Measurements of OH Reactivity Using a Chemical Ionization Mass Spectrometry Technique

Joshua McGrath
joshua.mcgrath@colorado.edu
MEASUREMENTS OF OH REACTIVITY USING A CHEMICAL IONIZATION MASS SPECTROMETRY TECHNIQUE

by

JOSHUA AARON MCGRATH

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Written by Joshua Aaron McGrath
has been approved for the Department of Atmospheric and Oceanic Sciences

______________________________
Darin Toohey

______________________________
Lee Mauldin

Date: ______________

A final copy of this thesis has been examined by the signatories, and we
find that both the content and the form meet acceptable presentation standards
of scholarly work in the above mentioned discipline.
ABSTRACT

McGrath, Joshua Aaron (Ph.D., Atmospheric and Oceanic Sciences)

Measurements of OH Reactivity Using a Chemical Ionization Mass Spectrometry Technique

Thesis directed by Lee Mauldin, Ph.D.

Typically tropospheric chemical models overestimate [OH] when compared to measurements. This discrepancy is usually attributed to incompletely modeling OH sinks due to a lack of measurements. The determination of OH reactivity provides an independent means to quantify the overall contribution of these unmeasured trace species to OH oxidation. Therefore, a new instrument was developed to measure the total loss rate of OH to chemical species in ambient air using the CIMS technique.

Measurements were performed as part of two field campaigns, the Nucleation in Forests (NIFTy) study in Indiana during May 2008 and the Ocean-Atmosphere-Sea Ice-Snowpack (OASIS) Spring 2009 intensive near Barrow, Alaska. The NIFTy study provided an opportunity to intercompare with a second OH reactivity system using the laser induced fluorescence detection technique as well as measure in an environment that has published results to compare to. The OASIS study provided an opportunity to measure in a previously unmeasured environment with a suite of complimentary measurements to allow for comparison between measured and calculated OH reactivity.

The results of the NIFTy study showed good agreement between the two instruments as well as previous published results for forest and mixed use environments. OASIS provided the
first ground based measurements of OH reactivity in the Arctic and the lowest average for measured OH reactivity of published results, about 2.5 s\(^{-1}\). OH reactivity was found to be lower during ozone depletion events than non ozone depletion events, but not significantly.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Photochemistry is a primary driver for many atmospheric processes, including the oxidation of biogenic and anthropogenic trace species (Thompson, 1995; Poppe et al., 1995), and the production and growth of aerosols (Petaja et al., 2009). A primary pathway of photochemistry is oxidation via the hydroxyl radical, OH (Thompson, 1995; Kovacs and Brune, 2001; Shirley et al., 2006; Yoshino et al., 2006). To gain a better understanding of this process, an understanding of hydroxyl radical concentrations and behavior was required, leading to a decade’s long development of instrumentation to measure OH radical in situ. This development culminated with the chemical ionization mass spectrometry (CIMS) (Eisele and Bradshaw, 1994; Tanner et al., 1997; Mauldin et al., 1998) and laser-induced fluorescence (LIF) (Wang and Davis, 1974; Hard et al., 1984; Faloona et al., 2001) techniques. These new instruments helped to gain insight into OH with regards to concentrations and diurnal and seasonal variations; yet new questions arose, particularly when comparing OH measurements to modeled behavior (Crosley, 1995; Mauldin et al., 1998; Shirley et al., 2006).

This thesis describes the work undertaken to adapt the hydroxyl radical (OH) loss measurement described in Kovacs and Brune (2001) to the Chemical Ionization Mass Spectrometry (CIMS) detection technique described in Eisele and Tanner (1991). Initial work began in January 2007 and led to an initial design that was field tested in Hyytiala, Finland that spring (and discussed by McGrath in Development of a Total OH
Los Rate Measurement Technique Using Chemical Ionization Mass Spectrometry (CIMS)). The work discussed herein, describes the revisions made to the system since that initial design along with results from two additional field experiments. An extensive discussion of revisions made to the system and the issues that occurred that lead to the modifications can be found in Chapter 2 along with basic operating parameters for the instrument. The chemical kinetics theory behind the measurement method along with detailed discussion of data analysis and processing can be found in Chapter 3. The two additional field experiments, one in May 2008 at Morgan Monroe State Forest in Indiana and the other from March and April 2009 near Barrow, Alaska, are discussed in Chapters 4 and 5, respectively, though a brief discussion of the reason for these two locations follows.

