve for regulating the dryer flow, a drying unit filled with $CaSO_4$ (W. A. Hammond Drierite Co. LTD, OH, USA), and a tank of breathing air. The water vapor content in the breathing air tank was less than 0.03 mmol mol⁻¹. The flow of the drying air in the Nafion system was maintained



Figure 2.2: The schematic of the laboratory setup. The red box in the upper-left of the figure shows where the sample air was humidified. Ambient air was scrubbed through a zero-air generator and run through a drying agent to remove any excess water vapor. The flow was varied through mass flow controller (MFC) 1 to produce dry air and MFC 2 to produce humid air. The humidifier was a Nafion membrane containing liquid water in the inner tube and the sample flow through the outer shell. Excess flow was released through the vent with a flow restrictor. MFC 3 controlled the flow to 8 L min⁻¹. This air was mixed with ozone-enriched air from the TEI 49i ozone generator (red box in upper-right of figure). Sample air was provided from a tank of dry breathing air. The flow through the ozone generator was controlled to 1 L min⁻¹. The Nafion drying system, FROI and LI-COR are shown at the lower portion of the figure. Switching valves directed the flow through or around the Nafion dryer. MFCs 5 and 6 controlled the flow to the FROI and LI-COR and were set at 1.5 L min⁻¹. All data were collected on the data acquisition computer housed in the FROI.

between two and three times the sample flow. The sample flow passing through the Nafion dryer was 3.0 Lmin^{-1} (FROI + LI-COR).

A tank of breathing air supplied ozone-free air to the TEI 49i which was used for generating ozone. Ozone was produced by setting the TEI 49i generator to a constant ozone output level. The flow rate was held constant at 1.0 L min⁻¹ by MFC 4. The ozone output was set to different levels by adjusting the intensity of the UV light source inside the TEI 49i. The resulting ozone output was checked with the TEI 49i regularly and found to be stable based on the comparison of measured ozone levels prior to and after experiments that used a particular ozone output level. The ozone generation process was kept separate from the humidifying process to ensure constant ozone production regardless of water vapor content. The ability to regulate the water vapor content in the air was accomplished by using a "zero-air" generator and a Drierite column and by changing the split ratio and balancing the total flow between MFC 1 and MFC 2. The combined flow through these two MFC was held constant at ~9 L min⁻¹. The introduction of water vapor in the sample air was accomplished by operating a Nafion dryer in reverse mode: liquid water was pumped through the inner tubing while dry air from MFC 2 flowed in the outer tube. Maximum water vapor mole fractions were achieved when MFC 2 was set to 9.0 L min⁻¹ and MFC 1 was closed. MFC 3 was set to 8.0 L min⁻¹, leaving an excess flow to the vent of 1 L min⁻¹. This configuration allowed for controlling a continuous range of water vapor mole fractions between < 0.1 and 28 mmol mol⁻¹.

This study used 4 ozone levels $(0, 30, 60 \text{ and } 100 \text{ nmol mol}^{-1})$ and 6 water vapor mole fraction levels (<0.1, 6, 12, 18, 23 and 27 mmol mol⁻¹) to mimic a range of atmospheric conditions. These levels were tested with and without the Nafion dryer installed, yielding 48 sampling periods. The ozone level was set to one of the 4 levels, then the water vapor was varied across each of the 6 water vapor levels. Water vapor levels were varied both from high to low and low to high. Each sampling period was run for at least 15 minutes after both the water vapor and ozone signals equilibrated to new conditions. All data were sampled and recorded at 10 Hz. Data from each sampling period were reduced to 15 minutes for consistency between sampling periods.

In our experimental configuration MFCs 3 and 5 were subjected to sample air with varying water vapor mole fraction. The changing humidity in the sample flow bears the potential to effect the ability of the MFC to maintain a constant volumetric flow rate, resulting possibly in a difference between the MFC set point flow and the actual flow rate. This effect could potentially bias the results from these experiments, in that changes in flow rate and dilution ratio could mistakenly be interpreted as a change in the FROI detection sensitivity. It has previously been noted that the effect of water vapor on MFC flow rates is nonlinear, making the scaling relations of the MFC particularly challenging [Wang 2012; B. Darby, Coastal Instruments, personal communication, March 5, 2013]. In order to investigate the effect of water vapor on MFC flow rates, MFC 3, a Tylan FC-2900 with a flow range of 0 – 30 L min $^{-1}$ was subjected to variable humidity levels while the setpoint flow rate was kept constant at 8 L min⁻¹. Reference flow rates were determined with a bubble meter, corrected for temperature and pressure to yield mass flow rates, and then compared with the set point flow rates. For dry air, at a MFC set point of 8 L min⁻¹, the MFC displayed flow was 7.98 L min⁻¹ while the bubble meter calibration gave 8.12 L min⁻¹. Water vapor was then introduced into the sample flow at 5 levels between 4 and 26 mmol mol^{-1} and 20 bubble meter flow readings were recorded at each level (Appendix Figure 2.8). At all tested water vapor levels above 0.1 mmol mol⁻¹, while the MFC reported that the flow remained constant at 7.98 L min⁻¹, the flow rate determined with the bubble meter was 7.93 L min⁻¹, a drop of 2.3 %. A one-way analysis of variance (ANOVA) found this difference to be statistically significant at the p < 0.05 level, F(5, 114) = 15.9, p = 1.35x 10^{-9} . Furthermore, post hoc comparison using the Tukey test [Hsu, 1996] indicated that the mean bubble meter reported flow for the dry air was significantly different than the individual results at each of the humidified air levels. The same calculations revealed that there was no significant difference between any of the tested humidified air levels.

The same analysis was conducted on MFC 5, a Tylan FC-260 with a range of 0 -5 L min⁻¹, yielding similar results, i.e. a drop of 2.6% (Appendix Figure 2.9) and statistical significance. Taken together, these results indicate that the MFCs exhibit a significant drop in flow between dry and humidified air level (2.3-2.6%), but that flows were not affected over a wide range of humidity once a threshold value (in our case ~ 4 mmol mol^{-1}) has been exceeded. For this manuscript, flow rates from experiments with dry air were corrected for this bias, but no further corrections were applied for experiments conducted at humilities >4 mmol mol⁻¹. It's noteworthy that in the experimental setup used here, the bias of MFC 3 was attenuated somewhat as the resulting ozone mole fraction delivered depends on the flow ratio of MFC 4/(MFC 3 +MFC 4). Furthermore, the MFC biases of MFC 3 and MFC 5 cancel out each other to a significant degree ($^{75\%}$). When MFC 3 experienced a drop in flow going from dry to moist air, the ozone mole fraction in the ozone standard sample slightly increased from the change in the dilution ratio as the output from the 49i remained constant. The response of MFC 5 in this transition was a slight reduction of the flow provided to the FROI, causing a reduction in the FROI response. The net effect of the MFC 3 and MFC 5 flow changes on the ozone signal was calculated as 0.54%.

Experiments under ambient conditions were conducted to test the effect of the Nafion dryer on high frequency fluctuations of the water vapor signal. This experiment took place behind the NOAA David Skaggs Research Center in Boulder, CO in October, 2008. The footprint of the sampling location consisted of a small parking lot surrounded by surface vegetation. The same FROI and Nafion drying system setup were used in this experimental setup. Water vapor was measured by two LI-7500 (LI-COR Inc., Lincoln, NE, USA) hygrometers. These hygrometers were converted to closed path instruments by inserting the calibration tube between the sapphire-glass windows. The FROI and the two LI-CORs were housed in a container for weather protection. Ambient air was drawn through a 23 m sampling line with an inlet located at 4 m A Teflon® membrane filter (5 μ m, Millipore, height on a meteorological tower. Billerica, MA, USA) was used during ambient air measurements to prevent contamination of the tubing due to air pollutants. The air passed through one LI-COR, then through the Nafion dryer followed by the other LI-COR, before sampling by the FROI. Prior to the experiment, an inter-comparison of both LI-CORs was conducted to determine the offset between the instruments. Ambient ozone mole fractions were ~39 nmol mol⁻¹ and the water vapor mole fraction varied between 4 and 6 mmol mol^{-1} .

2.3 Results and Discussion

2.3.1 Effects of water vapor on the chemiluminescence ozone signal

The water vapor mole fraction was varied across different ozone levels in order to determine the appropriate correction factor, α , for this instrument and to evaluate how the correction factor compares with previously reported results for other instruments. To determine the correction factor, a re-write of Eq. (2-1) is used, shown as:

$$O_{3,0} = O_{3,r}(1 + \alpha r) \tag{2-3}$$

where $O_{3,0}$ is the ozone signal in counts s⁻¹, when the water vapor mole fraction is <0.1 mmol mol⁻¹, and $O_{3,r}$ is the ozone signal at a water vapor mole fraction r. At each ozone level, the correction factor was calculated at each water vapor level with pairwise combinations of $O_{3,0}$ and $O_{3,r}$. Additionally, as seen by rearranging Eq. (2-3), the slope
of the linear regression analysis of the ratio $O_{3,0}/O_{3,r}$ and the water vapor mole fraction corresponds to the correction factor, shown in Figure 2.3. A consistent pattern was seen when water vapor was introduced to ozone-enriched air; an increase of water vapor caused a decrease of the ozone signal. Direct observations from this experiment showing the average ozone signal loss for each average water vapor level are presented in Appendix Table 2-2, the summary of these results are shown in Figure 2.3. At high water vapor mole fractions the ozone signal had a negative bias of over 11%.

The average correction factor based on the results from Figure 2.3 gave a mean value for α of 4.15 x 10⁻³ with a 95% confidence interval of 0.14 x 10⁻³. This result is within the range given by Lenschow et al. [1981] (5 x 10⁻³ ± 1 x 10⁻³) and Ridley et al. [1992] (4.3 x 10⁻³ ± 0.3 x 10⁻³). Our instrument was operated at 10 Hz; Lenschow et al. [1981] used a sampling frequency of 20 Hz and Ridley et al. [1992] sampled at 12 Hz. Despite their reaction chamber being half the size of ours at 17 cm³ at 2000 counts s⁻¹ ppbv⁻¹ it yielded a similar response to our instrument. The important conclusion from these comparisons is that, despite these differences in the instrument configuration, the correction factors determined by these three studies all agree within the margin of error provided by each study.

2.3.2 The removal of water vapor with a Nafion drying system

The Nafion dryer was installed in the sample line (Figure 2.2) upstream of the FROI and LI-COR. Switching values allowed for the flow to pass through or to bypass the Nafion dryer. The experiment from the previous section was repeated with the addition of the Nafion drying system. A time series of the water vapor mole fraction recordings in the sample flow as it bypassed the Nafion dryer and flowed through the Nafion dryer is shown in Figure 2.4. Each sampling period started with the flow bypassing the Nafion dryer to record the amount of water vapor in the sample. In



Figure 2.3: Ratio of ozone signal at water vapor level less than 0.1 mmol mol⁻¹ ($O_{3,0}$) to ozone signal at water vapor level r ($O_{3,r}$) versus water vapor mole fraction. The points are color-coded by the amount of ozone generated by the TEI 49i. The solid lines represent results from linear regression analyses. The slope results from the linear regression analyses are shown in the table insert.



Figure 2.4: The water vapor signal before, during and after switching the Nafion dryer into the sample flow.

Figure 2.4 the flow bypassed the Nafion dryer for the first 2 minutes, during that time the LI-COR recorded 12.2 mmol mol⁻¹. After two minutes the flow was switched to the Nafion dryer and the water vapor mole fraction dropped below 5 mmol mol⁻¹. It took between 7 and 12 minutes for the water vapor equilibrate at 4.6 mmol mol⁻¹. The flow was then switched back to bypass the Nafion dryer to ensure reproducible water vapor conditions throughout the experiment. This behavior was repeatable during operation of the Nafion drying system over a period of several days.

The amount of water vapor removed from the sample air under the range of applied conditions is shown in Figure 2.5. The drying efficiency was consistent across ozone levels. The Nafion dryer removed 50% of the water at the lower water vapor mole fractions. This is a higher rate than what was reported in a previous study with this Nafion setup that where a 28% removal rate of water vapor through the Nafion system using ambient outdoor air with a water vapor mole fraction of 5 mmol mol⁻¹ was observed [*Lang* 2008; *Bariteau et al.*, 2010]. Under the laboratory conditions tested here, the Nafion dryer became more efficient at higher water vapor mole fractions, removing up to 78% of the water vapor in the sample air at the highest humidity conditions that could be tested.

Additional tests were performed to determine the optimum configuration for the Nafion drying system. During the above described experiments, the sample flow through the Nafion drying system was 3.0 L min⁻¹ and the drying flow was set at 9.0 L min⁻¹. The drying flow was lowered to 6.0 L min⁻¹ to investigate the relationship between dryer flow and water vapor removal. The comparison between these two dryer flows revealed a statistical difference in the amount of water vapor removed. The 9.0 L min⁻¹ drying flow removed 77.4% of the water vapor while the lower drying flow of 6.0 L min⁻¹ removed 75.0%. There was not a statistical difference in the ozone signals between the high drying flow rate and low drying flow rate.

A comparison was also done between the 2.44 m-long (used for the entirety of



Figure 2.5: Fraction of water vapor removed by the Nafion dryer versus water vapor mole fraction upstream from the Nafion dryer. Data are color-coded by ozone level.

this experiment) and a 1.22 m-long dryer under similar conditions. At a water vapor mole fraction of 26 mmol mol⁻¹, the 2.44 m dryer removed 78% while the 1.22 m dryer removed 71%. Obviously, the removal rate of water vapor does not scale linearly with the drying gas flow rate and the length of the Nafion dryer. It is important to note that drying efficiency is variable and dependent on multiple operational conditions that do not scale linearly.

2.3.3 Effect of the Nafion dryer on the ozone signal

First, we tested if there was a loss of ozone as it passed through the Nafion dryer by comparing three configurations: 1) a control case without the Nafion dryer installed, 2) Nafion dryer installed with drying flow rate of 0.0 L min⁻¹, and 3) Nafion dryer installed with drying flow rate of 9.0 L min⁻¹. All three cases used a dry sample flow containing <0.1 mmol mol⁻¹ water vapor and 60 nmol mol⁻¹ ozone. The mean ozone signals measured for these three setups were basically the same, varying by 40 counts s⁻¹ (0.03% of 130,000 counts s⁻¹), which is within the sampling noise of the instrument and not statistically different. This confirmed previous research that reported that ozone passed through the Nafion dryer without any noticeable losses [*Wilson and Birks*, 2006; *Spicer et al.*, 2010].

After confirming that there is no ozone loss in the Nafion dryer, we investigated how much of the ozone signal loss seen in the experiments described above is restored by passing a humidified sample flow through the dryer. When using a Nafion drying system, there are two effects that need to be considered: 1) An enrichment (i.e. increase in mole fraction) of ozone resulting from the removal of water molecules and 2) The reduction of the quenching effect occurring in the reaction chamber.

The Nafion drying system operates on the principle of removing molecules of water vapor from the sample line by permeation through a semi-permeable membrane. Since this causes a reduction of the total amount of molecules while the number of ozone molecules remains constant, the use of the dryer results in an enrichment of ozone, i.e. an increase in the ozone mole fraction and the signal from the FROI. The enrichment effect is expected to be equal to the fraction of water vapor molecules removed by the Nafion dryer. In the previous section it was shown, for instance, that at a water vapor mole fractions of ~25 mmol mol⁻¹, the Nafion dryer removed ~77% of the water vapor, equivalent to ~20 mmol mol⁻¹ (or 20 parts per thousand = 2%). This enrichment would consequently cause an increase in the FROI signal of 2%. Figure 2.6 displays the inferred ozone enrichment as a function of the water vapor content, as measured upstream of the Nafion dryer, ranging from 0.3 - 2% under the water vapor mole fractions applied here.

The ozone signal that is restored when using the Nafion dryer was determined by comparing results from three different cases. Case 1 is the sample flow containing 30 nmol mol⁻¹ of ozone in dry air, < 0.1 mmol mol⁻¹ of water vapor, without the sample passing through the Nafion dryer. Case 2 is a humidified sample containing 30 nmol mol⁻¹ of ozone, a water vapor mole fraction of 6.04 mmol mol⁻¹, without passing through the Nafion dryer. Case 3 is for a sample flow with the Nafion dryer installed, containing 30 nmol mol⁻¹ of ozone, 26.5 mmol mol⁻¹ of water vapor upstream of the Nafion dryer and 6.04 mmol mol⁻¹ of water vapor downstream of the Nafion dryer. In Cases 2 and 3, the amount of water vapor entering the FROI reaction chamber is very similar, at ~6 mmol mol⁻¹. In theory, the ozone signal from Case 2 should be equal to the ozone signal from Case 1 after correcting for the quenching effect, and Case 3 should agree to Case 1 after correcting for the enrichment and quenching.

For Case 1, the FROI signal was 60645 counts s⁻¹ (Table 2-1). For Case 2, the corrected ozone signal was determined from the measured 59135 counts s⁻¹ by using Eq. (2-4), $\alpha = 4.15 \times 10^{-3}$, and $r = 6.04 \text{ mmol mol}^{-1}$ of water vapor. This yields a corrected ozone signal of 60617 counts s⁻¹. The ozone signal for Case 3 required corrections for



Figure 2.6: Increase in the ozone signal from the removal of water vapor molecules by the Nafion dryer as a function of the water vapor mole fraction in the sample air, using the drying efficiency ratios shown in Fig. 2.5.

Water Vapor Mole	Case 1	Case 2	Case 3
Fraction	$<0.1 \text{ mmol mol}^{-1}$	$6.04 \text{ mmol mol}^{-1}$	$26.5 \mathrm{~mmol~mol^{-1}}$
	No Nafion Dryer	No Nafion Dryer	Nafion Installed
Measured Counts	60645*	59135	60267
Corrected for Enrichment	N/A^{**}	N/A	59079
Corrected for Quenching	N/A	60617	60648

Table 2-1: The comparison of measured ozone signals (mean of 15 minute data) at 30 nmol mol⁻¹ (in counts s⁻¹) for Cases 1, 2 and 3, before each correction term.

 \ast Calculated from a raw count of 60975 after correcting for the dry air flow biases of MFC 3 and MFC 5.

** Not applicable

both enrichment and quenching. The difference in water vapor mole fractions upstream and downstream of the Nafion dryer was 20.1 mmol mol⁻¹ of water vapor, which corresponded to 2.01% of the total molecules in the sample flow being removed by the Nafion dryer. The measured ozone signal was 60267 counts s⁻¹ corresponding to an ozone signal of 59079 counts s⁻¹ after this correction. In order to account for the quenching effect, Eq. (2-4) was applied, with $O_{3m} = 59079$ counts s⁻¹, $\alpha = 4.15 \times 10^{-3}$, and r = 6.4 mmol mol⁻¹ of water vapor. This calculation resulted in a corrected ozone signal of 60648 counts s⁻¹.

With these considerations, the three cases gave close agreement, with the difference between the three cases of less than 32 counts s⁻¹ (or 0.02 nmol mol⁻¹ of ozone), which is well within the precision of the FROI. This consistency confirms the correctness of the determined quenching effect, developed correction algorithms, and the efficiency of the Nafion dryer in mitigating the quenching effects in the FROI ozone detection.

2.3.4 Reduction of atmospheric water vapor high frequency signals

The high sampling frequency of the FROI and LI-COR allowed for the investigation of high frequency behavior of the ozone and water signal with use of the Nafion dryer, specifically the reduction of water vapor fluctuations that determine the water vapor flux in Eq. (2-3). The following analyses are based on the experiments conducted on the mesa behind the NOAA-ESRL building.

The water vapor power spectrum distributions with and without the Nafion dryer shown in Figure 2.7a illustrate that the Nafion dryer was very efficient in damping the high frequency water vapor signal. The water vapor spectrum obtained without the Nafion dryer has both low and high frequency contributions. White noise was seen at frequencies higher than 2 Hz. The water vapor spectrum with the Nafion dryer installed has its primary contribution in the lower frequency range and a reduction of the higher



Figure 2.7: Spectral distribution plots using two hours of data with the same x-axis range for all three plots A) Power spectra of ambient water vapor with (red) and without (black) the Nafion drying system. B) Power spectra of the ozone signal with (red) and without (black) the Nafion drying system. C) Coherence spectral distribution of the ambient water vapor signal.

frequencies when compared to the water vapor signal without the Nafion dryer. The ratio of the integrals of the power spectra showed a 77% reduction of water vapor mole fraction, which confirmed the amount of water vapor removed as seen at the highest water vapor levels in Figure 2.5.