The study in Indiana provided an excellent opportunity not only to obtain reactivity values in the field with supporting measurements but also to compare results with an LIF based OH reactivity instrument and see how this environment compared to previously reported measured values of OH reactivity for forested environments. If good agreement existed between the two OH reactivity systems, with different detection techniques, it would lend credibility to the CIMS system being able to measure OH reactivity. Also, since the study was being conducted in a forest, it should have similar average and maximum values of OH reactivity to previously published results, though the presence of sizeable communities in the vicinity could push the values more towards those of a mixed use environment. Properly characterizing the chemical environment, purely forest vs. an anthropogenic intrusion environment, would be important in determining the chemical loss mechanisms for OH.
The study in Barrow, Alaska provided an opportunity to test several hypotheses about the behavior of OH reactivity along with instrumental sensitivity. The Barrow, Alaska site was chosen because it has a ‘clean’ chemical environment with anthropogenic pollution limited to the town of Barrow to the south of the measurement site, and predominantly northerly winds for that time of year. Further with no vegetation present due to the snowpack, there would be little biogenic chemical influence on the environment. Some of the hypotheses to be tested were:

Is the instrument sensitive enough to measure OH reactivity in what is expected to be a chemically clean environment? If so, is it sensitive enough to pick up changes in OH reactivity?

Is measured OH reactivity of the Arctic significantly different from what one would expect from the known chemistry of the Arctic and how well does it compare with calculated OH reactivity from the species measured during the study?

Does OH reactivity decrease with increasing daylight since OH is present for longer and there is a reduction in the amount of dark time for species to build up?

Does OH reactivity show a discernable difference between ozone depletion events (ODEs) and non ozone depletion event periods?

This chapter will discuss the primary OH production mechanisms together with a generalized overview of OH loss chemistry. A brief discussion of the techniques for measuring OH and OH reactivity in the atmosphere will follow. A review of OH reactivity measurements from the literature and a short discussion of known issues with
those detection methods conclude this chapter and provide the primary motivation for this work.

1.2 OH Chemistry

The hydroxyl radical is an important oxidant in the atmosphere. It exists at trace levels (sub ppt, levels) with many sink reactions but only a few source reactions. It is responsible for the oxidation of many trace species in the air including sulfur dioxide (SO2), nitrogen dioxide (NO2), carbon monoxide (CO), non-methane hydrocarbons (NMHCs), volatile organic compounds (VOCs), and hydrogenated chlorofluorocarbons (HCFCs) to name a few, thereby controlling their atmospheric abundance (Thompson, 1995; Kovacs and Brune, 2001; Sadanaga et al., 2005). Furthermore, oxidation of some species can also lead to the formation of secondary pollutants such as sulfuric acid (H2SO4), peroxy acetyl nitrate (PAN) and ozone (O3) (Kovacs and Brune, 2001). These products can then produce more hydroxyl radicals via one of its production reactions (Poppe et al., 1995). Figure 1.1, from Stevens et al. (1997), shows a simplified diagram of atmospheric OH chemistry. The remainder of this section will discuss the more important OH reactions described in Figure 1.1.
The primary OH production mechanism involves the photo-dissociation of ozone at wavelengths less than 320 nm (Poppe et al., 1995; Thompson, 1995). This pathway is generally considered to be the dominate source of hydroxyl radicals in both clean and polluted environments.

1.1) \( \text{O}_3 + h\nu \rightarrow \text{O}_2 + \text{O}(1^D) \)

1.2) \( \text{O}(1^D) + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \)
Another significant source of OH during the day is the photolysis of formaldehyde (Faloona et al., 2001.)

$$1.3) \quad \text{HCHO} + hv (\lambda<340 \text{ nm}) \rightarrow \text{H} + \text{CHO}$$

$$1.4) \quad \text{H} + \text{CHO} + 2\text{O}_2 \rightarrow 2\text{HO}_2 + \text{CO}$$

$$1.5) \quad \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$$

In polluted environments other photochemical mechanisms of OH production are also possible, such as the photolysis of nitrous acid (HONO) and hydrogen peroxide (H$_2$O$_2$) (Ren et al., 2003a; Sadanaga et al., 2005).

$$1.6) \quad \text{HONO} + hv (\lambda< 400 \text{ nm}) \rightarrow \text{OH} + \text{NO}$$

$$1.7) \quad \text{H}_2\text{O}_2 + hv (\lambda< 370 \text{ nm}) \rightarrow \text{OH} + \text{OH}$$

However, the latter reactions are not major contributors outside of polluted environments. In environments cold enough that thermal decomposition of pernitric acid has not occurred, the photolysis of pernitric acid (HO$_2$NO$_2$) can also be a source of OH or HO$_2$ via reactions 1.8 and 1.9.

$$1.8) \quad \text{HO}_2\text{NO}_2 + hv \rightarrow \text{OH} + \text{NO}_3$$

$$1.9) \quad \text{HO}_2\text{NO}_2 + hv \rightarrow \text{HO}_2 + \text{NO}_2$$

OH production is not limited to only photolysis driven reactions. It is possible to produce OH via so-called ‘dark’ reactions. In high NO environments, NO reacts with RO$_2$ (alkyl peroxy radical) and/or HO$_2$ (peroxy radicals) to produce OH (Thompson, 1995; Kovacs and Brune, 2001; Shirley et al., 2006; Yoshino et al., 2006).
1.10) $RO_2 + NO \rightarrow RO + NO_2$