The frequency response spectrum in Figure 2.7c shows the coherency between the water vapor with and without a Nafion dryer. The coherency is the ratio of the cospectrum between the two water vapor signals and the square root of the product of the power spectra. A coherency value of 1 is representative of a high correlation between two signals at a given frequency. The water vapor signals have high coherency between 10^{-3} and 10^{-2} Hz, a decrease between 10^{-2} and 10^{-1} Hz, and display low coherence above 0.1 Hz. These results clearly illustrate that the Nafion dryer is very effective at reducing the high frequency contributions of the water vapor flux was reduced by 97%.

It is imperative that the attenuation of fast fluctuations as observed in the water vapor signal is not seen in the ozone signal, as this would alter the ozone flux calculation. Figure 2.7b shows the power spectra of the ozone signal with and without the Nafion dryer installed in the sampling flow path. The ozone signal has a relatively large contribution from lower frequencies in the < 0.1 Hz range. The inertial subrange is between 0.1 and 0.7 Hz. White noise is seen at frequencies higher than 0.7 Hz. The spectral components of the ozone signal remained unchanged when using the Nafion dryer, which confirms earlier results presented in this manuscript that there is not an attenuation of the ozone signal by the Nafion dryer. A slight increase of the signal is apparent in the white noise frequencies greater than 0.7 Hz. This increase was observed in the other time periods examined and can be explained by the additional tubing required of the Nafion dryer. These results give confidence in the ability to use a Nafion drying system when measuring ozone surface fluxes.

In order to prevent contamination of the sampling line from salt water sea spray,

or other particulate matter, it has been a standard operating procedure to direct the sample air through a Teflon® membrane inline sampling line filter. Filters used in our field measurements are conditioned prior to use by purging ~300 nmol mol⁻¹ of ozone through the filter for ~15 hours at a flow rate of 4 L min⁻¹. Filters are typically changed daily on oceanic research cruises in order to minimize the buildup of particulate matter on the filter. The effects of the Teflon filter on both the ozone and water vapor signal were investigated in the controlled laboratory setting. The filter was inserted into the setup directly downstream from the mixing of air from MFCs 3 and 4. Ozone and water vapor were held constant at ~100 nmol mol⁻¹ and 26 mmol mol⁻¹ respectively. There was no significant difference in absolute water vapor or ozone mole fractions and fast fluctuations with and without the filter installed.

2.4 Conclusions

This investigation confirmed previously reported signal loss in an O_3 -NO chemiluminescence instrument from the presence of atmospheric water vapor. The quenching effect of water vapor resulted in up to an 11% loss in the ozone signal as measured by the FROI. A correction factor, α , according to Eq. (2-1), was calculated to be 4.15 x 10⁻³, which is of similar magnitude as results from previous researchers. We also demonstrated the effectiveness of a Nafion drying system to reduce the quenching effect of water vapor on the chemiluminescence signal. This was accomplished by a series of laboratory and outside ambient air experiments. The installation of a Nafion drying system significantly reduced the amount of water vapor in the sample air. The fraction of water vapor to over 70% above 18 mmol mol⁻¹ of water vapor. The drying efficiency was found to depend on operating conditions of the dryer, increasing with dryer length and drying flow rate. The removal of water vapor molecules by the Nafion dryer results in an ozone enrichment upwards of 2%. Most importantly, the Nafion

dryer was found to be effective at attenuating the fast fluctuations of the water vapor signal. The ozone mean concentration and ozone fast fluctuations were not affected by the Nafion dryer. Consequently, the Nafion dryer is an efficient means for eliminating the interference from the water vapor flux in the eddy covariance ozone flux measurement.

2.5 Acknowledgements

I thank K. Lang and L. Bariteau for conducting experiments and providing data for the ambient air water vapor and ozone flux experiments.

2.6 Appendix



Figure 2.8: Flow rate determined with a bubble meter plotted, corrected for ambient pressure and temperature, against water vapor mole fraction, for MFC 3 (Tylan FC-2900) operated at a constant set point. Each point shows the mean flow rate and the error bars represent the standard error with a sample size of 20. The numbers to the left of each point correspond to the water vapor content determined with the LICOR.



Figure 2.9: Flow rate determined with a bubble meter plotted, corrected for ambient pressure and temperature, against water vapor mole fraction, for MFC 5 (Tylan FC-260) operated at a constant set point. Each point shows the mean flow rate and the error bars represent the standard error with a sample size of 20. The numbers to the left of each point correspond to the water vapor content determined with the LICOR.

H_2O	Ozone Signal Loss	95% Confidence Interval
6.2‰	2.5%	0.2%
12.0%	4.7%	0.4%
17.9%	7.1%	0.7%
23.0‰	9.2%	0.6%
27.1‰	11.2%	0.9%

Table 2-2: Averaged loss of ozone signal at the 3 different ozone levels.

Chapter 3

Transport of Ozone in the Marine Boundary Layer

In-situ ozone measurements from four fixed island and coastal stations in the Atlantic Ocean along with ozone measured on board the R/V Ronald H. Brown were used to examine the transport of ozone in the marine boundary layer. Ozone measurements made at the Tudor Hill station were subjected to continental outflow from the east coast of the United States. Ozone mixing ratios were typically between 40 and 60 ppbv during the spring and 20 to 30 ppbv during the late summer. Ozone observations at the Tudor Hill station had the largest seasonal variability among the four stations. Ozone measurements at the Cape Verde station approached 40 ppbv in the springtime and had air influenced by the outflow of Northern Africa. Back trajectories showed the source of ozone measured at Ragged Point to be the middle of the Atlantic Ocean. Despite the nearby city, the ozone measured at Ushuaia did not indicate any influences from pollution. An analysis of annual ozone average mixing ratios at the Tudor Hill station revealed an annual increase of background ozone of 0.2 ppbv year⁻¹ from 1988 to 2010 due to anthropogenic emissions along the east coast and the subsequent transport to Tudor Hill.

3.1 Introduction and Motivation

Over urban and polluted areas tropospheric ozone mixing ratios frequently rise about natural background levels and occasionally exceed the National Ambient Air Quality Standard (NAAQS) of 75 ppbv. In urban areas the levels of nitrogen oxides and hydrocarbons are high, increasing the level of ozone during the daylight hours. At night nitrogen oxides are present only as nitrogen dioxide which is oxidized by ozone, resulting in a diurnal cycle of ozone over urban regions. Rural areas, including the open ocean, can experience high ozone levels by the transport of ozone and ozone precursors from polluted areas. With lower hydrocarbon and nitrogen oxide emissions, the production and destruction of ozone is reduced resulting in a dampened diurnal cycle. The transport of ozone has been observed over Europe at Mace Head, Ireland [Simmonds and Derwent, 1991] and Izania, Canary Islands [Schmitt et al., 1988]. The North Atlantic Regional Experiment (NARE) looked at the distribution of ozone at four island stations in the far North Atlantic Ocean [Parrish et al., 1998]. Transport of ozone depleted air, not local chemistry was found to be the cause of ozone depletion events (ODE) in the Arctic [Helmig et al., 2012]. Ozone and ozone precursors from mainland Asia have travelled across the Pacific Ocean and enhanced the already high levels of ozone in southern California [Lin et al., 2012]. There have been instances of ozone pollution transported from North America to Bermuda but the bulk of the observations suggest that transport from the stratosphere and natural photochemical destruction control surface ozone levels over much of the North Atlantic [Oltmans and Levy, 1992].

The lack of an ozone source over the open ocean simplifies the marine boundary layer ozone budget. Ozone sources include transport from the stratosphere, transport of ozone pollution, and transport of ozone precursors. Ozone is removed from the marine boundary layer by deposition to the ocean surface. It is estimated that 1010 Tg yr⁻¹ of ozone is lost to the Earth's surface through dry deposition [*Stevenson et al.*, 2006]. Ganzeveld et al. [2009] estimated that oceanic ozone dry deposition accounts for approximately 1/3 of the global ozone deposition sink, roughly 335 Tg yr⁻¹. An airborne study found that vertical transport from the upper troposphere and horizontal advection by the tradewinds were the important source terms while photochemical destruction through photolysis or reactions with HO_x provided a primary sink [*Conley et al.*, 2011].

Recent developments in ozone measurement techniques have resulted in the ability to measure ozone over the open ocean. This is accomplished by using a fast response ozone instrument, based on the chemiluminescence reaction of ozone and nitric oxide [Bariteau et al., 2010]. Water vapor is the primary interferent with the ozonenitric oxide reaction, limiting its use over the open ocean. Boylan et al. [2013] determined that using a drying membrane to remove water from the sampling line was a viable choice in order to conduct ozone measurements over the ocean. The comparison of shipboard ozone data with island locations can assist in further identifying how ozone is transported above the ocean and potentially explain the deposition to the ocean surface.

3.2 Study Methodology

3.2.1 Land Based Stations

Four stationary atmospheric observatories in the Atlantic Ocean provided surface ozone concentration measurements. The observations from these stations were used due to the proximity to simultaneous ship-borne ozone measurements. The Tudor Hill station is located in Bermuda (32.27° N, 64.87° W, 30 m) operated by the Bermuda Biological Station and managed by the Global Monitoring Division (GMD) as part of the Earth Systems Research Laboratory (ESRL) National Oceanic and Atmospheric Administration (NOAA). Continuous ozone measurements were made using UV photometry. Ozone data are available from October, 1988 to May, 1998 using a DASIBI UV ozone monitor for measurements and from February, 2003 to December, 2010 using a TEI 49C. The instrument has been calibrated to the National Standard Instrument at the National Institute of Standards and Technology (NIST). Data are available in hourly, daily, and monthly means.

The Ragged Point station is located in Barbados (13.17° N, 59.43° W, 45 m) operated by the University of Miami and managed by GMD/ESRL/NOAA. Continuous ozone measurements were made using UV photometry. Ozone data are available from January, 1989 to December, 1995 using a DASIBI UV ozone monitor for measurements and from August, 2006 to December, 2010 using a TEI 49C. The instrument has been

calibrated to the National Standard Instrument. Data are available in hourly, daily, and monthly means.

The Cape Verde Observatory is located in the Republic of Cape Verde (16.85° N, 24.87° W, 10 m) operated by the Instituto Nacional de Meteorologia e Geofisca, Republic of Cape Verde and managed by the University of York, UK. Continuous ozone measurements are made using UV photometry. Ozone data are available from January, 2006 to January, 2012 using a Thermo Scientific UV Ozone Analyzer model 49C. The instrument has been calibrated to the national standard in 2007 and again in May 2010. Zero air was added into the ozone inlet once a month and external calibrations using a photometer standard are applied every 6 months. Data are available in hourly, daily, and monthly means. Wind direction generally varied between northwest and northeast.

The Ushuaia station is located at the southern tip of Argentina (54.83° S, 68.30° W, 18 m) operated and managed by the Gobierno de Tierra del Fuego - Servicio Meteorologico Nacional. Continuous ozone measurements are made using UV photometry. Ozone data are available from November, 1994 to January, 2009 using two Thermo Scientific UV Ozone Analyzer model 49 running in parallel using the same inlet. System and performance audits were performed in 1994, 1997, 1998, and 2003 in addition to daily zero checks. A filter based on wind direction and velocity is applied to distinguish between background and polluted air masses. Data are available in hourly, daily, and monthly means.

3.2.2 Open Ocean Ozone Data

A ship-based eddy covariance ozone flux system [*Bariteau et al.*, 2010; reference figure 1] was deployed to investigate ozone concentrations and the magnitude and variability of ozone surface fluxes over the open ocean. The core of the eddy covariance

ozone flux system is a fast response ozone instrument (FROI) based on the chemiluminescence reaction of ozone with NO (nitric oxide). Sample air was pulled through 30 meters of 9.5 mm Teflon-PFA line from an inlet on the jackstaff onboard the ship at 10 l min⁻¹. From this sample line, two 6.45 mm Teflon-PFA tubes were connected; one ran to an UV absorption O_3 monitor, the Monitor Lab 8810 (Measurement Controls Corp. Englewood, CO, USA) and the other to the FROI. The mass flow controlled sampling flow rate to the FROI was set at 1.5 l min⁻¹ and the NO flow rate was set at 3 ml min⁻¹ (99.995% NO). Sample air was dried using a Nafion drying membrane which has been shown to be permeable to water vapor but not to ozone [Boylan et al., 2013]. FROI calibrations were carried out with a laboratorycalibrated Monitor Lab 8890 and showed a sensitivity of ~2800 counts s⁻¹ ppbv⁻¹. Data from the FROI were collected at 10 Hz. The system response time was 0.3 seconds. Extensive tests have been run on the FROI to determine the optimum set points and parameters. The flux experiments were conducted on five cruises on board the NOAA Research Vessel (R/V) Ronald H. Brown during 2006 to 2008 [Helmig et al., 2012]. Cruise details and a map showing cruise tracks are shown in Table 3-1 and Figure 3.1.

3.2.3 Back Trajectories

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model was utilized to compute air parcel back trajectories [*Draxler and Hess*, 1997; *Draxler* and Hess, 1998; *Draxler*, 1999; *Draxler and Rolph*, 2013; *Rolph*, 2013]. Back trajectories are used in this research to determine the approximate origin of air masses. A back trajectory does not provide any information pertaining to ozone concentration or air parcel dispersion, i.e. width or depth. Back trajectories were computed once daily at locations along the cruise track and at the height of the inlet on the ship, 18 m above the ocean surface. The model outputs the location of an air parcel for the previous 144 hours before arriving at the location of the ship. The meteorology is based on Global Table 3-1: Cruise name, ports and dates.

	<u>Cruise</u>	Start	End	Dates	Year
Α	TEXAQS	Charleston, SC	Galveston, TX	07/07 - 09/12	2006
в	STRATUS	Panama City, Panama	Arica, Chile	10/09 - 10/27	2006
С	GOMECC	Galveston, TX	Boston, MA	07/11 - 08/04	2007
D	GASEX	Punta Arenas, Chile	Montevideo, Uruguay	02/29 - 04/11	2008
Е	AMMA	Montevideo, Uruguay	Charleston, SC	04/27 - 05/18	2008



Figure 3.1: Cruise tracks and location of island ozone monitoring stations.

Data Assimilation System (GDAS) 1 degree data, which provides global coverage, including remote areas of the Atlantic Ocean. The HYSPLIT model was used to compute trajectories along the AMMA and GasEx cruises.

3.3 Results

The lowest ozone mixing ratios were measured in the Southern Atlantic during the GasEx cruise, with levels consistently between 15 - 25 ppbv. Ozone levels in the South Pacific (STRATUS) varied between 25 - 35 ppbv. When the *Ron Brown* sailed through Galveston Bay during the TEXAQS cruise, ozone mixing ratios during several occasions approached 100 ppbv when the ship was subjected to urban outflow from the City of Houston [*Bariteau et al.*, 2010; reference Figure 13]. During the GOMECC cruise ozone remained in the 20 - 30 ppbv range in the Gulf of Mexico when southerly winds were encountered. Significantly higher mixing ratios, i.e. 40 - 70 ppbv, were observed off the U.S. Atlantic Coast. During the AMMA cruise, ozone was in the 10 - 30 ppbv range off the coast of South America, while higher values, i.e. 40 - 60 ppbv were measured when the ship sailed towards South Carolina.

Open ocean ozone data from the ship were compared to measurements from four nearby island coastal surface ozone stations. Ozone measurements were taken on the AMMA cruise from April 29th through May 19th 2008. During this period the ship was within one thousand kilometers of three island stations.

3.3.1 Tudor Hill

The Tudor Hill station is the closest of the four stations to the continent of North America. Monthly ozone mixing ratio averages from 1988 to 2010 are shown in Figure 3.2. The data show a large seasonal variability with a maximum monthly average of ozone of 61 ppbv. Ozone measured at the Tudor Hill station has increased between 1998 and 2010. The average annual ozone mixing ratio between 1988 and 1992 was 35.1 ppbv while the annual average between 2006 and 2010 was 39.3. Ozone increased 4.2 ppbv between 1988 and 2010 which corresponded to an average increase of 0.2 ppbv per year. The largest variability in the ozone data was between January and April. The average ozone between January and April in 1988 through 1992 is 42.6 ppbv while the same winter period in years 2006 to 2010 had an average ozone of 47.6 ppbv, a difference of 5.0 ppbv. In contrast, during the summer months of June through September the average ozone mixing ratio between 1988 and 1992 was 26.4 ppbv. The average summer ozone mixing ratio from 2006 to 2010 was 29.6 ppbv. Over the 20 years of operation, summertime ozone mixing ratios increased 3.2 ppbv. Seasonally, ozone mixing ratios varied by ~18 ppbv.

The comparison between the ozone measured on the AMMA cruise and hourly Tudor Hill data are shown in the upper pane of Figure 3.2. The black squares are ozone measurements from the Tudor Hill station and the circles are ozone measurements made aboard the ship, color-coded to represent the distance between the ship and the station during the time of the measurements. The station data show a diurnal cycle of ~10ppbv although a 50 ppbv drop in ozone is observed on day 130. The ozone measured on the ship was 40 ppbv lower from day 122 to 136, although one would not expect to see agreement as the ship was more than 3000 km away. Interestingly, the ship-borne ozone data showed a similar diurnal cycle and a gradual decrease in ozone from day 122 to 127, when the ship was the furthest away from the station. Unlike the station ozone data, ship-borne ozone measurements did not show the drop in ozone at day 130 but had a dramatic increase at day 136 when the ship was within 1200 km of the station. Between days 137 to 139 the ship was less than 1000 km from the station. During this period the ship-borne ozone measurements were consistently 8 ppbv less than the station ozone; however, there was good agreement in the variability of ozone measurements.

The HYSPLIT back trajectory model was used to determine the source of the



Figure 3.2: Comparison of ozone data from Tudor Hill and the AMMA cruise. The lower panel shows the available monthly ozone data from the Tudor Hill station shows the seasonal cycle of ozone. The upper pane is the hourly ozone data from the Tudor Hill station (black squares) plotted with the 15 minute ship-borne ozone data (colored circles) from April 29, 2008 to May 19, 2008. The color-coding of the ship-borne ozone measurements represents the distance between the ship and station.

ozone that was measured aboard the ship. Each back trajectory starts at the time the ship was at a given location and works backwards to show the path of the air parcel. A map of the daily back trajectories for the AMMA cruise is shown in Figure 3.3. The solid red line is the cruise track, the maroon stars are the island ozone monitoring stations and the black, green and blue lines are the back trajectories. Symbols represent the location of the air parcel every 24 hours from the start. The three colors are only used to visually differentiate between the back trajectories. It should be noted that it is not the intent of the author to use the back trajectories as exact origins of air parcels but rather to give a general idea of the synoptic transport of air parcels.

The concentrations of ozone measured onboard the AMMA cruise and at Tudor Hill disagreed by more than 20 ppbv except for the last two days of the cruise. Figure 3.3 shows that the two back trajectories closest to North America (corresponding to the last two days of the cruise) showed air parcels that were transported near the Tudor Hill station. Trajectories before that period showed air parcels transported directly from the east. The change in air parcel trajectory corresponded to the increase in ozone seen on the AMMA cruise during the last two days. The general origin of these two air parcels was from Nova Scotia and eastern Canada. There was a drop in ozone of ~5 ppbv from the time the air parcel flowed near the Tudor Hill station to when it was measured aboard the ship. Conley et al. [2011] estimated daily loss of ozone over the marine boundary layer as ~1.9 ppbv day⁻¹. Based on the back trajectories during days 137 and 138, there was a lag of ~36 hours between measurements made at Tudor Hill and the ship. This corresponded to a 2.9 ppbv loss of ozone over the marine boundary layer.

3.3.2 Cape Verde

The Cape Verde station has less than four years of continuous ozone monitoring. The monthly ozone mixing ratios from the Cape Verde station are shown in Figure 3.4.



Figure 3.3: Map showing daily back trajectories for the AMMA cruise. The solid red line is the cruise track from Uruguay to South Carolina. The three north Atlantic island ozone monitoring stations are marked by a maroon star. The 144 hour back trajectories are the black, blue and green lines. The three colors and three symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 24 hours. Day of year is labeled next to each trajectory.



Figure 3.4: Comparison of ozone data from Cape Verde and the AMMA cruise. The lower pane of available monthly ozone data from the Cape Verde station shows the seasonal cycle of ozone. The upper pane is the hourly ozone data from the Cape Verde station (black squares) plotted with the 15 minute ship-borne ozone data (colored circles) from April 29, 2008 to May 19, 2008. The color-coding of the ship-borne ozone measurements represents the distance between the ship and station.

Even with the limited data, a seasonal cycle of ozone was seen with high concentrations approaching 40 ppbv in the spring and low concentrations of less than 20 ppbv in the fall. Due to the brief history of the stations ozone monitoring, annual averages and their change over time are not presented.