1.11) $RO + O_2 \rightarrow HO_2 + \text{carbonyl compounds}$

1.12) $HO_2 + NO \rightarrow OH + NO_2$

In a low NO$_x$ environment, peroxy radicals can also react with ozone to produce hydroxyl radicals (Poppe et al., 1995),

1.13) $HO_2 + O_3 \rightarrow OH + 2O_2$

The destruction pathways for OH, or sinks, fall into one of two categories: the consumption of OH to produce a product or products that are long lived, thereby being an almost permanent sink of OH, or the reaction of OH to produce shorter lived compounds, or so called ‘reservoir species’, that can then cycle back into OH (Poppe et al., 1995). While there are many loss mechanisms, they often involve the reaction of OH with a trace species that has an extractable hydrogen (Thompson, 1995). In a clean environment, the most abundant species in the atmosphere for hydroxyl radicals to react with are CO and methane (CH$_4$) (Eisele et al., 1994; Sadanaga et al., 2005). The reaction of OH with CH$_4$ leads to the production of formaldehyde which can either react further with OH, or be photolyzed via Reaction 1.3. While the reaction of OH + CH$_4$ is the major loss mechanism for CH$_4$, its contribution to OH loss is only about a third of that which occurs from the OH + CO reaction. The reason is that though the atmospheric concentration of CH$_4$ is greater than that of CO, the OH+CO rate constant is two orders of magnitude faster than that of OH+CH$_4$ and therefore CO is considered the major sink of OH with regards to background atmospheric species.
1.14) CO + OH → CO₂ + H

1.15) H + O₂ → HO₂

Generalizing methane to a generic hydrocarbon, RH, with R representing a methyl, alkyl or carbonyl group, OH leads to the production of a wide array of peroxo radicals (Kovacs and Brune, 2001). These reactions proceed via:

1.16) RH + OH → RO₂ + H₂O

The RO₂ can then recycle back to OH via reactions 1.10-1.12. An example of an OH sink that produces a long-lived product is the reaction of OH with NO₂. This reaction becomes important when NO₂ is present in concentrations larger than 1 ppb (Poppe et al., 1995).

1.17) NO₂ + OH + air → HNO₃ + air

Nitric acid can photolyzed to regenerate OH, but this process is very slow (2-4 weeks) compared to its atmospheric lifetime due to heterogeneous loss (mean lifetimes of a few days) (Levin and Schwartz, 1982; Logan 1983). OH can also react with the nitric acid to produce HO₂ which could then regenerate OH but this process is not much faster than nitric acid photolysis.

In summation, while the production of OH can be strongly correlated to the rate of ozone photolysis (Rohrer and Berresheim, 2006), with extra sources in more polluted environments; the loss of OH, and hence its lifetime, is highly dependent on the chemical environment. Irrespective of the environment however a minimum loss of OH
exists due to the global distribution of methane (approximately 1.8 ppm) and carbon monoxide, minimum monthly mean of about 150 ppb in the Northern Hemisphere and about 50 ppb in the Southern Hemisphere at surface, using MOPITT CO retrievals. As an environment increases in chemical compounds, most OH loss reactions can be described by reaction 1.16.

1.3 Measuring OH

The measurement of hydroxyl radicals has proven historically difficult due to their low atmospheric abundance and high reactivity (Tanner et al., 1997; Crosley, 1995; Schlosser et al., 2007). Early attempts to measure OH relied on chemical conversion via $^{14}$CO (Felton et al., 1988) or long-path laser absorption (Perner et al., 1976). Issues related to the large temporal and spatial variability of OH abundances hindered the sensitivity of these measurements to observations of short-term behavior in the concentration of hydroxyl radicals (Crosley, 1995). These issues were addressed by the development of chemical ionization mass spectrometry (CIMS) in the late 1980s (Eisele and Tanner, 1991) and with the development of laser induced fluorescence using full assay gas expansion (LIF-FAGE) in the mid-1990s (Stevens et al., 1994). These systems allowed for in situ measurements of hydroxyl radical in real time (Eisele and Bradshaw, 1993), and both have been used extensively in field campaigns since their development.
Real time, in situ measurements with high sensitivity to changes in hydroxyl radical concentration allowed for better understanding of atmospheric photochemistry but also raised new questions. The large number of sinks of OH, together with the multiple recycling pathways available and limitations on how many trace species can be measured simultaneously, has led to discrepancies between measurements and chemical models (Sinha et al., 2007). Comparison with measured hydroxyl radical concentrations has revealed discrepancies in model simulations, with the models typically overestimating OH concentrations by up to a factor of 2 (Maudlin et al., 1998; Shirley et al., 2006). These discrepancies were normally attributed to unaccounted for OH losses or sinks. While measurements in polluted environments would be expected to be incomplete, those in remote, ‘clean’ environments more adequately capture the dominant OH sinks, such as CO and CH4. These discrepancies hinted strongly that important unknown chemical pathways that were acting as hydroxyl sinks (Di Carlo et al., 2004), with important implications for accurate model treatments of oxidation by OH in the troposphere.