Figure 3.4 shows the comparison of ozone measurements between Cape Verde and the AMMA cruise. Ozone measurements at the Cape Verde station are 20 ppbv lower than observations at Tudor Hill. A similar diurnal cycle was seen in both the ship and station ozone data. The ozone measured at Tudor Hill had a drop at day 130 while the measurements at the Cape Verde station increased by 20 ppbv over two days. Agreement between ozone measured at the station and aboard the ship was seen on days 130 and 133-134. The ship-borne ozone data increased to over 25 ppbv on day 136 while the ozone data from the station continued to decrease. When the distance between the ship and station were at a minimum there was not better agreement between the ozone measurements than when the ship was further away.

The synoptic flow around the Cape Verde station was due to the northeast trade winds. Between days 129 and 136 air parcels come from the northeast. On days 130 and 131, air parcels were transported near the Cape Verde station before arriving at the ship location. This may include outflow from Saharan Africa. The lag time of an air parcel from the Cape Verde

station to the ship location on day 130 was 72 hours and on day 131 was 48 hours. Using a loss of ozone of ~1.9 ppbv day⁻¹, 3.8 ppbv to 5.7 ppbv of ozone was removed. During days 129 and 136 the difference in ozone between the Cape Verde station and the ship was between 2 and 8 ppbv. The estimated loss could explain the difference in ozone concentrations between the two locations.

3.3.3 Ragged Point

Monthly ozone measurements from the Ragged Point station, shown in Figure

3.5, had the smallest seasonal cycle when compared to Tudor Hill and Cape Verde. Springtime maximum ozone mixing ratios reached 34 ppbv and summer minimums were less than 13 ppbv. There was better agreement among the monthly data when compared to the Tudor Hill station measurements. The average annual ozone mixing ratio between 1989 and 1992 was 20.4 ppbv and between 2006 and 2010 was 21.4 ppbv. Over 20 years the ozone increased 1.0 ppbv or 0.05 ppbv per year. This was 25% less than the annual increase observed at the Tudor Hill station. Average monthly winter ozone (January through April) between 1989 and 1992 was 24.0 ppbv and between 2006 and 2009 was 25.6 ppbv, an increase of 1.6 ppbv. There was very little change in the summertime ozone mixing ratios. Between 1989 and 1992 the average summer ozone mixing ratio was 16.9 ppbv while between 2006 and 2009 the summer ozone was 17.2 ppbv. Over 20 years the summertime ozone mixing ratio has increased by only 0.3 ppbv.

The hourly ozone data from the station showed a diurnal cycle of 2-3 ppbv and a mean of 21 ppbv. The ozone data measured at the ship and at the station were within 5 ppbv between days 124 and 136, often when the ship was over 4000 km away from the station. Since the back trajectories in Figure 3.3 do not extend to the Ragged Point station, further inspection of the synoptic air parcel transport to Ragged Point is shown in Figure 3.6. The northeast trade winds carried air parcels over the location of the ship to the Ragged Point station. There was a lag of 36 to 48 hours from ship to station. This was the opposite of what has been seen at the Tudor Hill and Cape Verde stations; the air parcel was first transported over the ship location and 1 to 2 days later it reached the island location. Between days 132 and 136 the ozone measured aboard the ship was between 1 and 5 ppbv higher than ozone measured at Ragged Point.

Similar to the loss of ozone observed at the Tudor Hill station, there is a loss of 2.9 to 3.8 ppbv of ozone during the transport from the ship location to Ragged Point. These results are similar to what was seen during NARE [*Parrish et al.*, 1998].



Figure 3.5: Comparison of ozone data from Ragged Point and the AMMA cruise. The lower pane of available monthly ozone data from the Ragged Point station shows the seasonal cycle of ozone. The upper pane is the hourly ozone data from the Ragged Point station (black squares) plotted with the 15 minute ship-borne ozone data (colored circles) from April 29, 2008 to May 19, 2008. The color-coding of the ship-borne ozone measurements represent the distance between the ship and station.



Figure 3.6: Map showing daily back trajectories from the Ragged Point station. The solid red line is the AMMA cruise track from Uruguay to South Carolina. The three north Atlantic island ozone monitoring stations are marked by a maroon star. The 144 hour back trajectories are the black, blue and green lines. The three colors and three symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 24 hours. Day of year is labeled next to each trajectory.

3.3.4 Ushuaia

The Ushuaia station is the only station reported here in the southern hemisphere. The southern tip of the South American continent separates the ship from the station. Monthly averages of ozone measured at the Ushuaia station between 1994 and 2009 are shown in Figure 3.7. Ozone maximums of 33 ppbv were seen in the southern hemisphere winter, June through September and minimums of 9 ppbv were observed in the summer, January through April. The annual ozone average between 1995 and 1998 was 24.6 ppbv and between 2005 and 2008 the ozone average was 24.8 ppbv. Over the 15 year period, ozone has only increased by 0.2 ppbv. Winter ozone did not show a change between 1995 and 2008. The winter ozone average for 1995 to 1998 was 19.6. Between 2005 and 2008 the wintertime ozone average was 19.5 ppbv. Summer ozone averages were 31.0 ppbv between 1995 and 1998 and 31.3 ppbv between 2005 and 2008.

Data from this station were compared against ozone data from the GaxEx cruise. Ozone measurements were made on the ship from March 2 to April 6. A seasonal cycle was seen with higher ozone in the springtime. The hourly data were noisy and were due to local influences from the nearby city of Ushuaia. Despite the variability in the station data, there was generally good agreement between the two ozone measurements. Interestingly, when the distance between the ship and station were at a minimum was when the ozone measurements deviated. Once the ship was 2000 km away from the station the magnitudes corresponded.

A back trajectory model was used to find the origin of air parcels that affected the ozone concentrations measured at the Ushuaia station and on the ship. Figure 3.8 shows the back trajectories from the Ushuaia station for the period when the ship was nearby. Air masses generally came from the west and only briefly travel over the southern tip of South America. This region is known for high winds and turbulent seas. This keeps the atmosphere well mixed and keeps day to day variation in ozone to a minimum.

56



Figure 3.7: Comparison of ozone data from Ushuaia and the GasEx cruise. The lower pane of available monthly ozone data from the Ushuaia station shows the seasonal cycle of ozone. The upper pane is the hourly ozone data from the Ushuaia station (black squares) plotted with the 15 minute ship-borne ozone data (colored circles) from February 29, 2008 to April 9, 2008. The color-coding of the ship-borne ozone measurements represent the distance between the ship and station.


Figure 3.8: Map showing daily back trajectories for the GasEx cruise. The solid red line is the cruise track. The Ushuaia coastal ozone monitoring station is marked by a maroon star. The 144 hour back trajectories are the black, blue and green lines. The three colors and three symbols are used to differentiate various trajectories for ease of viewing. Symbols are placed on the trajectory lines every 24 hours.

3.4 Discussion

Ocean ozone measurements from locations both near and far from the North American continent revealed large differences in ozone mixing ratios. Average ozone mixing ratios measured on board the AMMA cruise increased from ~20 ppbv when the ship sailed around South America to over 50 ppbv as the ship approached the United States. In a more localized study, ozone measured aboard the GOMECC cruise was typically less than 30 ppbv in the Gulf of Mexico, up to 70 ppbv when the ship was directly off the east coast of the United States, and approached 100 ppbv in the Galveston Bay [*Bariteau et al.*, 2010]. This behavior is an indication of the variable influence of continental outflow that was sampled during those cruises. Of the four stations investigated, the ozone measurements at the Tudor Hill station had the highest annual average and the largest seasonal variability. Even though the Tudor Hill station is located ~1000 km from the coast of the United States, it is still susceptible to pollution outflow. Back trajectories indicated that during the study period air masses measured at the Tudor Hill station originated over the North American continent, where larger ozone mixing ratios were observed.

The seasonal cycle of ozone observed at the Cape Verde station was smaller than what was observed at the Tudor Hill station and was larger than at the Ragged Point station. Air masses that typically passed over the Cape Verde station originated off the western coast of Northern Africa, a source of aerosols and pollution. The ozone measured at the Cape Verde station was more than 20 ppbv less than the ozone measured at the Tudor Hill station, indicating that continental outflow had a larger contribution to the Tudor Hill station. The ozone measured at the Ragged Point station had the lowest average mixing ratios and the smallest seasonal cycle. The annual average mixing ratio at Ragged Point was ~21 ppbv, similar to background levels of ozone reported in the Caribbean [*Vingarzan*, 2004]. Back trajectories indicated that the source of ozone was from over the mid-Atlantic ocean, void of anthropogenic influence. The small seasonal cycle can be explained by the close proximity of the station to the equator. A larger seasonal cycle in ozone was seen at the Cape Verde station, which is located further north. The largest seasonal cycle was measured at the mid-latitude Tudor Hill station. The amplitude of the seasonal cycle in ozone from the Ushuaia station is less than half when compared to the Tudor Hill station and similar to Ragged Point. Ushuaia station has less than 7 hours of solar radiation in the winter and more than 17 hours in the summer. Despite its location next to a small city, there was not an increase of ozone or ozone precursors. Back trajectories from the GasEx cruise showed the erratic behavior of surface layer transport from strong winds through the Drake Passage. There was not a correlation between air mass source and ozone levels.

Photochemical destruction of ozone during daylight hours can be used to explain the loss of ozone during transport in the marine boundary layer. Between the Tudor Hill station and the ship there was an estimated ozone loss of 2.9 ppbv and an observed loss of 5 ppbv. Similar results were observed at the Ragged Point station with an estimated ozone loss of 2.9 - 3.8 ppbv and an observed loss of 2 - 5 ppbv. The distance between the Cape Verde station and the ship was further than the other two northern hemisphere stations. An estimated 3.8 - 5.7 ppbv of ozone was lost to the marine boundary layer while the observed loss was between 2 - 8 ppbv. For all cases, the estimated loss of ozone was less than the observed loss. Not included in the loss term is the dry deposition of ozone to the ocean surface. This term can be variable depending on location, season, and physical and biogeochemical controls, among others.

The decades of nearly continuous ozone measurements at the fixed stations can provide an insight to the changing background levels of ozone. Ozone measured at the Ragged Point station has increased ~1.0 ppbv over the 20 year period of measurements. The source of ozone was from the middle of the Atlantic Ocean, removed from any anthropogenic activities. Over time the natural background of the Northern Hemisphere has increased but the measurements at Ragged Point indicate that this station is not directly affected by continental outflow. Ozone measurements at the Ushuaia station only increased by 0.2 ppbv over a 15 year period, despite its location near a pollution source. The amount of pollution produced by the city of Ushuaia was diluted by the availability of "clean" tropospheric air. Annual average ozone measurements at the Tudor Hill station have increased by 4.2 ppbv between 1988 and 2010. The increase and subsequent transport of ozone and ozone precursors along the east coast of the United States was evident in the ozone data measured at Tudor Hill. The increase in ozone was more apparent during the springtime as ozone increased 5.0 ppbv between the late 1980's and the late 2000's. The work of Parish et al. [2013] report a changing seasonal cycle of ozone, with the occurrence of maximum ozone at mid-latitudes shifting earlier in the year. Between 1988 and 1992 the average ozone maximum was on April This has shifted nearly two weeks earlier between 2006 and 2010 to March 31. 13. Processes influencing climate change are affecting measurements made more than 1000 km away from the nearest pollution source.

3.5 Conclusions

The ozone concentrations measured at island monitoring stations and aboard a research vessel provided the basis for an analysis of the transport of ozone over the open ocean. Three monitoring stations in the North Atlantic Ocean showed a seasonal ozone cycle that was stronger in the mid-latitudes and less pronounced in the tropics. Ozone mixing ratios measured at the Tudor Hill station were the highest of the four island stations, approaching 60 ppbv. Ozone measured at the Cape Verde and Ragged Point stations were at a maximum in the springtime between 30 and 40 ppbv. During the AMMA cruise, the research vessel sailed within 1000 kilometers of the three northern hemisphere stations. Back trajectories showed air originating from the northeastern portion of the North American continent, increasing the background ozone. The source

of ozone that passed over the Cape Verde and Ragged Point stations was from the north central Atlantic Ocean, following the regional trade winds. Agreement in ozone measurements between the Ragged Point station and the ship were often less than 5 ppbv, even with the ship was over 4000 km away, suggesting that both were measuring the clean background levels of ozone. Measurements in the southern hemisphere had ozone mixing ratios between 15 and 20 ppbv while the ship and Ushuaia station agreed within 3 ppbv. The synoptic flows in this region are scattered, revealing that there are few sources of pollution in this region. The analysis of annual average ozone mixing ratios revealed an increase of 0.2 ppbv year⁻¹ at the Tudor Hill station, which is subjected to the continental outflow from North America. Neither the Ragged Point nor Ushuaia stations ozone measurements saw a measureable increase in ozone over the past two decades.

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Chapter 4

Biogeochemical Controls of Atmosphere-Ocean Ozone Fluxes

A recently developed ship-based eddy covariance ozone flux system was deployed to investigate biogeochemical and physical controls of ozone surface fluxes over the open ocean. The relationship between ozone fluxes and chlorophyll were studied during the GOMECC 2007 cruise when large gradients in chlorophyll concentrations were observed along the cruise track in both the Gulf of Mexico and Northern Atlantic. The motivation for this study can be broken into two sections: a) evaluate the agreement between in-situ and satellite derived chlorophyll concentrations and b) establish if either method can represent the chlorophyll concentration at the surface where the reaction with ozone occurs. The two chlorophyll observation methods showed good agreement ($\mathbb{R}^2 = 0.81$) when the wind speed was greater than 6 m s⁻¹ and differed in the magnitude of observed concentrations when the winds were less than 6 m s⁻¹. The agreement between the two data sets and the postulated dependency of the oceanic ozone flux on chlorophyll levels opens up new opportunities for utilizing satellite-derived oceanic chlorophyll fields for description of the large scale oceanic ozone uptake.

4.1 Introduction

Recent deployments of a newly developed ship-borne ozone flux system have yielded the first in-situ measurements of ozone uptake over the open ocean [Bariteau et al., 2010]. This research has provided compelling evidence that oceanic ozone uptake is driven by physical and chemical properties at the atmosphere-ocean interface i.e. surface conditions and chemical reactants in the ocean water. Current global scale atmospheric models only incorporate physical boundary layer conditions into the calculation of oceanic ozone uptake; however, it is estimated that nearly 50% of the uptake variability is determined by chemical enhancements [Helmig et al., 2012].

Ganzeveld et al. [2009] suggest that the chemical enhancement in the oceanic ozone uptake is predominantly driven by the reaction of ozone with biologically derived iodide and organic material in the oceanic surface microlayer. Several researchers have suggested that chlorophyll content may be an indicator, or itself the reactant for ozone uptake. Clifford et al. [2008] hypothesized that at low wind speed the reaction of ozone with chlorophyll might be the driving factor of ozone deposition. Chlorophyll can be measured on board a ship via an underway system, which is constantly flushed with water from the bow several meters below the surface. An alternative approach is to use inferred chlorophyll surface concentrations from remote sensing data. An important question is how the chlorophyll measurements in water taken at 3-10 m depth are indicative of chlorophyll concentrations at the surface micro-layer, which is where the reaction with ozone occurs [*Ryabov et al.*, 2009].

4.2 Data and Methods

Ozone and chlorophyll observations were recorded aboard the NOAA Research Vessel *Ronald Brown* during July and August, 2007, as it was sailing from Galveston, TX, USA to Boston, MA, USA during the Gulf of Mexico and East Coast Carbon Cruise (GOMECC) [Figure 4.1]. The purpose of this cruise was to gather information on biogeochemical processes in the transition zone between the coast and open ocean, where large gradients in chlorophyll have been observed along the US coast in both the Gulf of Mexico and Northern Atlantic. Data filtering and quality control processes and the protocol for ozone flux calculations are explained by Bariteau et al. [2010]. Ozone deposition velocity (V_d , which equals the ozone flux divided by the ozone concentration multiplied by -1) results from this cruise have been presented by Helmig et al. [2012]. Over 297 hours of quality controlled data were collected during the COMECC cruise,



Figure 4.1: Cruise track for the GOMECC cruise along the Gulf of Mexico and east coast of the United States.

with mean and median deposition velocities of 0.019 and 0.018 cm s⁻¹. In-situ ocean water chlorophyll observations were collected onboard the ship from a sub-surface inlet every minute and reduced to 10 minute averages. Chlorophyll surface concentrations were inferred from ocean color remote sensing data measured by the SeaWiFS instrument aboard the SeaStar satellite. The satellite-based chlorophyll data were obtained as monthly mean values at 9 x 9 km resolution along the cruise track. Due to the sun-synchronous orbit of the satellite, data are not always available for each 10 minute position of the ship, so the closest temporal data point to the ship position was used.

4.3 **Results and Discussions**

In Figure 4.2 the chlorophyll concentrations for the in-situ and remote sensing observations are plotted against the day of year during the cruise. During periods of low chlorophyll concentrations (< 0.5 μ g l⁻¹) the satellite-derived data are consistently three times higher than the in-situ data as shown in Figure 4.2 inset. During high chlorophyll events, both techniques pick up the increase in chlorophyll. The exception to this is on days 197, 198, and 205. In general there are two scenarios during the higher chlorophyll periods. The first is when the satellite derived chlorophyll is five to eight times higher than the in-situ observations. The other is when both observations match up in terms of magnitude as seen on days 201, 207, 209, 215.

I would not expect an exact match due to the retrieval techniques of the observations. Werdell and Bailey [2005] have shown that chlorophyll inferred from satellite observations is not always consistent due to the changing optical clarity of the ocean. During clear conditions, satellite observations sample from a deeper water column extending several meters below the surface while during other times they may only observe the first few centimeters of the ocean. The data used for this analysis are monthly averages, which may bias the in-situ conditions when the ship sailed by the



Figure 4.2: Comparison of satellite derived and in-situ chlorophyll observations during the 2007 GOMECC cruise from Galveston, TX to Boston, MA. The inset is from day 202 to 204 showing difference comparison during low concentration conditions.

particular position of the satellite measurement at a given time. The in-situ observation is taken from the fixed-position underway system, though its relative depth varies with the pitching of the ship. It appears that the satellite inferred chlorophyll concentrations during most times are equal to or greater than in-situ observation, which might point towards chlorophyll enhancements at the surface of the ocean.

Soloviev and Lukas [2006] have shown that the vertical chemical structure of the first few tens of meters of the ocean can be influenced by surface winds due to upwelling and downwelling. During high wind events the surface layer should be well mixed due to the induced water side turbulent mixing. This is especially evident on day 201 when the wind speeds reached over 15 m s^{-1} and to a lesser extent on day 215. On day 216 the winds drop to 5 m s^{-1} . Wind speeds were also low (variable between 0 and 6 m s⁻¹) during the first three high chlorophyll events in which there could be significant stratification of the surface layer. Further investigation of the relationship between wind speed and chlorophyll is examined in Figure 4.3. When the wind speed was below 6 m s⁻¹ the difference in chlorophyll observations varies between -1.3 and $13.9 \ \mu g \ l^{-1}$. The chlorophyll measurements generally agreed within 2 μ g l⁻¹ when the winds exceeded 6 m s^{-1} . A linear regression analysis of the two chlorophyll observations reported an R^2 value of 0.81 when winds were higher than 6 m s⁻¹. The agreement was much lower when the winds were less than 6 m s^{-1} , with a correlation coefficient of 0.44. During periods of high winds, corresponding to a well-mixed ocean surface layer, the satellite inferred and in-situ chlorophyll tended to agree. There was not a clear relationship between chlorophyll concentration and ozone deposition velocity, which suggests that other variables, for instance an unknown chemical mechanism, likely have an influence on the oceanic ozone flux.

Both measurement techniques sample from some depth in the water column whereas the reaction of ozone with chlorophyll occurs at the surface micro layer which is less than a millimeter thick. During high wind events the ocean surface water is well



Figure 4.3: The difference in chlorophyll concentrations from remote sensing satellite data and in-situ observations versus wind speed measured from the ship.

mixed so that the concentrations at the surface are expected to be quite similar to what is sampled by the in-situ measurements. High chlorophyll/low wind events would reduce the optical clarity of the ocean making the satellite inferred chlorophyll more representative of the surface micro layer. The results of a process-based modeling study suggest that nearly 50% of the variability in the modeled ozone deposition velocity can be attributed to chlorophyll levels [*Helmig et al.*, 2012]. This hypothesis has been tested with the GOMECC 2007 dataset utilizing both in-situ and satellite derived chlorophyll. Results showed no significant differences in utilizing the two different data sets. More in-depth analyses of ozone deposition observations with higher temporal resolution satellite derived surface chlorophyll data are highly desirable to further test these relationships and for improving our understanding of the controls of oceanic ozone fluxes.

4.4 Conclusions

Satellite derived chlorophyll observations exhibited similar peaks as the in-situ data, although inferred concentration levels at times varied by a factor of 2 to 3. It was difficult to determine which method is more representative of the ocean surface skin conditions in which ozone would react. During or just after high wind events the surface layer is well mixed giving similar results from both methods. During low wind events the surface layer may be stratified with a higher concentration of phytoplankton at the surface than just below it. An examination of current and future satellites that provide inferred chlorophyll observations is needed to provide a link between the temporal and spacial resolutions from satellite observations and in-situ measurements. Further investigations during low and moderate wind events are needed to provide a more robust analysis of the biogeochemical effects on the oceanic ozone uptake.

4.5 Acknowledgements

70

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Chapter 5

Boundary Layer Dynamics during the Ocean-Atmosphere-Sea-Ice-Snow (OASIS) 2009 Experiment at Barrow, AK

Three dimensional atmospheric turbulence measurements were conducted from seven sonic anemometers on two different towers in Barrow, AK, during the spring of 2009 as part of the Ocean-Atmosphere-Sea-Ice-Snow (OASIS) campaign. This was the largest number of side-by-side atmospheric turbulence measurements in the Arctic at one time. These analyses allowed for 1) a comparison of the instrumental measurement approaches and 2) a comparison of the variability of the lower atmospheric surface layer at these measurement heights and tower sites. Friction velocity estimates were affected for a sonic anemometer that was operated on the tower in the near vicinity of a building module. Boundary layer height (BLH) was estimated from sonic anemometer measurements based both on a turbulence variable estimator and a temperature gradient method. Results from both methods were compared to radiosonde-estimated BLH and generally underestimated the BLH for shallower depths. Conditions with low BLH (< 100 m) often lasted for several days. The seven ozone depletion events (ODE) that were observed during the OASIS campaign had a tendency of coinciding with BLH of less than 50 m and stable atmospheric conditions; however there was not a clear relationship between the occurrence of ODE and wind speed or wind direction as ODE occurred under a wide range of conditions of BLH, wind speed, local wind direction, and Comparisons of these surface layer dynamics to sites in atmospheric stability. Antarctica and Greenland reveal that boundary layer dynamics are not the primary driving force that fosters the unique ozone chemistry at this coastal Arctic site.

5.1 Introduction & Motivation

A particular focus of atmospheric research in the Polar Regions has been the study of snow-atmosphere interactions and how boundary layer dynamics affect local atmospheric chemistry [Grannas et al., 2007; Perrie et al., 2012]. Results from the Ocean-Atmosphere-Sea-Ice-Snow (OASIS) 2009 campaign have identified interactions between halogenated species, volatile organic compounds, ozone and nitrogen oxides [Sjostedt, 2009; Liao et al., 2011; Helmig et al., 2012; Liao et al., 2012]. Previous research on this subject at polar sites has shown a strong relationship between boundary layer stability and chemical tracers, with stable atmospheric conditions promoting the buildup of surface layer trace gas concentrations [Davis et al., 2004; Oncley et al., 2004; Helmig et al., 2008; Neff et al., 2008]. It has also been shown that the top of the boundary layer can be characterized by a sharp transition in water vapor and ozone concentrations [Helmig et al., 2002]. Springtime in the coastal regions of the Arctic presents unique conditions with low temperatures, stable atmospheric conditions, and the introduction of sunlight after a dark winter. These intriguing surface conditions allow for unique chemical phenomena including ozone depletion events (ODE) Bottenheim et al., 1986; Oltmans and Komhyr, 1986; Jones et al., 2006; Simpson et al., 2007; Jones et al., 2013.

Several studies on boundary layer dynamics have been conducted at polar sites, including Alert, Nunavut, Canada [Strong et al., 2002; Cobbett et al., 2007], Summit, Greenland [Helmig et al., 2002; Cohen, 2006; Bocquet, 2007; Van Dam et al., 2013], Ny-Alesund, Spitsbergen [Solberg et al., 1996], and South Pole, Antarctica [Neff et al., 2008]; however, none have investigated in depth the data quality and reproducibility of turbulence measurements from multiple towers at one site and multiple levels. Surface turbulence measurements have been used to estimate boundary layer height (BLH) with some success at South Pole [Neff et al., 2008]. Similar methods have been applied to Summit [Cohen et al., 2007; Van Dam et al., 2013], although there were fewer direct measurements to validate the BLH estimations. Van Dam et al. [2013] compared turbulence-derived and sodar BLH measurements and found the best agreement was during more stable conditions. Sodar measurements at Dome C, Antarctica, showed that a stably stratified atmosphere resulted in a very shallow BLH, often below 50 m during periods of low solar insolation [*Argentini et al.*, 2005; *King et al.*, 2006; *Pietroni et al.*, 2012].

During OASIS, seven ultrasonic anemometers (referred to as sonics from this point forward) on two towers were operated during the campaign. These measurements allowed defining conditions in the arctic springtime when eddy covariance measurements were reliable to derive fluxes [*Staebler et al.*, manuscript in preparation, 2013]. Due to the flatness and surface homogeneity of the study site, measurements made on the towers should compare well with one another; however, one of the towers was in close proximity to a building which potentially might influence turbulence measurements. This campaign was also unique due to the availability of over 100 radiosonde profiles which allowed further evaluation of the turbulence-derived BLH estimations. The results from Barrow will be compared with other polar sites to offer further insight on the role of boundary layer processes on local atmospheric chemistry, in particular on the occurrence of ODE.

5.2 Experimental Setup

5.2.1 Study Location

The OASIS study was conducted approximately 5.8 km northeast of Barrow, Alaska, at the former Naval Arctic Research Laboratory (NARL) (71.323 N, 156.663 W; 8 m a.s.l) from March 6 to April 15, 2009. The snow-covered experimental site was located ~600 m from the Arctic Ocean and ~100 m to the west of Imipuk Lake, which was frozen over and snow-covered during the course of the study (Figure 5.1). This site was selected for the predominantly easterly winds coming over clean, undisturbed snow.



Figure 5.1: Arial view of northern Barrow, Alaska. The primary study site (dashed black box) was located 150 m southeast of the Barrow Arctic Research Center (BARC) and 600 m from the Arctic Ocean (located to the north and west). The National Oceanic and Atmospheric Administration (NOAA) Barrow Observatory and the United States Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility were located 1.8 km east of the primary study site (dashed red box). Upper left inset shows wind speed and direction as measured from the top of Tower 2. Upper right inset is the primary study site layout – zoomed in from the black dashed box. The modules housed all of the chemical analyzers and data acquisition systems. Tower 1 was located 3.5 m upwind of Module 1. Tower 2 was 29 m to the southeast of Tower 1. The balloon system was 20 m to the north of Module 1.

The primary measurement location was ~150 m south of the Barrow Arctic Research Center (BARC). Power lines ran next to an ice road that led to two modules (3 m height, 4 m width, 6 m length) which housed the instrumental equipment. Tower 1, 6.1 m tall, was located 3.5 m to the east of the first module. Its close proximity to the module was due to the need for short chemical sampling lines for atmospheric short lived gas species. A 10 m-meteorological tower (referred to as Tower 2) was located 29 meters southeast of the instrument modules. This tower setup allowed Tower 2 to be the standard for turbulence measurements while Tower 1 was utilized for chemical measurements. The tethered balloon site was located ~50 m east-northeast of the modules (Figure 5.1 inset). The National Oceanic and Atmospheric Administration (NOAA) Barrow Observatory and the United States Department of Energy (DOE) Atmospheric Radiation Measurement (ARM) Climate Research Facility were located 100 m apart approximately 1.8 km east of the primary study site.

5.2.2 Instrumentation

Two sonics with a 15 cm path length [SATI-K 3-D, Applied Technologies Inc., (ATI)] operated by the National Center for Atmospheric Research (NCAR) were mounted at 1.5 and 5.4 m above the snowpack on Tower 1 (3.5 m from the module) pointing 10 degrees from true north. Data were collected at 10 Hz. Five sonics were operated on Tower 2, four by Environment Canada (EC) and one by the Institute of Arctic and Alpine Research (INSTAAR). The lowest anemometer at 0.58 m above the snow surface was a 5 cm path length instrument [TR90-AH, Kaijo Denki, Japan] operating at 20 Hz. The other three anemometers from Environment Canada were 11.5 cm path length instruments [CSAT3, Campbell Scientific Inc., USA] operated at 10 Hz and mounted at 1.8, 3.2, and 6.2 m above the snowpack. All four Environment Canada anemometers were mounted on booms in the prevailing wind direction, 60 degrees from true north. All analog signals were collected with a data logger [CR3000, Campbell Scientific Inc., USA] at 10 Hz. The INSTAAR anemometer [Gill Windmaster, Gill Instruments Ltd., UK] was a 15 cm path length instrument mounted at 2.54 m above the snow surface operating at 21 Hz and recording data at 10 Hz. The sonic was pointing 40 degrees from true north and ~1 m away from the tower to limit flow effects from the tower (Figure 5-2). During the calculation of fluxes, the coordinate system of the sonic data was rotated into the prevailing wind direction. Details of the sonics are summarized in Table 5-1.

The vertical profiling system used a 6.7 m diameter SkyDoc Balloon SkyDoc Systems, LLC, USA] and a second winch to raise and lower a Vaisala RS-80 radiosonde Electrochemical Concentration Cell Ozonesonde [DMT/EN-SCI ECC and anOzonesonde] up to a height of 150 m using the SkyDoc as a "sky hook". The ozonesondes were prepared according to the NOAA/ESRL Global Monitoring Division standard operating procedures [Johnson et al., 2002]. Daily radiosondes [RS-80, Vaisala, Finland] were launched in the early afternoon from the NOAA Barrow Observatory and twice daily from the DOE ARM site at 5:30 and 17:30 hrs Alaska Standard Time (AKST). A fast response ozone instrument (FROI) based on the chemiluminescence reaction of ozone with nitric oxide (NO) was used for measurements of ozone. FROI calibrations were carried out weekly with a laboratory-calibrated Monitor Lab 8810 (Measurement Controls Corp. Englewood, CO, USA), which was calibrated against the ozone standard at NOAA, GMD, Boulder. FROI measurements were archived at 10 Hz and 5 min averages were computed. All times are in AKST, GMT - 9 h, and use 15 minute averaging periods unless otherwise indicated. Only time periods when data exist for all 7 sonics will be used in comparisons (unless otherwise indicated) to prevent biased results.



Figure 5.2: Sketch (heights to scale) of sonic anemometer mounting heights and module height. The black arrows indicate the distance between the module and Tower 1 and between Tower 1 and Tower 2. Sonics NC1 and NC2 were operated by NCAR. Sonics EC1, EC2, EC3, and EC4 were operated by Environment Canada. Sonic IN1 was operated by INSTAAR.

Sonic Name	Height above the snowpack (m)	Tower	Operator	Brand	Path Length (cm)	Sampling, Acquisition (Hz)	Orientation from true north (Degrees)
EC1	0.58	2	EC	Kaijo Denki	5	20, 10	60
NC1	1.5	1	NCAR	ATI	15	10, 10	10
EC2	1.8	2	EC	CSAT3	11.5	10, 10	60
IN1	2.5	2	INSTAAR	Gill	15	21, 10	40
EC3	3.2	2	EC	CSAT3	11.5	10, 10	60
NC2	5.4	1	NCAR	ATI	15	10, 10	10
EC4	6.2	2	EC	CSAT3	11.5	10, 10	60

Table 5-1: Sonic anemometer technical details

5.3 Turbulence Observations

5.3.1 Meteorological conditions

Typical Barrow springtime wind regimes were observed with winds from the east (0-180 degrees) ~75% of the time and below 5 m s⁻¹ ~68% of the time. Higher wind speeds were observed from the east between 78° and 124° (Figure 5.1 inset). Sonicderived temperatures (calculated from the speed of sound and are equivalent to the virtual temperature) varied between -39 and -14°C (Figure 5.3). During low wind speeds (< 2.0 m s⁻¹), mean and median temperatures varied between -30 and -26°C and were lower at lower sonic heights due the presence of a surface temperature inversion. Higher median and mean sonic temperatures (-25 and -24°C respectively) were measured during moderate to high winds (> 4.0 m s⁻¹). There was very good agreement between the mean temperatures during high winds. A one-way analysis of variance (ANOVA) demonstrated no significant difference in sonic temperature between the seven anemometers during winds greater than 4.0 m s⁻¹ at the $\alpha = 0.05$ level. Meteorological conditions during the OASIS study are discussed in further detail in Staebler et al. [manuscript in preparation, 2013].

In order to calculate gradients of sonic anemometer measurements between heights, inter-comparison periods are necessary to identify offsets between instruments. The Environment Canada sonics underwent a 44 h inter-comparison at 1.8 m. Wind speeds during the inter-comparison varied from 0.6 to 4.9 m s⁻¹. A one-way ANOVA showed no significant difference of means or variances of the uncorrected sonic temperature and wind speed at the $\alpha = 0.05$ level. The comparison of sonic IN1, operated at 2.5 m, and the EC sonics during the 44 hour EC inter-comparison period showed a significant difference at the $\alpha = 0.05$ level in wind speed and sonic temperature. For this reason, sonic IN1 will not be used for gradient calculations.



Figure 5.3: Boxplots showing sonic anemometer derived temperatures. The median is the center horizontal line in rectangle, square is the mean, 25 and 75 percentiles are the ends of the rectangle, whiskers capture 5 and 95% of the data, 'X's are 1 and 99%, and horizontal lines are minima and maxima. Temperatures are broken apart into light ($< 2.0 \text{ m s}^{-1}$) and strong (> 4.0 m s⁻¹) wind regimes. Sonics are arranged in order of height (0.6, 1.5, 1.8, 2.5, 3.2, 5.4, and 6.2 m).

The NCAR sonics did not undergo an inter-comparison period during the campaign. To account for this, we compared sonic temperatures during well mixed (i.e. windy) conditions - using the assumption that temperature would be approximately uniform between the heights under such conditions. This was tested on a high wind day (Mar 9, average wind speed 12.92 m s⁻¹) and a low wind day (Mar 24, average wind speed 1.12 m s⁻¹). There was no significant difference in the temperature means and variances calculated from the sonic measurements on the high wind day; however, there was a significant difference at the $\alpha = 0.05$ level on the low wind day. Before the campaign, the NCAR sonics underwent a two day side-by-side comparison at their facility in Boulder, Colorado. During this inter-comparison the conditions were not representative of Barrow: the average temperature was 10°C and winds were below 5 m s⁻¹. During these conditions there was excellent agreement of sonic temperature (R² = 0.99), wind speed (R² = 0.98), friction velocity (R² = 0.98), and sensible heat flux (R² = 0.97) between the sonics. The results of these tests give confidence in the ability to include the two NCAR sonics in temperature gradient calculations.

5.3.2 Comparison of turbulence measurements

Surface layer theory is used to describe the thermal stratification scaling in the near-surface atmospheric layer [*Kaimal and Finnigan*, 1994]. The stability regime is based on Monin-Obukhov Similarity Theory (MOST) which describes turbulence using the dimensionless height:

$$\zeta = \frac{z}{L} \tag{5-1}$$

$$L = -\frac{u_*^3 T_o}{kgQ_o} \tag{5-2}$$

where u_* is the friction velocity, T_0 is the ambient temperature, k is the von Karman constant (nominally 0.40), g is the acceleration due to gravity, and Q_0 is the kinematic heat flux. Sorbjan and Grachev [2010] defined ζ values of 0.0 - 0.02 as nearly neutral, 0.02 - 0.6 as weakly stable and > 0.6 as very stable. Sonics except for NC2 had at least 60% of the data fall into the weakly stable regime (Figure 5.4). In a constant flux layer the Monin-Obukhov length, L, is constant with height, which can be seen in sonics EC2, EC3, and EC4 in Figure 5.4. Sonics IN1 and NC2 extended further into the unstable range and will be investigated further in the next sections. A time series of the Monin-Obukhov stability parameter showed periods with a strong diurnal cycle and good agreement between measurements (Figure 5.5). A diurnal cycle was observed Mar 9 -Mar 14 and Mar 26 - Apr 1 when nighttime values of ζ were nearly neutral and daytime values were in the weakly stable regime. These periods were consistent with higher wind speeds (> 4.0 m s^{-1}), higher temperatures, and often corresponded with the beginning of an ozone depletion event as described in Oltmans et al. [2012]. The periods of scatter among measurements in Figure 5.5 were during low wind speed events, often below 2.0 m s⁻¹. It was during these stable periods that an ozone depleted air mass can sit over the measurement site for hours to days [Helmig et al., 2012].

Stable conditions were often characterized by low wind speeds and low wind stress on the ground. Separating friction velocity by stability revealed that during unstable and nearly neutral conditions the median friction velocity was higher and the range was larger than during stable conditions (Figure 5.6a, 5.6b). There was a clearer distinction in the sensible heat flux when separated by stability regime. Stable conditions were marked by a transfer of heat to the ground with a sensible heat flux of - 26 to 6 W m⁻²; the middle 50% of the data ranges from -13 to 0 W m⁻² (Figure 5.6c, 5.6d). During unstable conditions transport of up to 20 W m⁻² from the surface occurred although all sonics showed over 25% negative heat fluxes during those conditions. Sonic



Figure 5.4: Boxplot of 1/L where L is the Monin-Obukhov length with 25, 50, and 75 percentiles with 5 and 95% of the data covered by the whiskers.



Figure 5.5: Time series of 1/L where L is the Monin-Obukhov length. Colors represent individual sonic anemometer calculations. A) Linear y-axis from -0.45 to 1.00. B) Logarithmic y-axis from 0.0001 to 10 to show detail in the nearly neutral stability range.



Figure 5.6: Boxplots showing friction velocity and sensible heat flux median, 25 and 75 percentiles, and 5 to 95% whiskers separated by unstable (z/L < 0.02) and stable $(z/L \ge 0.02)$ regimes. Sonic NC2 does not follow the general pattern of the other sonics. A) Friction velocity during unstable atmospheric conditions. B) Friction velocity during stable atmospheric conditions. C) Sensible heat flux during unstable atmospheric conditions. D) Sensible heat flux during stable atmospheric conditions.

IN1 showed a similar range of sensible heat fluxes as EC1 even though the median was nearly 10 W m⁻² higher. Sonic NC2 does not follow the general pattern of the other sonics. The friction velocity derived from sonic NC2 was ~50% lower when compared to the other sonics. The direction of the sensible heat flux derived from sonic NC2 agreed with other sonics with respect to the stability regime; however, the magnitude was considerably smaller (-6 to +7 W m⁻²). Diurnal patterns for the sensible heat flux and friction velocity from this campaign can be seen in Staebler et al. [manuscript in preparation, 2013]. The agreement that was seen in the median sonic temperature gradients did not carry over into the friction velocity and sensible heat flux data. These discrepancies with NC2 calculations will be investigated in the next section.

5.3.3 What is the effect from the building on tower 1 measurements?

Median values of sonic temperature, friction velocity, and sensible heat flux measurements among sonics tended to agree although there were some suspect data that could be due to the building module next to tower 1. To further investigate this question, friction velocity measurements from sonics NC1 and NC2 on tower 1 were compared with results from sonics on tower 2 of similar height, EC2 and EC4. Friction velocity was used to compare the sonics as it removed the effect of height and can describe the atmospheric boundary layer conditions better than wind speed in a constant flux layer.

The comparison of friction velocities between EC4 at 6.2 m and NC2 at 5.4 m showed good agreement ($\mathbb{R}^2 = 0.69$) except when winds were coming from the WSW as shown in Figure 5.7a. The tower was downwind of the building for winds from the 170 to 290 degree sector. The red dashed line represents the 1:1 agreement. The linear line of best fit is shown in black along with the equation and correlation coefficient. Friction velocities derived from NC2 never exceeded 0.4 m s⁻¹ and were enhanced at lower friction velocities compared with those from EC4. Figure 5.7b shows the comparison of



Figure 5.7: Regression analysis of friction velocity using: A) Sonics NC2 vs. EC4. 1:1 line is shown in red. The best fit line is shown by black dashes. Color coded by wind direction. B) Sonics NC1 vs. EC2. C) Sonics EC4 vs. EC2. D) Sonics NC2 vs. NC1. For reference, the inset shows a sketch of the sonic anemometer heights and locations.

friction velocities from EC2 (1.8 m) and NC1 (1.5 m). There were similar trends as seen in the higher sonics: higher friction velocities were seen during winds coming from the SE, moderate wind speeds coming from the E, and an atypical distribution of data during WSW winds ($R^2 = 0.69$). During WSW wind events, the median friction velocity for EC2 was 0.15 m s⁻¹ while the median friction velocity for NC1 was more than double (0.33 m s⁻¹). Sonic NC1 had a 9% loss of friction velocity when compared to EC2 and experienced an increase in friction velocity when the wind was coming from the west. Further comparison confirmed that sonics EC2 and EC4 on tower 2 had very good agreement ($R^2 = 0.97$, slope = 1.02) (Figure 5.7c) while N1 and N2 had a slope of 0.44 with increased disagreement when winds were from the WSW and N (Figure 5.7d). This indicated that turbulence variables derived from NC2 were suspect.