The longstanding discrepancy between OH measurements and models motivated the development of techniques to measure and quantify the lifetime of OH in the atmosphere or put another way the reactivity of OH with regards to ambient air.

Before delving further, a definition of OH reactivity is needed to focus the discussion. In this case OH reactivity means a change in an initial [OH] after time \( t \), during which OH is exposed to ambient air. The slope of this change, \( k \), is the reactivity while \( 1/k \) gives the lifetime of OH. A further discussion of the mathematics of the
measurement can be found in Chapter 3. A method to measure OH reactivity required four conditions to be met:

1) A method of measuring [OH]

2) A method of producing OH to react with ambient air and in sufficient quantities to be measurable

3) A means of introducing the produced OH to ambient air in a controlled manner, but also fast enough so that a change in [OH] is measurable given its short lifetime, <1 sec.

4) Additionally, it must be practical to perform said measurements in the field.

Condition 1 is easily met using either the LIF or CIMS instrumentation. Condition 2 is also easily met using the calibration technique for OH systems which involves photolyzing water at 184.9 nm (Mauldin et al., 1998; Faloona et al., 2004). This left the conditions of how to introduce OH to ambient air and be able to measure \( \Delta [OH] \) and make the technique practical for use in the field. These conditions were met by adopting a discharge flow-technique (Kovacs and Brune, 2001). This involved producing OH at the tip of a movable injector rod inside a flow tube that is filled with ambient air. Moving the injector rod allowed to change the time that OH was exposed to ambient air allowing for the change in [OH] to be determined. By flowing ambient air through the flow tube fast enough, the total time of OH exposure to ambient air could be kept to 1 sec or less.
Later, a method using LIF was developed that eliminated the injector rod and produced OH by photolyzing ozone with a 266 nm laser (Yoshino et al., 2006). These two techniques are discussed further and compared in Chapter 2. Soon thereafter an indirect relative rate measurement measured the decay rate of hydroxyl radicals in the presence of a compound not normally found in the atmosphere in the absence and presence of ambient air was developed (Sinha et al., 2007). Since the CIMS technique is a direct measurement technique, the indirect method is not discussed in this paper.

1.4 OH Reactivity Field Results

Several studies have been carried out using a total OH reactivity measurement technique. Most of these have been carried out in urban environments including the Southern Oxidant Study (SOS) Campaign in Nashville, Tennessee (Kovacs et al., 2003; Martinez et al., 2003), the Tokyo Metropolitan University study in Tokyo, Japan (Yoshino et al., 2006), the Mexico City Metropolitan area study (MCMA) in Mexico City, Mexico (Shirley et al., 2006), the Texas Air Quality Study (TexAQS 2000) in Houston, Texas (Di Carlo et al., 2004) and the multiyear PM 2.5 Technology Assessment and Characterization Study-New York (PMTACS-NY) in New York City, New York (Ren et al., 2003a, 2003b, 2006a). A study in a semi-agrarian location was carried out in central Pennsylvania at a Penn State University agricultural research farm (Ren et al., 2005). There were also two forest reactivity measurements carried out, one as a part of the PROPHET 2000 study in northern Michigan (Di Carlo et al., 2004) and the other PMTACS-NY at Whiteface Mountain in 2002 (Ren et al., 2006b). In the case
of PROPHET, the measurements were made approximately 10 m above the forest canopy, while for PMTACS-NY at Whiteface Mountain the instruments were in the tree canopy of Whiteface Mountain. A summary of the findings of the average reactivity and maximum reactivity of OH from each study is presented in Table 1.1.

Table 1.1 Compilation of measured OH average and maximum reactivity measured in various OH reactivity studies.

<table>
<thead>
<tr>
<th>Study / Location</th>
<th>Average reactivity (s⁻¹)</th>
<th>Max Reactivity (s⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>Nashville SOS</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>PROPHET 2000</td>
<td>N/A</td>
<td>13</td>
</tr>
<tr>
<td>PMTACS-NY 2001</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Agrarian Pennsylvania</td>
<td>6.1</td>
<td>15</td>
</tr>
<tr>
<td>PMTACS-NY Whiteface</td>
<td>5.6</td>
<td>12</td>
</tr>
<tr>
<td>Mexico City, Mexico</td>
<td>33</td>
<td>200</td>
</tr>
<tr>
<td>Tokyo, Japan</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>PMTACS-NY 2004</td>
<td>30</td>
<td>N/A</td>
</tr>
</tbody>
</table>