The friction velocity calculation is based on the covariance of the three-axis wind vector and not on the absolute wind speed magnitude. Flow disturbances caused by the location of the building can interfere with the friction velocity calculation even with minimal disturbances on the scalar wind speed. There was an interesting relationship between sonic NC2 and EC4 wind speeds during WSW winds: EC4 measured wind speeds between 5.0 and 7.5 m s⁻¹ while NC2 measured between 0.25 and 9.5 m s⁻¹ (Figure 5.8a). Wind speeds derived from NC2 deviated during western winds above 4.0 m s⁻¹; however, below 4.0 m s⁻¹ there was generally agreement with wind speeds derived from EC4. The comparison of wind speeds between sonics EC2 and NC1 showed good agreement $(R^2 = 0.95)$ except during WSW winds when the module was physically blocking the wind (Figure 5.8b). Sonic NC1 was located slightly lower than EC2 and experienced slightly slower wind speeds, which can explain the slope of 0.98. From these results it is obvious that the observational differences in wind speed between towers 1 and 2 was due to the building on tower 1, which significantly interfered with measurements performed from this tower, especially during westerly winds.

Scalar variables obtained from direct sonic measurements, such as sonic



Figure 5.8: Regression analysis of wind speed using: A) Sonics NC2 vs. EC4. 1:1 line is shown in red. The best fit line is shown by black dashes. Color coded by wind direction. B) Sonics NC1 vs. EC2. For reference, the inset shows a sketch of the sonic anemometer heights and locations.

temperature, were not affected by the location of the building module. The sonic temperature dataset from sonics NC1 and NC2 did not require filtering. Wind vector variables, consisting of wind speed and direction, experienced disturbances when the flow was physically blocked by the building module. Therefore, for further analyses of wind speed and wind direction, periods when the wind direction was between 180fl and 315fl were removed from the sonics NC1 and NC2 datasets. Filtering based on wind direction removed 19% of the data from NC1 and NC2. Without the wind direction filter the correlation coefficient of friction velocities between NC1 and EC2 was 0.69 and with the filter the agreement rose to 0.94. The slope of the linear regression analysis of friction velocity between NC1 and EC2 increased from 0.91 to 0.98 as a result of the wind direction filter. This improvement in agreement between NC1 and EC2 gives confidence in the ability to use turbulence-derived variables, i.e. the Monin-Obukhov stability parameter, friction velocity, and sensible heat flux, from the wind direction filtered NC1 dataset. The correlation coefficient of friction velocities between NC2 and EC4 increased from 0.69 without the wind direction filter to 0.89 after being filtered; however, the slope remained nearly unchanged. Turbulence-derived variables were more sensitive to flow disturbances from all directions around the building module and data from sonic NC2 were removed from these further analyses.

5.3.4 Evaluation of the turbulence measurements

It was evident that the location of the building had an effect on the turbulence measurements, but how much did this affect the chemical measurements that were made? Due to the fact that westerly winds were suspected to bring in contaminated air from the city of Barrow to the study site, chemical data during these wind regimes were eliminated before further analyses. Since the lowest NCAR sonic was only affected when the wind was coming from the WSW, there is not a concern for the chemical flux measurements with this sonic. The highest NCAR sonic proved to be more difficult to evaluate even though it was not directly blocked by the building. Turbulence data for this sonic were compromised for all wind speeds and directions. Based on these observations we recommend not using sonic NC2 data for chemical eddy covariance flux measurements. Since mean scalars were not as affected by the module presence, it could be possible to take chemical gradient measurements (mean value) and use eddy diffusivities derived from Tower 2 to compute gradient fluxes. Accounting for complex distortion effects of structures is beyond the scope of this work. Rather, we edited out the data affected by distortion.

This unique dataset consisting of seven simultaneous measurements allowed for the calculation of the deviation of measurement results between sonics. A 95% confidence interval for each sonic variable was determined by calculating the standard deviation of the sonic calculations at each time step, dividing by the square root of the number of sonics, and multiplying by 1.96 (based on the standard normal curve) (Table 5-2).The third column describes the effect of the building on the specific variable before filtering. Once the building contaminated data were removed the seven sonic anemometers compared surprisingly well considering that they were from four different manufactures and located at different heights on two towers. The relative error in the wind speed measurement among the sonic anemometers decreased as the wind speed increased from 0 to 4 m s⁻¹ (Appendix Figure 5.13). Above 4 m s⁻¹ the relative error remained constant. The absolute error of the wind speed measurement was 0.29 m s^{-1} when the wind speed was less than 1 m s⁻¹. This absolute error increased ~ 0.05 m s⁻¹ per unit increase in wind speed. Wind direction was difficult to determine at low wind speeds. The 95% confidence interval for wind direction was 25° when wind speeds were less than 1 m s⁻¹. During periods when the wind speeds were between 1 and 4 m s⁻¹ the confidence interval for wind direction dropped from 14° to 4°. The confidence interval drastically improved to less than 3° at wind speeds above 4 m s⁻¹. The agreement

Variable	95% Confidence Interval	Building Effect	
Sonic Temperature	0.42°C	None	
Wind Speed	Average: 0.42 m s^{-1} < 1 m s ⁻¹ : 0.29 m s ⁻¹ Increasing at ~ 0.05 m s ⁻¹ per 1 m s ⁻¹ > 9 m s ⁻¹ : 0.72 m s ⁻¹	Minimal	
Wind Direction	Average: 6.2° < 1 m s ⁻¹ : 25° 1 - 2 m s ⁻¹ : 14° 2 - 3 m s ⁻¹ : 7° 3 - 4 m s ⁻¹ : 4° > 4 m s ⁻¹ : j 3°	Minimal	
Friction Velocity	All: 0.028 m s ⁻¹ Unstable: 0.033 m s ⁻¹ Stable: 0.023 m s ⁻¹	Significant	
Sensible Heat Flux	All: 3.2 W m^{-2} Unstable: 4.5 W m^{-2} Stable: 2.8 W m^{-2}	Significant	
$(Monin-Obukhov Length)^{-1}$	0.33 m^{-1}	Significant	

Table 5-2: Absolute uncertainties in sonic calculations after filtering by wind direction.
among friction velocity and sensible heat flux measurements was worse during unstable compared to stable atmospheric conditions. This is partially due to the fact that both variables had a wider range of median and quartile values during unstable conditions when compared to stable conditions (Figure 5.6).

5.4 Boundary Layer Height

5.4.1 Calculation of boundary layer height from turbulence

Because of the small heat fluxes (Figures 5.6c, 5.6d) in the Arctic springtime, wind speed rather than convective processes is the driving force of boundary layer growth during stable atmospheric conditions. Simple approximations using friction velocity obtained from sonic measurements can approximate the BLH. Neff [1980] and Neff et al. [2008] found that an expression from Pollard et al. [1972] could be used to estimate BLH at South Pole. The equation, originally developed for the stable mixed layer of the ocean, is:

$$BLH = 1.2u_*(fN_B)^{-0.5}$$
(5-3)

$$N_B = \sqrt{\frac{g}{T} \frac{\partial \Theta}{\partial z}} \tag{5-4}$$

where f is the Coriolis parameter (at the latitude of the study site the Coriolis parameter equals 1.38e10⁻⁴), N_b is the Brunt-Vaisala frequency, and $\partial\theta/\partial z$ is the potential temperature gradient. The Pollard equation is not sensitive to the potential temperature gradient, as it occurs as a fourth root. The Pollard equation assumes a sensible heat flux of zero and BLH is directly proportional to the friction velocity. The Brunt-Vaisala frequency is defined for stable atmospheric conditions with a positive temperature gradient between two sonics. Neff et al. [2008] found that this estimation gave reasonable results when compared to sodar-observed BLH at South Pole, although it overestimated BLH when the mixing layer became deeper. An alternative estimation describes an eddy viscosity scaling height for strongly stable regimes [*Zilitinkevich and Baklanov, 2002; Zilitinkevich et al.*, 2002]:

$$BLH = C_s^2 (u_* L/|f|)^{0.5}$$
(5-5)

where C_s (estimated as ~0.7) is an empirical constant and L is the Obukhov length (Eq. 5-1). The Zilitinkevich equation BLH is proportional to the friction velocity and the Obukhov length. This estimation is defined for strongly stable atmospheric conditions and negative sensible heat fluxes. Results of this estimation at South Pole had more scatter and tended to overestimate the BLH when compared to Equation 5-3 and SODAR-observed BLH. Both South Pole and Barrow have low heat fluxes but Barrow has a diurnal solar cycle that does not exist at South Pole.

These diagnostic equations are defined for stably stratified atmospheric conditions. After applying the wind direction filter approximately 26% of the data fall in the unstable regime and ~18% represent nearly-neutral atmospheric conditions. The depth scaling equations are not defined for unstable conditions; however, in this investigation we will extend the range of applied stability to include nearly-neutral atmospheric conditions.

5.4.2 Use of surface turbulence variables to approximate the boundary layer height in Barrow during springtime

A comparison of BLH estimated from Eq. 5-3 (Zilitinkevich method) and Eq. 5-5 (Pollard method) is shown in Figure 5.9. Boxplots show BLH estimates from each individual sonic using the Zilitinkevich method and from a pair of sonics using the Pollard method. Periods when the winds were from 180° - 315° were removed from all

95



Figure 5.9: Boxplot of boundary layer height estimations showing 25, 50, and 75 percentiles and 5 to 95% whiskers using the Zilitinkevich and Pollard methods. The Pollard method uses a gradient between two heights - the label 'EC41' defines data derived from EC4 and EC1.

BLH estimations; each boxplot has the same number of points. Sonic NC2 is included in Figure 5.9 to demonstrate that the friction velocity distortion propagated through the Zilitinkevich method BLH calculation, but these results will not be included in any further analyses. The sonic-derived temperature from NC2 was not affected by the presence of the building module and can be used for the calculation of temperature gradients used in the Pollard method, explicitly for 'NC21'. The Zilitinkevich BLH results display a dependence on the height of the sonic. Further investigation of the Zilitinkevich method showed that sonics located closer to the surface estimated a higher BLH and a larger range and that this effect was amplified when the BLH was over 100 m. The Pollard method estimated a lower BLH when compared to the Zilitinkevich method and did not show a correlation between measurement height and estimated BLH.

To evaluate the accuracy of the BLH equations, data from several series of radiosondes launched at or nearby the study site were used as a comparison. Researchers at the NOAA Barrow Observatory launched 26 radiosondes during the campaign, around noon local time. This yielded 19 usable temperature profiles after filtering for incomplete or erroneous profiles. Twice daily radiosondes were launched at the DOE ARM Climate Research Facility in Barrow, resulting in 70 temperature profiles out of 72 radiosondes launched during the timeframe of the campaign. At the study site, the INSTAAR group collected 17 tethered balloon temperature profiles between 0 and 135 m. At the top of the boundary layer the atmosphere transitions from This transition was determined using the gradient turbulent to laminar flow. Richardson number, which was calculated between each temperature and wind speed data point of the radiosonde profile, approximately every 9 - 12 m depending on the rate of ascent. The height at which the Richardson number exceeded the critical value of Ri > 0.25 was set as the boundary layer height for that profile. Varying the *Ri* critical value by ± 0.05 resulted in a change in the radiosonde-estimated boundary layer height

by ~ 20 m. Each profile and associated BLH were then visually checked for irregularities in the data. If irregularities existed the boundary layer height was instead estimated from the height of the temperature inversion [*Stull*, 1988].

An ensemble average and standard deviation were calculated at each time step for both BLH estimations. A time series of the sonic-derived BLH averages is shown with the radiosonde-determined BLH in Figure 5.10. To preserve as much data as possible, only sonic NC2 was filtered for wind direction. The sonic-derived BLH are color-coded by the coefficient of variation (CV), which is defined as the ratio of the standard deviation to the mean or simply the inverse of the signal-to-noise ratio. This normalizes the error estimate and allows for a comparison of the variability of the seven sonics over the entire range of heights. Values approaching zero indicate a general After April 9 sonic IN1 was the only sonic that was agreement between sonics. operated, consequently it does not have a corresponding CV. Both methods inferred a range of BLH from 1 m to 1000 m and showed a similar variability. Many spikes in BLH were distinct in both estimates. The Pollard method had a tighter range when compared to the Zilitinkevich method. Both methods tended to underestimate the radiosonde-derived BLH. The CV was low for the Pollard method although there tended to be more disagreement below 20 m and above 200 m. The Zilitinkevich method had a higher CV when compared to the Pollard method but visually matched up better with the radiosonde BLH estimates.

A frequency distribution of the difference between radiosonde-estimated BLH and sonic-estimated BLH is shown in Figure 5.11. The data are binned every 10 m and are classified by absolute radiosonde height. Each radiosonde-derived BLH was matched to a sonic-derived BLH within 8 minutes, and the sonic-derived BLH were averaged for a 30 min window bracketing the radiosonde result. Data shown in Figure 5.11 are from March 6 to April 9. Data with a difference greater than 200 m were combined into the bin '> 200'. Positive values indicate the radiosonde BLH was higher than the sonic



Figure 5.10: Time series of estimated boundary layer heights color-coded by the coefficient of variation. NOAA radiosonde BLH are represented by black squares, ARM radiosonde BLH by black circles and INSTAAR radiosonde BLH by black triangles. After April 9 the IN1 sonic was the only one operated. A) Turbulence derived BLH by Zilitinkevich method. B) Turbulence derived BLH by Pollard method.



Figure 5.11: Frequency distribution of radiosonde-estimated BLH minus mean sonicestimated BLH, bin size 10 m, classified by absolute radiosonde height. A) Radiosonde minus mean Zilitinkevich BLH estimation. B) Radiosonde minus mean Pollard BLH estimation. C, D) Scatterplots of the difference between sonic-derived and radiosonde estimated BLH plotted against 1/L where L is the Monin-Obukhov length. The left vertical axis shows the absolute difference while the right vertical axis shows the relative difference.

BLH. The Pollard method BLH was within 40 m 63% of the time and underestimated the radiosonde BLH 62% of the time. In comparison, the Zilitinkevich method BLH was \pm 40 m 81% of the time and underestimated BLH 67% of the time. Both methods tended to severely underestimate when the BLH was over 200 m. Interestingly, when the BLH was below 50 m both methods occasionally overestimated the BLH by more than 100 m.

Originally, both BLH estimation methods were defined for a stably stratified boundary layer. In our analysis here these methods were extended to include nearlyneutral atmospheric conditions. An analysis of the difference between radiosondeestimated BLH and sonic-estimated BLH against the median local atmospheric stability derived from the sonics is included in Figure 5.11. The blue points represent the absolute difference while the red points correspond to the relative difference. The Pollard method had 10 cases where it underestimated the BLH by more than 150 m whereas the Zilitinkevich method only had two instances. During these periods of severe underestimation, the local atmospheric stability was nearly-neutral, with ζ ranging between <0.001 and 0.008. This analysis shows that better agreement was seen during stable conditions for both methods. Higher occurrences of larger differences were seen when stability shifted towards nearly-neutral and slightly unstable conditions; however, there were still many incidences with good agreement in the nearly-neutral to slightly unstable stability regime. The Zilitinkevich method was robust to nearlyneutral atmospheric conditions which allowed the previously defined range of atmospheric conditions to be extended without a loss of agreement. Van Dam et al. [2013] found that both methods scaled well with sodar-derived BLH at Summit during weakly stable and stable atmospheric conditions although both models overestimated the BLH. At Summit, the Zilitinkevich method tended to overestimate the BLH more than the Pollard method. Similar to Barrow, the bias in the sonic-derived BLH estimates increased when atmospheric stability conditions transitioned from weakly stable to nearly-neutral. Similar results were observed at South Pole where the Pollard method gave reasonable results when compared to sodar BLH but overestimated the height as the boundary layer became deeper [*Neff et al.*, 2008]. In contrast to Summit and South Pole, both methods tended to underestimate the BLH at Barrow.

An inherent limitation of the radiosonde-derived-BLH was that radiosondes only provided a snapshot of the BLH throughout the day. A NOAA radiosonde was launched daily between 10.45 and 15.30 hrs, providing a single point in the early afternoon. The ARM radiosondes were launched at 5.30 and 17.30 hrs daily. Using only the three radiosonde observations to understand the BLH behavior could dampen the daytime and nighttime signals. A composite BLH can be modeled to provide a continuous record of BLH that can be used to further investigate surface ozone chemistry.

The composite BLH was based on the two sonic-derived BLH estimates and 115 direct observations. For both methods, the matched-pairs data of radiosonde-estimated BLH and individual sonic-estimated BLH were separated into 4 groups, 0 - 50 m, 51 -100 m, 101 - 200 m, and > 200 m. For each group, a bootstrapped bisquare weighted least squares regression was run 500 times and then averaged to provide a correction for the sonic-derived BLH for each method. The bootstrapping method also provided an estimate of the uncertainty in the correction term. A confidence interval of the correction term was constructed and the correction term was tuned within the confidence interval to minimize the bias. The correction term was applied to each group to yield the best agreement between the two sonics-derived BLH and radiosondes. These resulting BLH were averaged into a composite BLH for Barrow for the springtime The composite BLH provided a continuous measurement campaign (Figure 5.12). estimate during periods when BLH measurements were otherwise unavailable, in particular during the daytime unstable conditions and during missed radiosonde profiles.



Figure 5.12: Time series of: A) Five minute ozone mixing ratio from the FROI measured at 2.5 m on tower 2. B) Composite boundary layer height after regression analysis and bias correction.

Seven ozone depletion events (ODE), when the ozone mole fraction dropped to less than 5 ppbv, were observed during the campaign [*Helmig et al.*, 2012]. In previous studies at the coastal Halley Station, Antarctica, some observed ODEs were associated with regional-scale transport while other occasions were influenced by the buildup and decline of the stable boundary layer [Jones et al., 2006]. There was not a clear correlation between the stages of an ODE and BLH at Barrow (Figure 5.12). The onset of ODE on March 15 and April 14, and a drop in ozone on March 27 correspond to a drop in the BLH from 100 - 200 m to less than 50 m. The ending of these ODE occurred while the BLH was still less than 50 m. The occurrence of ODE on March 21, April 4, and April 6 occurred when the BLH was sustained at below 50 m. The onset of the ODE on March 26 and March 31 correspond to a drop in BLH to less than 50 m while the recovery of ozone coincided with a growth in BLH. The periods of low ozone tend to correspond with stable conditions associated with a low BLH. Highly stable conditions corresponded to ODE with the exception of the March 31 ODE, which had a longer onset and recovery. The relationship between BLH and ozone was further examined by investigating the local wind speed, wind direction, day of year, and local atmospheric stability (Appendix Figure 5.14). In general, there was not a clear relationship between low and high ozone and BLH nor was there a relationship between shallow and deep BLH and ozone mole fraction. Ozone depleted air was observed at low to moderate local surface wind speeds. Easterly winds were more abundant although low ozone mole fractions were not exclusively tied to the easterly winds. Deeper BLH were generally observed during northern to easterly winds. Deeper BLH were associated with slightly unstable, neutral, and nearly neutral atmospheric stability conditions; however, there was not a clear association of low or high ozone mole fraction with atmospheric stability conditions and BLH. In summary, the conclusion from these analyses is that BLH does not appear to exert a primary forcing on ozone at the OASIS site and ODE cannot be directly explained by the meteorological variables that were considered here. This finding suggests that synoptic transport is the primary controlling factor for ODE occurrences at this site, which has been suggested previously by other studies conducted at Barrow [*Oltmans et al.*, 2012] and over the frozen Arctic Ocean [*Bottenheim et al.*, 2009].

5.4.3 Comparison of boundary layer height behavior with other polar sites

In this section we investigate how boundary layer dynamics at Barrow compares with other polar locations and if there are particular features seen at Barrow that can possibly relate to the ODE seen at this site. Barrow experienced several days of sustained low BLH (less than 100 m) followed by periods of BLH growth with BLH extending to over 500 m. Shallow BLH days coincided with low wind speeds, stable atmospheric conditions, and a small diurnal cycle of BLH. BLH greater than 100 m rarely lasted for more than 48 hours before dropping below 50 m. Between March 9 and March 13 the BLH varied between 80 and 500 m before dropping to 20 m on March 14. A similar trend was seen between April 10 and April 13 where the BLH remained between 100 and 400 m. Occurrences of sustained shallow boundary layers are a common condition for polar environments. Low BLH at night were observed during the summertime at Dome C, but there the BLH grew from 30 to 350 m during the day due to convection [Argentini et al., 2005; King et al., 2006; Pietroni et al., 2012]. At Halley Station, similar conditions were observed as in Barrow (i.e. low convection and a weak diurnal cycle) but the atmosphere was well mixed up to 200 – 300 m [King et al., 2006]. At Summit, conditions were similar to Dome C but had intermittent days when the boundary layer grew to over 200 m [Helmig et al., 2002]. These low BLH were not seen during the summer, which was marked by stronger diurnal cycles in convection and BLH [Cohen et al., 2007; Van Dam et al., 2013]. A unique situation exists at South Pole where lacking a diurnal cycle, BLH lacks forcing from diurnally changing heat fluxes. During extended periods of high stability, BLH at South Pole were between 20 and 80 m [*Neff et al.*, 2008].

There is also the possibility that differences in topography influences the BLH dynamics. Barrow in this respect is very different than the Antarctic and Greenland stations. Air mass transport at Barrow is typically dominated by flow over the Arctic Ocean. Dome C and Summit both sit upon the topographic high on an ice sheet with a near zero slope. South Pole receives air draining from the Antarctic Plateau, yet tends to have the best agreement in BLH behavior with Barrow as South Pole and Barrow both exhibited shallow BLH and multi-day periods of sustained stability.

Several studies have investigated the BLH – atmospheric surface chemistry connections at polar snowpack sites. Van Dam et al. [2013] examined the relationship between BLH and ozone and nitrogen oxides ambient air mole fractions at Summit (72°N) and found that BLH is not a primary factor in driving ambient trace gas levels at this site. Frey et al. [2013] found that at Dome C (75°S), NO emissions from the snowpack exhibited a diurnal cycle and maximized around solar noon. Nonetheless, nitrogen oxide mole fractions in the atmospheric surface layer were lower during the day, driven by the growth of the daytime BLH. Both of these sites showed a different BLH – surface chemistry association than South Pole where shallow BLH were associated with enhanced levels of nitric oxide and ozone production near the surface [*Crawford et al.*, 2001; *Davis et al.*, 2001; *Neff et al.*, 2008; *Helmig et al.*, 2008]. Our results presented here show that Barrow, despite having similarity to South Pole in multi-day shallow BLH, does not show the strong relationship between boundary layer dynamics and ozone surface chemistry and in that respect appears to behave more similar to Summit.

5.5 Summary and Conclusions

The investigation of measurements from seven sonic anemometers provided

insights into the dynamics of the boundary layer at this coastal arctic location. Sonic temperature calculated from seven sonic anemometers agreed well across two towers and multiple measurement heights. Sonic temperature results did not show interference from the building module in the proximity of one of the towers. Wind speed and wind direction showed disturbances during westerly and southerly winds due to the proximity of the building module. Large discrepancies were observed in friction velocity calculated from sonics located near the building. All turbulence-derived data from sonic NC2 were found to be contaminated and are recommended not to be used for chemical flux calculations.

Concurrent observations of BLH from sonic-derived measurements and radiosonde estimations allowed for an in-depth comparison of the BLH at this site. BLH calculated from the filtered sonics turbulence data proved to estimate the radiosonde-derived BLH within 40 m over 60% of the time. During weakly stable atmospheric conditions, the variability in the turbulence-derived estimations for BLH tended to scale well with the variability of heights estimated from radiosonde profiles, although both methods tended to underestimate the BLH. The Pollard method severely underestimated the BLH during nearly-neutral atmospheric conditions, often by more than 150 m. A composite BLH was modeled from the two sonic-derived BLH and radiosonde estimations. This model showed sustained periods of BLH below 50 m with minimum BLH of 20 m. During unstable conditions the BLH reached 500 m and had a diurnal cycle that varied by over 300 m. When compared to other polar observations, Barrow and South Pole showed similarities in having multi-day periods in sustained shallow BLH, despite the differences in topography between these sites.

There was not a clear dependency of ozone on directly measured meteorological parameters, including wind speed and local wind direction. The periods of low ozone showed a tendency of corresponding with stable conditions associated with low turbulence-derived BLH, however there were multiple occasions of low ozone occurrences during slightly unstable and mixed BLH conditions. A change in ozone mole fraction often coincided with a change in atmospheric stability. Consequently, despite frequent occurrence of sustained shallow BLH at Barrow, a clear relationship between boundary layer dynamics and surface layer chemistry could not be established.

5.6 Acknowledgements

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Figure 5.13: Plots of error versus wind speed binned by 1 m s⁻¹. Black symbols and lines represent absolute errors and red symbols and lines represent relative errors. Relative errors are calculated by dividing the absolute error by the wind speed bin. Upper plot: wind speed. Lower plot: wind direction.



Figure 5.14: Scatter plot of composite BLH and surface ozone, color-coded by wind speed, local wind direction, day of year, and local atmospheric stability.

Chapter 6

Ozone Dynamics and Snow-Atmosphere Exchanges during Ozone Depletion Events at Barrow, AK

The behavior of lower atmospheric ozone and ozone exchanges at the snow surface were studied using a suite of platforms during the Ocean-Atmosphere-Sea Ice-Snow (OASIS) Spring 2009 experiment at an inland, coastal site east of Barrow, Alaska. A major objective was to investigate if and how much chemistry at the snow surface at the site contributes to springtime ozone depletion events (ODEs). Between March 8 and April 16, seven ODEs, with atmospheric ozone dropping below 1.0 ppbv, were observed. The depth of the ozone-depleted layer was variable, extending from the surface to $\sim 200-$ 800 m. ODEs most commonly occurred during low wind speed conditions with flow coming from the Arctic Ocean. Two high-sensitivity ozone chemiluminescence instruments were used to accurately define the remaining sub-ppbv ozone levels during ODEs. These measurements showed variable residual ODE ozone levels ranging between 0.010 and 0.100 ppby. During the most extended ODE, when ozone remained below 1.0ppbv for over 78 h, these measurements showed a modest ozone recovery or production in the early afternoon hours, resulting in increases in the ozone mixing ratio of 0.100 to 0.800 ppby. The comparison between high-sensitivity ozone measurements and BrO measured by longpath differential absorption spectroscopy (DOAS) during ODEs indicated that at low ozone levels formation of BrO is controlled by the amount of Measurements of ozone in air drawn from below the snow surface available ozone. showed depleted ozone in the snowpack, with levels consistently remaining less than 6 ppbv independent of above-surface ambient air concentrations. The snowpack was always a sink of ozone. Ozone deposition velocities determined from ozone surface flux measurements by eddy covariance were on the order of 0.01 cm s^{-1} , which is of similar magnitude as ozone uptake rates found over snow at other polar sites that are not subjected to ODEs. The results from these multiple platform measurements unequivocally show that snow-atmosphere chemical exchanges of ozone at the measurement site do not exhibit a major contribution to ozone removal from the boundary layer and the formation of ODE.

6.1 Introduction

There are many remaining open questions about the atmospheric dynamics and chemical processes that determine the late winter/early spring occurrences of ozone depletion events (ODEs) [Simpson et al., 2007b] in the coastal Arctic, despite the fact that numerous research campaigns have been conducted to investigate the cause of the ODE chemistry since their first discovery [Oltmans and Komhyr, 1986; Bottenheim et al., 1986]. Since above-surface and ozonesonde measurements have been a centerpiece of this previous research, relatively little information has been obtained on the role of ozone depletion and exchanges at the snow surface. Interestingly, research at the far inland polar sites Summit, Greenland, and South Pole, Antarctica, as well as at snow covered sites outside the Polar Regions has shown that ozone is influenced by a number of processes occurring inside the snowpack and at the snow surface. Ozone levels in air withdrawn from inside the snowpack were found to vary significantly depending on site characteristics. Very little ozone was observed inside the seasonal midlatitude snowpack at a Colorado Rocky Mountain site [Bocquet et al., 2007]. Similarly, measurements by Albert et al. [2002] at Alert, Nunavut, showed that ozone was depleted in the snowpack interstitial air, with no evidence for a photochemical mechanism, although snow chamber experiments showed a faster loss rate in the presence of irradiation. A much more dynamical ozone behavior was seen in the polar snowpack covering glacial ice where ozone levels were found to be influenced strongly by solar irradiance and wind pumping [*Helmig et al.*, 2007b]. Furthermore, a strong seasonal cycle has been observed.

The inland polar snowpack appears to be rather unreactive during the colder and dark winter months. During the warmer, sunlit period, daily cycles of ozone destruction were observed. Furthermore, the measurements at Summit showed that ozone photochemistry inside the snowpack can be a determining process for driving ozone deposition fluxes at the snow surface [*Helmig et al.*, 2009].

The ozone chemistry above the snowpack becomes further complicated by the fact that the snowpack can be a significant source of nitrogen oxides (NO_x) [Honrath et al., 1999; Jones et al., 2000]. Under the typically observed stable and shallow boundary layer conditions encountered over snow, NO_x released from the snow tends to get trapped within the lowest tens of meters above the snow surface [Neff et al., 2008; Helmig et al., 2008b]. Resulting enhancements in ambient NO_x, in concert with high radiation and elevated concentrations of radical species, can result in significant ozone production chemistry, which, under the most extreme conditions, can result in up to a doubling of ozone above the snow [Crawford et al., 2001; Helmig et al., 2008a]. This phenomenon, of course, is much in contrast to what has been described for ODE conditions, where just the opposite, i.e., ozone loss, resulting in removal of boundary layer ozone above the snow surface, occurs. In this environment, halogen radical chemistry is the culprit for the chemical destruction of ozone causing at times destruction of boundary layer ozone to below instrument detection limits over several days [Simpson et al., 2007b].

The Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) spring 2009 experiment entailed the deployment of a multitude of comprehensive chemical observing platforms for the study of ODE atmospheric chemistry at a coastal Arctic site. This opportunity was used for investigating the ozone dynamics from an extensive array of ground and balloon experiments. A particular goal was the characterization of the magnitude of ozone fluxes preceding, during, and after ODE to answer questions about the role of surface fluxes and for a more detailed contrasting of the coastal Arctic ozone chemistry with the aforementioned observations from other snow covered sites.

6.2 Experimental Setup

6.2.1 Study Site

The OASIS study was conducted approximately 5.5 km northeast of Barrow, Alaska, at the former Naval Arctic Research Laboratory (NARL) site (71.323 N, 156.667 W; 8 m above sea level) from March 8 to April 14, 2009. The snow covered experimental site was located 600 m from the Chukchi Sea to the west and $^{-100}$ m to the west of Imipuk Lake, which was frozen over and snow covered during the course of the study. A map of the study area is presented in Boylan et al. [2013]. This site was selected for the predominantly northeasterly winds coming from clean, undisturbed snow and from the direction of the Beaufort Sea. The primary measurement location was ~150 m south of the Barrow Arctic Research Center (BARC). Power lines ran next to an ice road that led to two trailers that housed the instruments. A 10 m meteorological tower for flux measurements was located 29 m SE of the instrument trailers. A second tower, 6.1 m tall, was located 2 m to the NE of the first module. The tethered balloon site was located ~50 m N-NE of the trailers. Data from the NOAA Barrow Observatory were obtained 8 km east of the city of Barrow and ~2 km southeast of the Arctic Ocean. The NOAA Barrow Observatory was located 1.9 km east of the OASIS site. All measurements are reported in Alaska Standard Time (AKST), i.e., GMT -9 h.

6.2.2 Instrumentation

6.2.2.a Ozone in the Snowpack

Ozone was measured in air withdrawn from within the snowpack using a sampling technique previously detailed and characterized [*Bocquet et al.*, 2007; *Seok et al.*, 2009], with ozone measured by an ozone UV absorption monitor (2B Technologies,

Colorado). Sample air was pulled through two lines of 6.4 mm o.d. Teflon-PFA tubing at a rate of 1.0 L min⁻¹ and measured every 10 s. The two sampling inlets had glass fiber filters (13 mm Acrodisc, Pall Corporation, U.S.) and were positioned at 0.50 m above the ~0.5 m-deep snowpack, and 0.35 m below the snow surface, approximately 5 m SE of the instrument building (see Chapter 5 for a site layout map). All sampling lines, inlet filter holders, and inlet filter materials used for the snowpack and ambient air sampling were conditioned in high ozone (\geq 250 ppbv) for at least 24 h prior to the experiment. Extensive tests have shown that ozone sampling losses are less than 1% after this treatment for the materials used in this experiment. A timed switching valve accommodated the alternating sampling between each of the inlets at ~5 min intervals.

6.2.2.b Surface Ozone Monitoring

Surface ozone was monitored by a continuously operating TEI (Thermo Environmental Corp.) Model 49C UV absorption analyzer at the NOAA Baseline Observatory from an inlet at 12 m above the ground. NOAA measurements are traceable to a Standard Reference Photometer (SRP) maintained by the U.S. National Institute of Standards and Technology (NIST).

6.2.2.c Surface Ozone Fluxes

Ozone surface fluxes were measured using the eddy covariance method. Wind and turbulence measurements were collected with a sonic anemometer (Gill Windmaster, Gill Instruments Ltd., UK) at 2.54 m above ground on the flux tower. The sonic anemometer was mounted into the prevailing wind direction (ESE) and ~1 m away from the tower to limit flow effects from the tower. A fast response ozone instrument (FROI) based on the chemiluminescence reaction of ozone with nitric oxide (NO) was used for measurements of ozone variability. The sampling inlet for the FROI was located ~20 cm behind the head of the sonic anemometer, minimizing disturbances due to the sampling line. Sample air was pulled through a 30 m, 9.5 mm o.d. Teflon-PFA line from the meteorological tower to the second module inside a conduit (arctic pipe) buried beneath the snow. From this purge line, one 6.4 mm Teflon-PFA tube connected to a Monitor Lab 8810 (Measurement Controls Corp. Englewood, CO, USA) UV absorption O₃ monitor. This monitor was calibrated against the ozone standard at NOAA, GMD, Boulder, Colorado. A second line connected the FROI to the purge line. The purge line flow rate was controlled to 12.5 L min⁻¹ with a mass flow controller. The sampling flow rate to the FROI was set at 1.5 L min⁻¹. The NO reaction gas $(2\% \text{ NO in } 98\% \text{ N}_2)$ was delivered at 150 ml min⁻¹. FROI calibrations were carried out weekly with the laboratory-calibrated Monitor Lab 8810. The instrument sensitivity was ~ 2060 counts s⁻¹ ppbv⁻¹, yielding a detection limit of ~0.051 ppbv (3σ) for a 5-min averaging time. Data from the FROI and sonic anemometer were collected at 10 Hz. There is a delay in the acquisition of the ozone signal in the FROI due to the transport time between the inlet and the reaction chamber. The lag time was determined regularly using a "puff-system" [Bariteau et al., 2010] and found to be 5.9 s. The overall response time for the sampling and signal detection was determined from the signal change of NO [Bariteau et al., 2010; these tests resulted in a signal drop to 1/e in 0.3 s (~3 Hz).

6.2.2.d Ozone Vertical Gradient Measurements from a Stationary Tower and Tethered Balloon Tower

Two sonic anemometers were located at 1.5 and 5.4 m on the second tower directly outside of module one. Three heated sampling inlets connected to 0.64 cm o.d. Teflon tubings were located at 0.61, 1.83, and 5.49 m above the snow surface. A second vertical profiling system relied on a tethered balloon system. A 6.7 m diameter SkyDoc Balloon (SkyDoc Systems, LLC, USA) was raised to 150 m above the ground. Stationary inlets were attached to a secondary tether line and raised to heights of 45, 90, and 135 m. Sampling lines were made of black, thin-wall 0.79 cm o.d. Teflon (PFA) of tubing. Each line was 183 m long to maintain similar sampling characteristics between inlets. Each of the six sampling lines ran into a manifold located in the first trailer. Samples from each inlet were collected sequentially for a period of 10 min at 5.8 L min⁻¹. Ozone was measured every 1 s using an NCAR-built chemiluminescence instrument, also operating with 2% NO reaction gas. Sample flow from the switching manifold to the ozone instrument was 500 mL min⁻¹.

6.2.2.e Ozonesonde Profiles

A second winch was used with the tethered balloon system to raise and lower electrochemical concentration cell (ECC) ozonesondes from the surface to the balloon as it was kept stationary at a height of 150 m. EnSci 2Z ozonesondes (EnSci Corp., Boulder, Colorado) paired with a Vaisala RS- 80 radiosonde were prepared according to NOAA/ESRL Global Monitoring Division standard operating procedures. The ozonesonde was placed in a Styrofoam box along with a small heat pack to keep the battery and sensor at a constant temperature. The ozonesonde package was run for several minutes at the surface to compare with surface ozone measurements. The ascent and descent of the ozonesonde package was controlled between 0.1 and 0.4 m s⁻¹ resulting in profiles lasting 12–40 min. Daily release ozonesondes were launched from the NOAA Barrow Observatory. The same EnSci ozonesondes were used. The ceiling height of these profiles was ~30 km.

6.2.2.f BrO Measurements from Longpath-DOAS

The Longpath-DOAS instrument determined the average bromine monoxide (BrO) concentration along two light paths defined by the distance between the telescope and retro-reflector arrays sited at 1074 m and 3623 m distance, respectively, using the method of Differential Optical Absorption Spectroscopy (DOAS) [*Platt and Stutz*, 2008]. The total light path lengths were thus 2148 m and 7246 m, respectively, and the

height of the light paths above ground was approximately 2 m. The long light path was used under favorable meteorological conditions, whereas the short light path was used during periods of low visibility owing to fog, blowing snow, or occasionally occurring mirages. Depending on meteorological conditions, spectra were recorded with integration times ranging between 1–50 s. For further details on the DOAS measurements, see Liao et al. [2011] and Frieß et al. [2011].

6.2.2.g Meteorological Measurements

Incoming and upwelling shortwave and longwave radiation components were quantified with a radiometer mounted 2 m above ground on a boom facing south (CNR1, Kipp & Zonen, Netherlands).

6.3 Results and Discussion

Results from these various ozone experiments are presented in the order of the instrument description, starting with the below-surface measurements, and from there going up in measurement height with the release ozonesonde data being presented last.

6.3.1 Ozone in the snowpack

Ozone measurements in air withdrawn from the snowpack were collected from March 8 to April 9, 2009; however, there are some gaps in this record due to the intermittent failure of the switching manifold. A data example, displaying both the data from the inlet below and above the surface is shown in Figure 6.1. The results from the above surface (2 m) sampling with the FROI are also included in this figure for reference. The comparison of the intermittent, switched inlet measurements from the above-snowpack inlet (blue data) with the FROI data shows that these two measurements showed good agreement, with deviations between the two measurements remaining \leq 5 ppby during most times. While the data from the above-surface inlet



Figure 6.1: Sub-snow surface (-35 cm, red points) and above surface (+1 m, blue points) ozone mixing ratios from the switched inlet ozone experiment. Ambient air results from the FROI, shown in black are included for comparison.

showed a high variability, with ozone dropping from ~ 40 ppbv to ≤ 1 ppbv during several ODEs, ozone in air withdrawn from the snowpack (red data points) was less variable, falling within the narrower range of 1-12 ppbv, and remaining around ~ 6 ppbv during most times. Specifically, there was relatively little change in ozone measured in the snowpack air during ODEs, except that during ODEs snowpack O_3 was even less variable, which can be explained by the lack of O_3 exchange between ambient and snowpack interstitial air. During ODEs ozone in air from above the surface and in air withdrawn from within the snowpack showed little difference. During times when there were sudden and rapid changes in ozone in the ambient air above the surface, the below surface measurements showed a smaller response. If ozone destruction occurring in the snowpack would contribute to ODEs then one would expect a change in ozone concentration in snowpack air preceding changes in ozone above the surface. The data in Figure 6.1 show that air drawn from within the snowpack at ~ 50 cm depth was depleted in ozone during all times and that the residual amount of ozone in the snow was largely independent of surface ozone conditions. Consequently, there is no clear indication of ozone concentration drops in the snowpack prior to above-surface ODE. Based on this behavior it can be concluded that this snowpack is a sink of ozone, however snowpack processes do not appear to play a major role in determining the ozone dynamics above the surface. Furthermore, since ozone mixing ratios in the snowpack were during most times equal or less than atmospheric ozone, ozone surface fluxes are expected to be predominantly negative, i.e., toward the snow surface (downward/positive deposition velocity).