The 1999 SOS campaign in Nashville was the first reported field measurement of total OH reactivity. The environment was a mixed-use landscape comprised of an airport near deciduous forests and pastures within an urban setting with measurements made during midsummer. Kovacs et al. (2003) found a diurnal variation in OH reactivity mainly during the morning and afternoon rush hours. The authors found
modest variability in OH reactivity during the midday, but large variation in nocturnal OH reactivity. A single large source was ruled out as the cause of the variability since it occurred with northerly, westerly and southerly winds, though wind speed was generally less than 4 m s\textsuperscript{-1}. Therefore the variation was attributed to changes in [NO\textsubscript{2}], and the stability of the nocturnal boundary layer. Comparisons of measured OH reactivity to calculated values found that measured OH reactivity was equal to 1.3 times the modeled OH reactivity using species measured during the study. The forty chemical species used to calculate OH reactivity can be found in Table 1.2. The measured OH reactivity was also compared to model simulations. The modeled reactivity was found to be 20% lower than measured reactivity rates for overlapping data points (Martinez et al., 2003). This discrepancy was attributed to short lived VOCs. This conclusion was drawn from measurements done in a nearby tunnel where VOC concentrations were high enough to measure. Here comparisons between measured and modeled reactivity in the tunnel resulted in a discrepancy of only 10%.

**Table 1.2 Chemical species used to calculate OH reactivity during Nashville SOS.**

*From Kovacs et al., 2003.*

<table>
<thead>
<tr>
<th>Chemical species</th>
<th>OH reactivity used in calculations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>trans-2-Butene</td>
</tr>
<tr>
<td>Propane</td>
<td>Isoprene</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>cis-2-Pentene</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>trans-2-Pentene</td>
</tr>
<tr>
<td>i-Butane</td>
<td>Benzene</td>
</tr>
<tr>
<td>n-Butane</td>
<td>Toluene</td>
</tr>
<tr>
<td>2-Methyl pentane</td>
<td>Ethyl benzene</td>
</tr>
<tr>
<td>3-Methyl pentane</td>
<td>o-Xylene</td>
</tr>
<tr>
<td>Acetylene</td>
<td>1,3-Butadiene</td>
</tr>
<tr>
<td>Ethene</td>
<td>m,p-Xylene</td>
</tr>
<tr>
<td>Propene</td>
<td>Acetone</td>
</tr>
<tr>
<td>1-Butene</td>
<td>Methylvinylketone</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>Methylethylketone</td>
</tr>
</tbody>
</table>

\(a(m) = 1\) min. All others hourly.
During the summer of 2001, OH reactivity measurements were carried out as part of the PMTACS-NY study. The measurement site was set-up at Queens College in Queens, NYC atop a tower in a parking lot with the sampling port approximately 6.4 m above the ground. Westerly winds brought polluted air from Manhattan to the site, while easterly winds brought in cleaner air from the Atlantic Ocean. Ren et al. (2003a) found the typical OH reactivity was 20 s$^{-1}$. Peaks in reactivity, ~25 s$^{-1}$, were generally associated with the morning rush hour, while minimums of ~15 s$^{-1}$, were generally observed between 1300 and 1900 hours. The minimums coincided with minimums in NO$_x$ concentrations. These average loss rates equated to an average lifetime of about 50 ms and were half of what was measured in Nashville and Houston.

A megacity urban environment was studied in April 2003, when the Penn State total OH loss rate measurement instrument was deployed in Mexico City, Mexico as part of the Mexico City Metropolitan Area study. The instrument was located atop one of the campus buildings at the Autonomous Metropolitan University sampling at approximately 18 m above street level. Measurements of OH reactivity showed a pronounced diurnal cycle, with peak reactivity centered near 600 (CST), Shirley et al. (2006). The average reactivity was found to be ~120 s$^{-1}$, with measurements as high as ~200 s$^{-1}$. By midday, the reactivity had dropped off significantly, to an average of 25 s$^{-1}$. A smaller second peak was found to occur at night around 2200 (CST) averaging around 40 s$^{-1}$. Around this time individual reactivity measurements were as high as 180 s$^{-1}$. When compared to the measurements from New York City, another megacity, these measurements were quite startling. Rush hour reactivity in Mexico
City was almost five times larger than in New York City. Also peak reactivities during this time were four times higher for Mexico City than New York City.

In Japan, Yoshino et al. (2005) at Tokyo Metropolitan University began using their OH reactivity instrument to make periodic measurements in Tokyo from July 2003 through November 2004, providing a seasonal sampling for an urban environment. The plots from their paper are presented in Figure 1.2. The measurements show interseasonal variability between 10 s$^{-1}$ and 90 s$^{-1}$. The summer increase was attributed to increases in the concentrations of CO and NO$_x$ during the same period. Winter observations had reactivity rates centered around 20 s$^{-1}$. Elevated reactivity levels during winter were again attributed to elevated NO$_x$ concentrations. Similar patterns held for the spring and autumn measurements, where reactivity rates stayed in a fairly consistent range but would increase with increases in the NO$_x$ concentration. When measured reactivity rates were compared with model calculations, a difference of about 30% was found in the reactivities for all seasons but winter. Winter observations had a difference of about 5% which fell within the error of measurements and model. Comparing the calculated OH reactivity for each species measured and comparing the discrepancy between measured and modeled OH reactivity overall showed that only OVOCs and ozone correlated. Therefore it was believed that oxidation of VOCs into OVOCs is a part of the missing OH reactivity story for Tokyo.
Figure 1.2 Measured and Calculated OH Reactivities from Tokyo, Japan

From Yoshino et al. (2005)
From early January to early February 2004, Ren et al. (2006a) returned with the Penn State total OH loss rate measurement instrument to the campus of Queens College as part of the PMTACS-NY winter intensive. OH reactivity observations showed two peaks, during the morning and evening rush hours. Here average OH reactivity during winter observations were about 10 s\(^{-1}\) higher than those observed during the summer intensive in 2002. Comparisons between measured OH reactivity and the calculated activity using VOC measurements from the last week of the intensive showed good agreement in variation of reactivity. The calculated reactivities, however, generally were lower than those measured, particularly during the morning and evening rush hours.

These studies, which have added greatly to the knowledge of OH reactivity in different urban environments, raise important new questions. While the PMTACS-NY studies showed an increase in OH reactivity during the winter, the same cannot be said for Tokyo. During winter time in Tokyo, the reactivity generally stayed below 40 s\(^{-1}\) and did not peak above ~50 s\(^{-1}\). This observation is in contrast to the summer and autumn months where reactivities were measured above 80 s\(^{-1}\) occasionally. Differences in part can be attributed to the fact that only a handful of days had measurements in Tokyo whereas PAMTACS-NY measurements were taken continuously over a month’s time. However, this discrepancy does exist. Additional OH reactivity observations in other urban areas throughout the year would shed light on how variable OH reactivity is throughout the year and what generalizations can be made about these environments.
Total OH reactivity measurements were carried out at two different locations during the summer of 2000. From 5 July to 3 August 2000, OH reactivity was measured as part of PROPHET 2000. During this study, Di Carlo et al. (2004) discovered that when compared to the calculated values, there was a temperature dependence on the measured OH reactivity. Over an increase in temperature of 15 K, this discrepancy increased from 0.5 s\(^{-1}\) to 3.7 s\(^{-1}\). When compared to terpene emissions, OH reactivities were found to have the same temperature sensitivity factor. This result led to speculation that unknown BVOCs were present and reacting with OH. Anthropogenic VOCs not being measured at the site were ruled out because their concentrations would be dependent on transport to the site rather than temperature (Di Carlo et al., 2004).

The Penn State total OH loss measurement instrument was deployed at Whiteface Mountain in upstate New York as part of PMTACS-NY from mid-July to early August. The measurement site was at an elevation of 600 m within the forest canopy. Ren et al. (2006b) measured an average reactivity of 5.6 s\(^{-1}\), which is comparable to the study done at the Penn State research farm. Reactivity had a maximum near midday and a minimum at night. The variability in measured reactivity was greater during the day than at night. Comparison between calculated OH reactivities and measured values agreed well, with differences being within the uncertainty of the calculations and measurements. Unlike the previous measurements in a forest environment, there was no temperature dependence found for the reactivity.

The two forest studies also raise some interesting questions, the most prominent being why does one study find a temperature-dependence to OH reactivity while the
other does not. Forest composition is a large part of this issue since different flora can emit VOCs in varying quantities, and under different conditions (Ren, et al., 2006b; Fuentes et al., 2007). So having measurements in multiple forests helps to determine which have a temperature-dependence and which do not. Differences in flora at the locations can help identify the missing reactants. Furthermore, both of the above studies were carried out during the summer months when most budding has already occurred. It would be interesting to see how OH reactivity behaves during the spring when new growth is just starting and autumn as leaves are shed and plant activity shuts down for the winter.

During the late spring of 2002, OH reactivity measurements were carried out as part of a larger study in semi-agrarian part of Pennsylvania. The research site was an agricultural research farm belonging to Penn State University. Local anthropogenic sources were primarily from the city of State College about 11 km away and a state highway approximately 200 m from the site. Ren et al. (2005) found a daily average of OH reactivity to be 6.1 s\(^{-1}\). When compared to the other studies in Table 1.1, the daily average OH reactivity value is higher than those values seen during PROPHET for a forested region (Di Carlo et al., 2004) but much lower than for the urban environments measured. Like the PMTACS-NY 2001, the study in Pennsylvania saw OH reactivity highest during the morning rush hour and the lowest during mid-afternoon, though not nearly as pronounced.
1.5 Known Issues with LIF Technique in OH Detection

Though the LIF system has been used extensively in the field to measure OH concentrations, it has suffered from a series of technical issues. Early incarnations of the LIF technique suffered from artifacts that affected the detection of OH. Since early systems used the 282 nm wavelength to excite OH for detection, ozone photolysis in the beam’s path was leading to hydroxyl radical production. Also fluorescence from aerosols and trace gases were leading to background issues with the measurements (Crosley, 1994). These issues were alleviated to a degree by moving the laser wavelength to 308 nm, which reduced ozone’s photolysis cross section by a factor of 30 (Faloona et al., 2001). Unfortunately, using the 308 nm wavelength led to increased light scattering within the detection cell along with nonresonant fluorescence that could not be filtered out and thereby increased difficulty in isolating the hydroxyl radical signal (Stevens et al., 1994).