There have been several other experiments in which ozone withdrawn from interstitial air was compared with above-surface concentrations. At Alert, Nunavut, ozone was always depleted below the snowpack surface, in dark or light conditions [*Albert et al.*, 2002]. At Summit, Greenland, ozone in the snowpack showed a dynamical

120

diurnal and seasonal behavior, with the level of ozone depletion in air withdrawn from the snow determined by the degree of solar irradiance [Helmig et al., 2007b]. Ozone in snowpack air showed distinct diurnal cycles, with minima occurring a few hours after solar maximum. Furthermore, there was a clear trend toward lower ozone (higher rate of depletion) in the summer [Van Dam et al., 2010]. During the dark winter months the snowpack appeared rather inert toward ozone, with ozone interstitial air levels mirroring above surface ambient air levels. A much different ozone behavior has been reported from sites with seasonal snow cover. Ozone in air withdrawn from inside the snowpack at Alert, Canada, Toolik Lake, Alaska, a Rocky Mountain site, Colorado Bocquet et al., 2007] and from a snowpack at a forest site in Michigan [Seok et al., unpublished data, 2009 did not show obvious photochemical dependencies, but instead was depleted to well below ambient levels at all times. In conclusion, the ozone behavior in the snowpack at the OASIS site, lacking a clear diurnal signature and showing high depletion levels throughout resembles much more what has been seen in the seasonal snowpacks than the characteristics that were seen in the year-round polar snowpack at Summit.

6.3.2 OASIS Surface Ozone

Continuous surface ozone data were collected at the OASIS site by the FROI from the ECM flux tower, from the three gradient tower inlets by the NCAR chemiluminescence instrument, and at the NOAA Barrow Observatory with the UV absorption monitor. The data from these measurements, plotted together in Figure 6.2, show a high level of agreement. During most times, deviations between instruments and sites are well below 5%. This behavior indicates a relatively homogeneous spatial ozone distribution on the geographical scale of these measurements.

A striking feature is that on several occasions ozone recorded from the highest NCAR tower inlet dropped up to ~ 10 ppbv below the other measurements, e.g., on



Figure 6.2: Time series of ozone mixing ratio (5-min mean data) from three independent measurements. Data from the NCAR tower are labeled for indication of the three tower inlet heights. The INSTAAR data are from a flux tower, approximately 40 m south of the NCAR tower. NOAA data are from the NOAA Barrow observatory. Seven ozone depletion events identified during this campaign are indicated at the top of the figure.

April 3 and 5 (see Figure 6.14 in the auxiliary material for a detailed presentation of the April 5 event). The strong gradient between the surface and the 5.5 m gradient inlet was not seen between the two lower inlet heights. Boylan et al. [2013] present an indepth comparison of turbulence measurements from the two towers and demonstrate that measurements on the NCAR tower were compromised during certain conditions by the building proximity. The departure of the agreement between ozone data from the tower inlets points toward a potential chemical interference in the ozone measurements from the NCAR tower, particularly during NW to SW wind conditions.

Figure 6.3 shows a 12-hour window of surface ozone data for a more detailed evaluation. While the five measurements display the same main features, closer inspection shows that during several occasions there was a systematic deviation in the hourly ozone concentrations. For instance, at 13:30 and 19:00 h increases in ozone were recorded at the NOAA site first, but on two other occasions, i.e., at 15:00 and 16:00 h rises in ozone were first observed at the OASIS site. This feature is somewhat surprising, as winds were originating from NE to E during this entire period. With the NOAA observatory being upwind under these conditions, a more consistent behavior, with changes at the NOAA site preceding observations (by ~ 10 min at the 3–4 m s⁻¹ surface winds) would be expected. Another interesting feature is the divergence in the ozone readings seen at $\sim 18:30$ h. This event appears to be the onset of an atmospheric stratification that caused lower ozone levels near the surface. The wind speed and wind direction data do not provide an obvious explanation for this feature, i.e., the change in wind direction was relatively small, and winds actually increased slightly during this period. The degree of atmospheric mixing was assessed by calculating the Monin-Obukhov Length (z/L) from the turbulence data. These results, added to Figure 6.3, show a sharp transition from near-neutral/moderately stable mixing conditions before 17.30 h to mostly stable conditions thereafter. Since this change was not driven by a strong drop in wind speed, the obvious cause must be the formation of a strong



Figure 6.3: (top) Twelve hours of surface ozone data from March 16, 2009. Time is in Alaska Standard Time (AKST). (bottom) The graph shows wind speed (blue) and wind direction (green) during the same period, as well as the Monin Obukhov Length (pink 'X') calculated from the turbulence data. The dotted line indicates the threshold where atmospheric mixing transitions from moderately stable (for $0 \le z/L \le 0.5$) to strongly stable conditions ($z/L \ge 0.5$).

temperature inversion from infrared radiative surface cooling likely associated with a cloud-free period (see discussion in *Persson et al.* [2002] and *Grachev et al.* [2005]). The comparison of stability calculations with the ozone record suggests that the lack of vertical mixing promoted a loss of ozone (depletion) near the snow surface that is seen in these data. Interestingly, the occurrence of the elevated ozone gradients observed in the evening of March 16 coincides with an increase in BrO from below the detection limit in the morning to more than 15 pptv at 18:00 h within a shallow layer of less than 100 m vertical extent (observed by the co-located MAX-DOAS instrument).

Remarkably, this ozone behavior at the OASIS site is opposite to what was observed at Summit, where negative ozone gradients (i.e., higher ozone near the surface) were seen during conditions with high atmospheric stability, typically during evening and nighttime. These contrasting features point toward different chemical mechanisms determining the ozone chemistry at these two sites, with near-surface ozone chemistry at Barrow likely being driven by halogen chemistry versus NO_x chemistry at Summit.

Overall, the OASIS ozone record spans 844 h of surface ozone data. The ozone concentration frequency from the three measurements (Figure 6.4), in 2.5 ppbv ozone mixing ratio bins, shows that for all records there was a predominance of low ozone events, with the largest fraction (25% for NOAA, 29% for others) of the data falling in the less than 2.5 ppbv ozone bin. Interestingly, this comparison reveals that the NOAA Barrow observatory was subjected to slightly fewer low ozone and more high ozone occurrences. At the NOAA observatory there were 12% fewer hours of ozone in the 0.0–2.5 ppbv range window and 47% more hours with ozone falling in the 30–42.5 ppbv range when compared to the OASIS site. This possibly reflects the further inland location of the NOAA observatory (~2000 m versus 700 m), making it subjected to slightly less ozone depleted air with ocean footprint origin than the OASIS site.



Figure 6.4: Histogram showing the 2.5 ppbv bin statistical distribution of observed ozone mixing ratios from the three NCAR tower inlets, the flux tower at the OASIS site, and from the 1.9 km east located NOAA Barrow Baseline Observatory.

The examination of the dependence of ozone on wind conditions in Figure 6.5shows that during OASIS there was a predominance of NE-E-SE winds. Barrow is surrounded by the Arctic Ocean from SW-N-SE, and has a land footprint in the SE–SW quadrant. It is noteworthy that these data do not show an unequivocal correlation of low ozone with oceanic footprint, as low ozone levels were also seen during times when winds were from the south (although such conditions were rare and associated with low winds). Ozone depleted air was observed during transport from a wide range of direction, i.e., 10–220°. There is a preponderance of lower ozone during calm conditions and higher ozone when winds were elevated. Other recent work suggested that blowing snow associated with higher wind speeds provides a larger surface area for heterogeneous release of bromine, and that this bromine mobilization fosters ozone destruction and lower ozone levels from ozone + bromine reaction. This hypothesis is supported not only by a model approach [Yang et al., 2010], but also by BrO measurements during the OASIS campaign [Frieß et al., 2011; Liao et al., 2012]. The OASIS ozone data suggest that the enhanced mixing during higher winds likely provides a stronger ozone source than the possible enhanced ozone removal rate from bromine reactions under such conditions.

6.3.3 Ozone during ODE

The full length OASIS ozone record (Figure 6.2) shows a number of events when ozone dropped below 1 ppbv, labeled 1–7. Overall seven ODEs (here defined as periods when ozone was less than 1 ppbv) were identified. The comparison of the 2009 data with the historical 38-year Barrow surface ozone record showed that the number of 2009 ODEs was well above the average [*Oltmans et al.*, 2012]. The time it took for the full development of an ODE was quite variable, ranging between 6 and 22 h. Similarly, there was a high variability in the full recovery at the end of an ODE (4–47 h). The



Figure 6.5: Hourly mean ozone plotted against wind speed and direction. Data from the 210–10 degree sector were excluded as that footprint was influenced by camp facilities and the town of Barrow.

overall length of the ODE ranged from 5 to 78 h. Characteristic features of the ODEs during OASIS 2009 are summarized in Table 6-1. Only one of the 7 ODEs lasted for more than one day (ODE #4, 78 h total). Figure 6.6 shows the residual ozone that was measured with the three instruments during this period. The two chemiluminescence instruments have a limit of detection of below 0.100 ppbv mixing ratios. The UV monitor is listed for a ≥ 0.05 ppbv measurement range, but has rarely been characterized for sub-ppbv levels. The comparison between these two measurement techniques, and three instruments, shows a remarkable agreement, despite the lower time resolution and higher noise in the UV monitor data at these low ozone levels. The data depicted in Figure 6.6, as well as the details on the other five ODE (Table 6-1) show that remaining ODE ozone levels during most times are in the 0.05–0.20 ppbv range. Closer inspection of the ODE record shows a pattern of ozone increases occurring during mid-day to afternoon hours. For instance, on both March 26 and 27, ozone increased from levels of 0.05-0.1 ppbv to $\sim 0.5-0.7$ ppbv during mid-day. On March 28, the increase was not as large, but a doubling of ozone from 0.1 to 0.2 ppbv observed. The incoming solar radiation data added to Figure 6.6 show that the onset of the ozone increase occurred $\sim 4-6$ h after sunrise and peaked $\sim 0-6$ h after solar noon. During all three days a reversal of this trend, leading to a decline of ozone in the late afternoon/evening was evident.

During previous field experiments in polar regions [e.g., Hausmann and Platt, 1994; Tuckermann et al., 1997; Hönninger and Platt, 2002; Simpson et al., 2007a], usually an anti-correlation between ozone and BrO was observed, which has been attributed to photochemical ozone destruction by bromine radicals in autocatalytic cycles. The BrO-HO₂ cycle, hypothesized to be dominant at low BrO, is expected to lead to an ozone destruction rate that is proportional to the BrO concentration, whereas this rate depends on the square of the BrO concentration at high BrO, when the BrO-BrO
ODE	Onset	Recovery	Length of ≤ 1 ppbv	Median Residual Ozone
Number	$(\mathrm{hours})^{\mathrm{a}}$	(hours)	Depleted Ozone	with interquartile range
			(hours)	(ppbv)
1	13	8.5	20.5	$0.12 \ (0.0817)$
2	14	9	6.8	$0.69\ (0.63\ -0.78)$
3	10	18	10.5	$0.59\ (0.37$ - $1.04)$
4	8	4	78	$0.11 \ (0.08 - 0.16)$
5	22	30	19	$0.43\ (0.28$ - $0.58)$
6	6	31	5	$0.17\ (0.13$ - $0.58)$
7	10	47	24.5	$0.23\ (0.15$ - $0.35)$
a The onset of an ODE event was set to when ozone levels began dropping more				
than 5 ppbv from the average of ozone levels seen in the preceding days.				

Table 6-1: Length of Ozone Decline during an ODE Onset, Recovery Time, Overall Duration, and Median Residual Ozone during the Seven ODEs.



Figure 6.6: Ambient air ozone (5 min mean data) measured by three instruments during ODE #4. Incoming shortwave radiation is shown in green.

catalytic cycle dominates [*Platt and Honninger*, 2003]. Photochemical models predict ozone destruction rates of 2–3 ppbv h^{-1} during an ODE [*Piot and von Glasow*, 2008], which leads to the complete destruction of ozone within approximately one day.

However, BrO cannot be produced from Br in the absence of ozone at very low ozone concentrations. Thus, the steady state involving BrO and Br is shifted toward Br, which is subsequently converted to reservoir species, such as HBr, and a proportionality between BrO and ozone can be expected. This behavior has been found during previous studies in Barrow [Simpson et al., 2007b]. However, a more detailed investigation of bromine chemistry at very low ozone concentrations was not possible owing to the lack of sensitivity of the ozone measurements at the sub-ppb level. The high sensitivity ozone measurements during OASIS and BrO measurements by DOAS allow for a more in depth re-examination of this question. The data from these measurements for ODE #4 are plotted together in Figure 6.7.

The onset of ODE #4 during the sunset of March 25 is characterized by a decrease in ozone mixing ratios from more than 20 ppbv to below 1 ppbv during less than 6 h. The rate of ozone decrease was much higher than predicted by photochemical models. It is therefore likely that part of the observed drop in ozone was caused by advection of air masses already depleted in ozone rather than by in situ photochemistry. The decrease in BrO mixing ratios from more than 25 pptv to values below the detection limit was always observed during sunset and the simultaneous decline in ozone for March 25 is most likely coincidental. The same applies to the increase both in ozone and, with a delay of 4 h, in BrO at the end of this ODE in the night from March 28–29.

During most of this time, however, ozone and BrO showed a positive correlation. The diurnal variability of both species agrees remarkably well, indicating that, as expected, the formation of BrO is controlled by ozone concentrations at these low ozone levels.

Stability and boundary layer height estimation from the sonic anemometer



Figure 6.7: Surface ozone measured with the INSTAAR ozone chemiluminescence instrument and BrO mixing ratios measured by LP-DOAS from March 25–29. Open and closed black symbols indicate BrO measurements (scale on left axis) performed along the short and long light path, respectively. The ozone surface mixing ratio (blue line) is shown on logarithmic scale (right axis). Nighttime periods are shaded in gray.

turbulence data (shown in Figure 6.15 in the auxiliary material) were used to examine if the ozone increases during ODE #4 were possibly influenced by a growth in boundary layer depth with advection of ozone-richer air from aloft. The comparison of these data, however, clearly showed that the daytime ozone increases were not correlated with boundary layer growth. Instead, the increases in ozone were observed independent of particular atmospheric stability conditions. Consequently the ozone growth seen in these data is probably from chemical production and not from advection of air from aloft with higher ozone into the surface layer at the site. J. Orlando et al. [manuscript in preparation, 2013] show that radical and NOx levels that were observed at the site during daytime hours were sufficient to sustain ozone production on the order of 0.100 ppby h⁻¹, which is consistent with the behavior seen in these data.

6.3.4 Ozone Surface Fluxes

A number of data quality control filters were applied to filter the INSTAAR flux tower ozone data record for conditions when requirements for surface flux calculations were met. Periods when instrument calibrations, zero tests, power outages, or problems with data acquisition occurred removed 23% of the data. Data were filtered based on several meteorological conditions. Conditions with winds coming from the N-SW (210– 360 degrees) were eliminated due to flow disturbances created by the upwind location of the modules and other site facilities. Periods when wind speed dropped to ≤ 0.5 m s⁻¹ were removed due to problems with expressing a streamwise wind vector under those conditions. Altogether 19% of the data were removed due to bad/shifting wind direction and low wind speeds. Another filter, testing for stationarity in ozone conditions, eliminated data from periods when ozone changed by more than 1.5 ppbv per 15 min period, removing 62% of the data. In addition, situations when the measurement height divided by Monin Obukhov Length was ≥ 0.2 were eliminated, as conditions were

deemed too stable to allow for a constant flux surface layer (22% of the data) [Sorbjan] and Grachev, 2010]. Many of the data points were eliminated by more than one of the filters, leaving 19% of the data suitable for eddy covariance flux calculations. Ozone fluxes (F_{03}) were calculated by the eddy covariance method for 15-min data increments. In order to remove the effects of mixing ratio on the flux (F_{O3}) , fluxes were converted to deposition velocity (v_d = $-F_{\rm O3}/[\rm O_3],$ in cm s^-1). A positive deposition velocity implies transport to the surface (deposition). The resulting ozone flux results are shown in Figure 6.8. In order to investigate the possible influence of surface fluxes on the variation of ozone above the snow and ODEs, flux results were binned into non-ODE and ODE conditions. A histogram of the deposition velocity when ozone was greater than 28 ppbv (non-ODE) versus ozone during ODE (here ≤ 5 ppbv) is shown in Figure 6.9 along with statistics describing the data. N_0 is the initial number of points, N_f is the number of points after filtering and quality control, and $N_f < 0$ is the number of points below zero (signifying upwards ozone flux, or more realistically statistical noise in the ozone deposition velocity results). The median/mean($\pm 95\%$ confidence interval) ozone deposition velocity outside of ODE of $0.005/0.02 \pm 0.015$ cm s⁻¹ is lower than the ozone deposition velocity of $0.11/0.16 \pm 0.047$ cm s⁻¹ during ODE. Please note that the uncertainty interval reflects both the combined variability of the ozone deposition as well as the measurement precision. The mean $v_{\rm d}$ for O_3 greater than 28 ppbv and the mean and median for O_3 less than 5 ppbv are statistically above zero, but the median vd for O_3 greater than 28 ppbv is not. In evaluating this comparison, it must also be noted that due to the deposition velocity calculation (as $v_d = -F_{03}/[O_3]$) the relative uncertainty in the ozone deposition velocity result increases with decreasing ozone mixing ratio. Consequently, while we estimate the uncertainty (considering accuracy and precision of the determination) in the ozone deposition measurement to be on the order of 0.05 cm s^{-1} during regular conditions, it is higher for the ODE results.



Figure 6.8: Time series record showing the ozone flux results after applying all quality filters, with ambient ozone mixing ratio at the top, ozone flux in the middle, and ozone deposition velocity results at the bottom.



Figure 6.9: Results of the ozone deposition velocity calculation binned for ozone mixing ratios (top) greater than 28 ppbv and (bottom) less than 5 ppbv with statistical evaluation. The vertical dashed red line shows the median of the data distribution. N_o lists the total number of 15-min flux measurement results, N_f the number of remaining values after applying all filters, and N_f less than 0 gives the number of results with negative deposition velocity.

Therefore, while there appears to be a tendency toward an overall larger ozone deposition velocity during ODE (Figure 6.9b), given that both data groups have standard deviations larger than the median values, and given the much smaller number of data points for ODE conditions, this comparison does not present a convincing case to argue for larger ozone deposition velocities during ODE. Overall, these ozone deposition rate results are small in comparison to ozone deposition rate values obtained for other surfaces [Wesely and Hicks, 2000]. These results indicate a very low ozone uptake rate and that the snow surface footprint of the flux tower is rather inert toward ozone. For example, for loss of O_3 within a 400 m thick layer (typical of the depleted layers, see below), this corresponds to a ≥ 1 month lifetime for O_3 in this layer, via loss by dry deposition. The magnitude of these ozone deposition velocity results is on the same order as observed for conditions at Summit, where ozone $v_{\rm d}\, was\,\,{\sim}0.01$ during winter/spring, and 0.01–0.05 cm s⁻¹ during summer [Helmig et al., 2009]. The potential for snowpack photochemical processes contributing to surface ozone fluxes is investigated in Figure 6.10, where all ozone flux results for greater than 28 ppbv conditions were binned hourly. There appears to be a higher variability, with a higher ozone deposition flux during morning hours, and again higher variability, with more occurrences of ozone upward flux in the late afternoon. The added radiation data show that this increase in the ozone flux happened predominantly during the first 3-4daylight hours. A hypothesis explaining this behavior could be that nighttime, dry deposition of HOBr, with subsequent production of Br_2 in snowpack air and the nearsurface layer during morning hours, rapidly destroys ozone in that layer, creating a downward ozone flux from aloft. It should also be noted that this timing typically coincided with the loss of stability in the surface layer |Boylan et al., 2013|. Consequently, this effect could also be driven by the breakup of the stable surface layer that is occurring at this time and the mixing of air from aloft with higher ozone into the



Figure 6.10: Whisker plot showing the distribution of the ozone deposition velocity as a function of the time of day from March 8 through April 14. Whiskers depict the median result in the center, the 25 and 75 percentile as the box edges, and 5 and 95 percentile as the cross bars on the staggered lines. The time axis scale uses Alaska Standard Time.

ozone-depleted surface layer. Again, this behavior is different than what was observed at Summit, where deposition fluxes peaked in the mid to late afternoon. Please note that we produced a similar graph for conditions when ozone was less than 5 ppbv. These results did not show a clear diurnal cycle and were noisier than the results shown in Figure 6.10, which likely reflects the smaller sample size and the larger relative error of the ozone deposition velocity determination at lower absolute ozone concentrations.