Faloona et al. (2001) also documented a measureable OH signal when the system was sampling zero air. While it was only one test that fell outside of 1 sigma of zero, the fact that OH was being seen is a concern since zero air is used in OH reactivity measurements to determine the instrumental contribution to the decay, and therefore adds more uncertainty to the overall technique. Another issue with the LIF technique is the continued detection of OH at night by the system (Faloona et al., 2001; Schlosser et al., 2009). It is suspected of being a wall reaction when a large concentration of unsaturated hydrocarbons is present with O₃. While it is possible to have some production of OH at night from non-photochemical sources, simultaneous
measurements with CIMS systems have not seen this nighttime, or dark, OH (Schlosser et al., 2009). Therefore it is possible that for nighttime measurements of OH reactivity, the reported decay rates are inaccurate.

1.6 Summary

In an attempt to better understand OH’s behavior in the atmosphere, methods of measuring OH reactivity have been developed. Measurements of OH reactivity have been successful carried out multiple times in a variety of environments adding to the knowledge of the photochemical budget. They have helped explain some of the discrepancy in OH model to measured comparisons as well as helping to quantify missing reactivity. At the same time new questions have been introduced such as the temperature dependence on decay rates during PROPHET and large variations in nighttime reactivity. With LIF systems being the only systems currently in use for the direct determination of OH reactivity, there is some question of how well these systems are capturing total OH reactivity in the atmosphere due to their known technical issues. The addition of a system that relies on the CIMS detection technique will not only add validity to the LIF measurements but also provide an alternative system for use where LIF is not feasible, i.e. limited power availability or limited working space. For example, the current CIMS configuration uses about 1 kW of power, whereas LIF uses between 3.5 and 5 kW of power. The dimensions of the CIMS are 1.2 m by 1.2 m compared to 1.3 m by 2 m for an LIF system (Robert Hansen, private communication).
Chapter 2
Instrumentation

2.1 LIF OH Reactivity Systems

Before detailing the system used to perform OH reactivity measurements it will be helpful to briefly describe the systems currently in use and which provided the best option for adapting to the CIMS detection system. At Penn State in the late 1990s, a method for measuring the lifetime of hydroxyl radicals was developed. Figure 2.1, taken from Kovacs and Brune (2001), shows the setup of the Penn State instrument. The system is comprised of an injector tube, flow tube and detection system. At the tip of the injector tube is a source to generate hydroxyl radicals. Ultra high-purity nitrogen is flowed through a bubbler containing de-ionized water. The humidified nitrogen then flows, at a rate of about 4 L min\(^{-1}\), into the injector tube made of stainless steel with a diameter of 1 cm. At the end of the injector tube, a mercury lamp is housed in a larger chamber which is shielded to prevent photochemistry from occurring in the flow tube. The lamp photolyzes water producing OH via reaction 2.1 and peroxy radicals via reaction 2.2.

\[
2.1) \text{H}_2\text{O} + h\nu \rightarrow \text{H} + \text{OH} \\
2.2) \text{H} + \text{O}_2 \rightarrow \text{HO}_2
\]

This flow then enters the main flow of the flow tube via a piece of Teflon with radially drilled holes.
The flow tube is a 5 cm diameter glass tube with a 10 cm diameter glass cross-piece at each end. The upstream cross provides the injector tube with access into the flow tube. The two openings in the cross perpendicular to the injector tube provide the access for the introduction of ambient air or calibration gases. The downstream cross-piece provides access for the detection system, the blower and a hot wire anemometer. The detection system sits perpendicular to the flow with the hot wire anemometer opposite the detection system. The blower provides the flow through the flow tube.

Figure 2.1. Penn State TOHLMS from Kovacs and Brune, 2001.

The detection system is comprised of a detection inlet, detection cell, micro-channel plate and vacuum pump. The detection inlet has a 0.675 mm diameter opening
through which the air is drawn into the cell which is maintained at approximately 16 hPa. The cell is cubic in shape with its walls painted black. Each face of the cube has an aperture in it to form three perpendicular axes. The first axis is for the laser bean to enter a multipass white cell. Perpendicular to that axis, on the same plane, is a gated micro-channel plate (MCP). The third axis perpendicular to the laser-MCP plane is the opening through which the sample gas is drawn. The hydroxyl radicals at this point are then measured using laser-induced fluorescence for 10 s on the 308 nm absorption line and 10s off the absorption line. A complete decay measurement, with 10 residence times, can be accomplished in 4 minutes.