6.3.5 Boundary Layer Ozone Dynamics

Boundary layer profiles of meteorological variables, ozone, and selected other trace gases not reported here (nitrogen oxides, volatile organic compounds, gaseous elemental mercury) were derived from three experiments: (1) stationary 3-height continuous monitoring from the tethered balloon inlet, (2) moving a meteorological/ozonesonde package up and down by the stationary balloon (at 500 feet), and (3) from the NOAA ozonesonde launches.

Operation of the tethered balloon and ozonesonde releases were somewhat compromised by inclement weather and airspace restrictions under high wind and low visibility conditions. We also experienced some material failures of the tethered balloon components when temperatures dropped below -30° C. The summary of all available vertical profiling and surface observations is shown in Figure 6.16 in the auxiliary material. Between March 3, 2009, and April 4, 2009, more than 100 h of the long sampling line profiling (over 18 days) and 24 ozonesonde profiles were obtained from the tethered balloon at the main OASIS site. Sampling heights of the long-line inlets fluctuated by up to $\sim 20\%$ at times due to the drag and height of the balloon from changing winds and payloads. This change in sampling height was not corrected in the data displays. A total of 29 sondes were launched from the NOAA observatory. The NOAA ozonesondes do not have the high resolution of the tethered balloon observations due to the faster balloon rise rate. Furthermore, the slight delay in the ozone response to changing atmospheric ozone conditions can result in a ~ 100 m upwards shift of recorded ozone profiles.

A color contour plot incorporating all of the available ozone data within the height probed by the tethered balloon, also incorporating continuous surface observations is presented in Figure 6.11. Figure 6.12 shows some selected profile examples from the tethered balloon. Graphs of all ozone, water vapor, and potential temperature profiles are provided in Figure 6.17 in the auxiliary material. Outside of ODEs (and conditions with airflow from the City of Barrow), ozone mixing ratios were on the order of 30–40 ppbv, and during most times ozone variability within the 180 m column was less than 5 ppbv during those conditions. A much different behavior was seen in ODE event profiles. Here, a highly variable ozone distribution was observed. Several profiles showed near complete destruction of ozone (less than 2 ppbv) throughout the entire profile (to 180 m). But on other occasions, the ozone depletion was constrained to a much shallower column near the surface. Some profiles (Figure (6.12) show plumes with ozone-containing air sandwiched by ozone-depleted air below and above (profile from 13.05 h, also see profiles from March 7, April 4, and April 7 in the auxiliary material). There were several occasions when plumes with 10–20 ppbv enhanced ozone within a narrow 20–50 m band (in height) were observed. The examples in Figure 6.12 nicely capture the end of ODE #7. During the time window of these observations surface ozone rose from less than 1 ppbv to ~ 5 ppbv. The sequence of these profile data show that the breakup of the ODE was driven by a plume of ozoneenhanced air being transported in at ~ 100 m height, and that the plume then slowly descended to lower heights (as shown in the release sonde data in Figure 6.13a).

The NOAA ozonesonde system captured ozone to heights well above the tethered balloon ceiling height. Therefore these data, albeit at lower temporal resolution, provided details of the ozone structure to the top of the mixed layer and beyond. A



Figure 6.11: Composite of ozone measured at the surface (2 m, flux tower), from the stationary tethered balloon inlets, and vertical ozonesonde profiles. Also included are results from the approximate daily NOAA release ozonesonde launches. Squares represent ozonesondes launched from the NOAA Observatory. Stationary tethered. Balloon inlets are shown as periods of sampling at each of the three inlet heights. Tethered balloon ozonesonde profiles are shown with circle markers.



Figure 6.12: A sequence of ozone profiles (ascent in blue, descent in brown) obtained from the tethered balloon within a three-hour period on April 7, 2009 (launches (from top to bottom) are at 12:20, 13:05, 14:20, and 14:50 h AKST) that shows the variable vertical ozone structure. Each graph shows a pair of profiles (ascent and descent) that typically was obtained within half an hour.

contour plot incorporating the data from the first 2000 m of the flights is shown in Figure 6.13. This graph also includes corresponding data for potential temperature recorded from the sondes. Data for wind speed and wind direction from the twice daily radiosonde launches at the Barrow ARM site (adjacent to the NOAA observatory) were included for further interpretation. Over the 1-month observation period ozone in the 0-2000 m column ranged from less than 1 ppbv in depleted air near the surface to >60 ppbv at 2000 m. Outside of depletion events there is a consistent gradient of ozone with lower mixing ratios at the surface. This behavior is in agreement with the surface flux measurements, which showed that the air layer right above the snow surface primarily behaves as ozone sink. Ozone depleted air extended from the surface to variable heights between 100 and 800 m with most ODEs reaching up to 400 m. There appears to be a tendency of an increasing depth of the ozone-depleted column toward the later part of the observation period. The ozone-depleted layer was on average ~ 400 m deep in early March. Moving toward mid-April the depth of the ODE layer appears to become deeper, reaching approximately twice this height during the April 14 ODE. A similar pattern with increasing depth of the ozone-depleted column was seen in the 3-weeks long ozonesonde record from April 2008 [Oltmans et al., 2012]. Comparison of the two years of ozone records shows about 2-3 times more frequent and more pronounced ODE in 2009 [Oltmans et al., 2012]. There is, however, similarity in the vertical structure of the ozone-depleted area. Both years show variability in the ozone-depleted column, with low ozone air extending from the surface to 400–800 m height. This consistent behavior in the two years of Barrow data, is, however, distinctly different from a similar record obtained at Alert Nunavut, during spring 2000. The Alert data show at least one episode with ozone-depleted air reaching up to 1400 m [Bottenheim et al., 2002]. This can be explained by the complex terrain around Alert, resulting in stronger mechanical mixing in the boundary layer.



Figure 6.13: Observations from the release sondes. Displayed data are for ozone (a) from the NOAA ozone sondes and meteorological variables of (b) potential temperature, (c) wind speed, and (d) wind direction measured from meteorological radiosonde launches undertaken at the Barrow ARM site.

The sharp transition/steep gradients of ozone at the top of the ozone depleted air layer is remarkable. During several occasions changes of ~ 40 ppbv were seen over a narrow 50 m height band. This feature implies that ozone-depleted air was confined within a mixed boundary layer that was capped by an inversion. The ODEs in March have a defined beginning and ending that is mostly independent of height. During an event the height of the depleted air mass varied no more than ~ 50 m. The abrupt beginning and ending of ODEs appears to result from changing air masses and not from mixing of air from higher altitudes. The start of an ODE was typically marked by wind speeds below 4 m s⁻¹ in the 0–2000 m layer and winds coming from the E-NE over the Arctic Ocean. Typically, ODEs ended due to a wind regime change bringing in ozonerich air. For ODE # 1–4 the recovery time for ozone to rise from less than 1 ppbv to background levels of 25–35 ppbv was between 4 and 18 h. The April ODE #7 took 30– 47 h to fully recover to background levels of ozone. Here the ozonesondes show ozone rich air moving in from the top of the depleted air mass. The wind regime shift was not as pronounced as for the recoveries in March, providing time for ozone rich air aloft to mix with the depleted air mass. There is no consistent correlation between ODE and surface wind speed conditions. While winds were relatively calm during the shorter ODE, the longest ODE (#4) had sustained winds of $8-15 \text{ m s}^{-1}$ throughout the BL. The wind speed and wind direction contour plots, with the exception of decreasing winds lowest to the surface (50 m), show relatively homogeneous conditions in the 2000 m column. Wind shear and wind-shear driven mixing appear not to be significant factors at this site most of the time.

6.4 Summary and Conclusions

The ozone concentration and flux data from the multiple experimental platforms provide a number of new insights into ozone chemical and dynamical behavior in the coastal arctic environment. The snow covered tundra was found to be a sink of ozone. Ozone in snowpack air was depleted of ozone regardless of surface concentrations. There was no indication that ozone chemistry occurring in the snowpack at this site plays a significant role in determining the ODE dynamics seen above the surface. Ozone surface deposition rates were relatively low, on the order of $\leq 0.02-0.05$ cm s⁻¹ during most times. which is of similar order as seen at other snow covered arctic sites. There was no clear evidence of ozone in interstitial air being influenced by photochemical processes; ozone in the snowpack did neither show increases (from production) nor decreases (from chemical depletion) associated with diurnal radiation cycles. This behavior is in contrast to the snowpack ozone chemistry at Summit. Ozone production chemistry driven by NO enhancements over the snow, as seen most clearly at South Pole, does not play a determining role at Barrow. This finding is in accord with the results from the measurements of nitrogen oxides during OASIS, which showed levels of NO in surface layer air well below the 100 pptv level, which is approximately an order of magnitude lower than peak values observed at South Pole during stable conditions. The ozone insnowpack and surface flux measurements clearly showed that processes in the snowpack or at the snow surface are *not* a major determinant in ODE occurrences at Barrow.

Residual ozone in ambient air during ODEs was found to be in the 0.010-0.100 ppbv range. During three days of the most pronounced ODE, ozone increases of 0.100-0.500 ppbv during the daytime were seen. The comparison between measurements of ozone and BrO from longpath-DOAS showed that this rise in ozone correlates with increases in BrO measured in the surface layer. This behavior suggests that the formation of BrO is determined by the amount of available ozone, which controls the production of BrO by reaction of Br with ozone, and that the Br/BrO steady state is shifted toward Br (which is subsequently converted to HBr by reaction with e.g., HO₂ or HCHO) when ozone drops to sub-ppbv levels.

Ozone-depleted air masses extended to a height of $\sim 400-800$ m. Occasionally, narrow bands with higher ozone were seen in boundary layer profiles. While it took hours to days for complete removal of ozone in the boundary layer, small changes at the surface were observed on timescales of minutes to hours. The dynamical changes seen in tethered balloon profiles and ozonesonde data are in agreement with the work by *Oltmans et al.* [2012] who concluded from their analyses of back trajectories that ozonedepleted air masses are transported to the Barrow area, with the primary source region of ozone-depleted air being the Arctic Ocean. Likely, these air masses have been exposed to ozone-depleting chemical conditions for several days before reaching the site.

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Figure 6.14: Ozone measured from three heights on the NCAR tower, the flux tower (INSTAAR), and the NOAA Barrow Observatory (upper graph). The lower graph shows the record of wind conditions and stability, expressed at the Monin-Obukhov length during the same period.



Figure 6.15: Surface layer ozone, stability parameter z/L, and estimated boundary layer height during ODE #4. Boundary layer height was estimated from the turbulence data according to (Zilitinkevich et al. 2002).



Figure 6.16: Record of available vertical profiling observations. The brown lines show the days/times when the tethered balloon was up, green lines show vertical ozone sonde profiles from the tethered balloon, pink labels show available observations from the long sampling line experiment, and grey lines show the NOAA release ozone sonde launches.

























Figure 6.17: Ozone, water vapor, potential temperature vertical profiles measured from the tethered balloon during OASIS. Ascent data are labeled in brown, descent data in blue.

Chapter 7

Conclusions

The work described in this thesis provides valuable insights to our understanding of ozone dynamics in the lower boundary layer. Some of the findings are entirely new while others confirm and extend the understanding of tropospheric ozone. This research has answered some questions and provides a direction for future work.

7.1 Summary

This thesis used a combination of laboratory experiments, remote sensing and satellite derived data, and in-situ measurements over the ocean and in the arctic to look at the behavior of tropospheric ozone. Chapter 2 examined the effects of water vapor on the nitric oxide and ozone chemiluminescence reaction. To further increase the limited number of oceanic ozone flux measurements, the quenching effect of water vapor on the fast response ozone instrument needed to be identified. Previous attempts to quantify the quenching effect during a cruise proved to be operationally difficult and ambient air measurements in Boulder, Colorado lacked the humidity representative of the atmosphere above the ocean. This resulted in a series of laboratory tests. Water vapor caused over a 10% negative bias in the measured ozone signal. A correction factor previously defined in the literature was further refined to 4.13, indicating a 4.13%correction to the ozone signal is required for every 10% increase in water vapor. A Nafion drying system was installed and found that it removed over 77% of the water vapor from the sampling line with conditions similar to that over the open ocean. At lower water vapor mixing ratios the Nafion dryer removed 50% of the water vapor in the sampling line. Using the laboratory setup, the Nafion dryer removed fast fluctuations of the water vapor signal which were later determined to be white noise.
Using data from ambient air measurements, the removal of fast fluctuations was confirmed. The Nafion dryer did not have an effect on the ozone signal. The Nafion dryer was determined to be an effective method of reducing the effect of water vapor in the sampling line. The ozone instrument used here has been on several research cruises without a complete quantification of the effects of water vapor and the Nafion dryer. This experiment removed any doubt regarding the validity of ocean ozone measurements from this instrument.

The transport of ozone over the open ocean was investigated in Chapter 3. The highest ozone measurements, up to 60 ppbv, were made at island stations closest to the North American continent, which was a result of pollution outflow. Mid-Atlantic stations measured ozone maxima between 30 and 40 ppbv while the Ushuaia station in the southern hemisphere measured a maximum ozone mole fraction of 25 ppbv. Ship based measurements were compared to measurements made at fixed ozone monitoring stations. This comparison revealed that ozone could travel several thousand kilometers. Observed ozone loss was less than 6 ppbv. Using an estimated photochemical loss of ozone of 1.9 ppbv day⁻¹, estimated ozone losses were less than observed losses. The long term change of marine boundary layer ozone was examined and found to be most significant at the fixed station closest to the United States. Over the past 20 years average annual ozone mixing ratios have increased by 4.2 ppbv. During the late winter/early spring, average ozone mixing ratios have increased by 5.0 ppbv, or 0.25ppbv year⁻¹.

Concurrent measurements of ocean ozone fluxes and surface chemistry have been extremely limited. In Chapter 4 I examined the feasibility of using satellite derived ocean chemistry observations when in-situ measurements were unavailable. The reaction of ozone with chlorophyll could be the driving factor of ozone deposition. During the GOMECC cruise, chlorophyll concentrations were measured on board. I found that satellite derived chlorophyll measurements had similar spikes as seen in the in-situ data although satellite derived measurements were often two to three times larger. Further investigation revealed that during high winds chlorophyll measurements were within 1 μ g l⁻¹. When the winds were less than 6 m s⁻¹ the two measurements would deviate as a result of the stratification of the ocean surface layer. The results of this study revealed that satellite derived chlorophyll concentrations can be effective used to parameterize ozone fluxes. Current chemical climate models do not account for ocean chemistry in the determination of oceanic ozone fluxes. The agreement between the two data sets and the postulated dependency of the oceanic ozone flux on chlorophyll levels opens up new opportunities for utilizing satellite-derived oceanic chlorophyll fields for description of the large scale oceanic ozone uptake.

Measurements of ozone and boundary layer dynamics at a coastal arctic site were presented in Chapters 5 and 6. Measurements from seven sonic anemometers were examined in Chapter 5. Two of the sonic anemometers were within 3.5 m of a building. As suspected, data from sonic anemometers in close vicinity of the building were jeopardized. Sonic derived temperature was not affected by the nearby building. Wind speed and wind direction were affected only when the winds were coming from behind Contaminated data were filtered out by wind direction. the building. Turbulence measurements such as friction velocity and heat flux were severely affected by the proximity of the building. Friction velocity calculations from a sonic anemometer near the building were on average 50% lower than from a sonic anemometer located away from the effects of the building. It was advised not to use the building affected sonic anemometers for chemical flux measurements. Turbulence measurements from the same seven sonic anemometers were used to estimate the height of the boundary layer. These sonic derived estimations were compared to boundary layer heights based on radiosonde The application of scaling relations between surface turbulence and measurements. boundary layer height showed that the boundary layer height is generally underestimated when compared to radiosonde measurements. In Barrow, the primary scaling parameter of the boundary layer height was friction velocity.

The dynamical behavior of ozone was examined in Chapter 6. Seven ozone depletion events were observed during the field campaign in Barrow, AK. Interstitial air in the snowpack was depleted of ozone regardless of surface ozone mole fractions, indicating that snowpack ozone chemistry did not play a major role in ozone depletion During the longest ozone depletion event, ozone dropped to 0.01 ppbv and events. ozone production was seen in the early afternoon increasing ambient ozone to 0.08 ppbv. Due to the dramatic changes in ozone mole fractions, eddy covariance ozone fluxes were difficult to calculate. Deposition velocities ranged from 0.01 to 0.05 cm s⁻¹ regardless of ambient ozone mole fraction. The deposition velocities measured in Barrow were similar to those seen at other arctic locations. It was found that it was not local chemistry but transport of ozone depleted air masses that caused ozone depletion events at this coastal site. Ozonesonde measurements from the surface to 2000 m revealed that ozone depleted air masses extended from the surface up to 400 m. Dramatic changes in the surface ozone mole fraction were seen on the timescale of hours. A comparison of the estimated boundary layer height and ozonesonde measurements confirmed that low wind speeds in the lower boundary layer were typical when the boundary layer height was below 50 m. Since the primary mechanism for ozone depletion events at Barrow was the transport of ozone depleted air masses, one would expect a relationship between ozone and boundary layer height. This was not the case as boundary layer height during ozone depletion events ranged between 20 and 200 m while ozonesonde profiles showed that the ozone depleted layer extended to over 400 m.

While the surface chemistry and meteorology of oceans and the arctic are completely different, this research has identified several similarities. Neither the Atlantic Ocean nor snow surface in Barrow are sources of ozone. Ozone reacts with the ocean surface while the snow surface does not play a role in ozone production or

168

destruction. In both locations transport of ozone was the primary mechanism for changing ozone concentrations. Ozone depleted air masses were transported over the study site in Barrow while ozone enriched air from urban outflow was measured thousands of kilometers over the ocean. This research has provided insight to two underrepresented areas of atmospheric chemistry and micrometeorological measurements.

7.2 Future work

Several questions were left unanswered and many new questions have arisen. I found that water vapor can negatively bias chemiluminescence ozone reactions. Several researchers have used chemiluminescence ozone instruments but failed to mention whether water vapor corrections were used in their final data. With limited oceanic ozone flux data available, there needs to be a push for researchers to clarify if their measurements compensated for the effects of water vapor.

The results from Chapter 3 show the transport of ozone across the open ocean yet leave questions about ozone deposition. Further investigation is required to determine if ozone loss is due to dry deposition, photolysis, or changes in air masses. The understanding of the variability of oceanic ozone fluxes is still in its infancy. Further work is needed to more accurately determine the physical and biogeochemical controls of oceanic ozone fluxes. Relationships between ozone and chlorophyll have only been hypothesized based on model simulations. More research is needed to determine where this relationship holds true and the variability in the relationship. It is known that ozone reacts with the ocean surface microlayer; however, it is not clear if in-situ or satellite derived measurements better describe the surface microlayer. Consideration for satellite measurements depends on optical depth, sea surface state, and surface mixing while in-situ measurements are made several meters below the surface. Another method to isolate the biogeochemical enhancements of ocean ozone flux variability without direct chemical measurements has been hypothesized. This method uses the ratio of ozone fluxes to fluxes of a more chemically inert gas, such as carbon dioxide or dimethyl sulfide (DMS). The solubility of carbon dioxide in water is a factor of two higher than ozone while the solubility of DMS is a factor of ten higher, making carbon dioxide the preferred measurement in this hypothesis. The ratio of these fluxes should follow a close relationship due to physical processes and any deviations from this behavior will point towards reactions of ozone with the chemistry of the surface microlayer. The only addition to the typical ozone flux system is the addition of a LI-COR to measure carbon dioxide, which is often already installed with the micrometeorological instrumentation.

The results from the field campaign in Barrow revealed effects of flow disturbances on sonic anemometer measurements. Further questions were raised when the sonic not directly blocked by the structure experienced disturbances in its turbulence measurements. This warrants investigation to the flow distortion around structures and the compromise between chemical and meteorological measurements. Currently there is not a standard protocol for determining boundary layer height from radiosonde measurements. The Atmospheric Radiation Measurement (ARM) Climate Research Facility is currently developing a standardized method for extracting estimated boundary layer heights from radiosonde measurements, allowing for consistent reporting and less ambiguity in future research. A similar approach could be taken for sonic anemometer derived boundary layer height measurements at specific scientific Atmospheric research sites typically have at least one sonic anemometer in sites. operation. Determining boundary layer height would only require further processing of the data and would not require any additional equipment. While the sonic derived boundary layer heights may not provide an exact height of the surface layer, they may provide researchers with another tool to explain surface meteorology and chemistry. Comparisons of sonic derived boundary layer heights over deserts, grasslands and forests would reveal the ability of the estimations to handle a wider range of surface roughness, heat fluxes, and surface stability regimes.

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