When [NO] > 1 ppb a correction factor is necessary to account for the hydroxyl radicals formed by reaction (1.5) due to HO$_2$ in the source (Shirley et al., 2006). This correction is determined from measured [HO$_2$]/[OH] ratios (HO$_2$ is measured by adding a large excess of NO to the flow, and assuming that the ratio of HO$_2$ to OH remains stable between such measurements). The OH produced by reaction of HO$_2$ to ambient abundances of NO reaction is calculated using a simple kinetics model for each point measured. The first measurement, denoted M1, after $t=0$ is corrected by subtracting out the created OH calculated by the kinetics model, producing M1$^*$. The next step is to reduce the value of the subsequent point, M2, such that the slope between points M1 and M2 is preserved between M1$^*$ and M2. Once that is done, the created OH calculated from the model can be subtracted from the M2 value to produce M2$^*$. This is repeated for all points in the decay. Figure 2.2 shows the setup of the hydroxyl radical reactivity measurement that was developed at Tokyo Metropolitan University (Sadanaga et al., 2004). The principles of this system are the same as that of the Penn State system,
though the method is slightly different. The system is comprised of a flow tube where hydroxyl radicals are produced and then measured using a fluorescence detection system modeled after the one from Penn State. In lieu of a movable injector rod to produce OH, ozone is introduced into the flow tube and then pulsed by a 266 nm laser to create hydroxyl radicals via reactions 1.1 and 1.2. The hydroxyl radicals then have approximately 1 s to react with trace species in the air before entering into the fluorescence detection cell. To reduce heterogeneous losses of hydroxyl radicals and other trace species the interior of the flow tube is coated in Teflon.

Figure 2.2. Tokyo Metro University OH Loss Instrument from Sadanaga et al., 2005.
2.2 CIMS Flow Tube System

The OH reactivity measurements described in this thesis were performed using a flow tube system similar to the Penn State design. This design was chosen for its simpler OH production mechanism and ability to be more readily adapted to the CIMS system. The system is composed of a glass flow tube, an injector rod to create and introduce the hydroxyl radicals to the sampled air, and a small cart rack that supports the system while connected to the CIMS and houses the pumps, flow controllers and other components used to perform the measurements. A description of each component will be presented and an overview of the system configuration used during studies Indiana and Alaska, previously mentioned in Section 1.1.

2.2.1 Glass Flow Tube

The flow tube is made up of three glass sections joined together with O-Ring clamps. A schematic of the set up used in the lab can be found in Figure 2.3 and is described below. The main section of the flow tube is made of thin-walled glass with a #40 O-ring joint located at the upstream end for attachment of the next section. There are two access ports along the flow tube for insertion of a hot wire anemometer to measure the velocity through the center of the tube and have an inner diameter of 12.7 mm. They were spaced as such to provide measurements at two points along the flow tube to see if the flow velocity varied. When not in use, the ports are capped off using ¾” inch to ¼” Swagelok reducing unions.
The next section is a glass tee with an arm set at a 45° angle. This piece allows access for the injector rod into the flow tube as well as a means to bring in ambient air or to use a gas to fill the flow tube. Each end has a #40 O-ring joint for attachment and sealing to a component piece. The inner and outer diameters of this section are the standard dimensions for the Kontes O-ring joint. End caps, also made of #40 O-ring joints, are then attached. Each has a stem about 5.0 cm long with an inner diameter of 1.3 cm. These stems provide a method of attaching a zero gas line by means of Ultra Torr fittings as well as allowing for injector rod movement in the flow tube without allowing in ambient air via a modified Swagelok fitting. This modified Swagelok fitting is a three quarter inch to half inch union that has been bored through so the injector can pass through.

![Figure 2.3 Schematic of OH Reactivity flow tube system](image)

The glass stem end uses a Teflon ferrule in place of the standard metal ferrule to avoid damaging the glass. The injector rod end also uses a Teflon ferrule but reversed from its normal direction. A small o-ring is placed between the ferrule and union to form an air tight seal without preventing the injector from moving smoothly through the fitting.

---

1 The glass stem end uses a Teflon ferrule in place of the standard metal ferrule to avoid damaging the glass. The injector rod end also uses a Teflon ferrule but reversed from its normal direction. A small o-ring is placed between the ferrule and union to form an air tight seal without preventing the injector from moving smoothly through the fitting.
Shortly after returning from Indiana and following some additional testing in the lab, a few minor modifications were made to the flow tube. The flow tube length was shortened from 76.2 cm to 71.1 cm to allow the injector rod to be closer to the detection instrument’s sampling inlet thereby reducing the distance in the flow tube between the \( t=0 \) position and the CIMS inlet. The shorter distance reduces the amount of OH loss that occurs before the measurement positions. The dual access port design was dropped in favor of a single port following testing which showed that flow speed or velocity did not vary much between the two points and most variation in the measured velocity could be attributed to the proximity of the injector rod to the hot wire anemometer. In addition, having a single port reduced the disruption of the flow caused by the presence of the ports themselves. The single access port was also moved further back from the detection instrument on the flow tube to 49.5 cm from the first port position of 30.5 cm.

### 2.2.2 Injector Rod

The injector rod is a thin-walled, 1.27 cm OD stainless steel tube. One end is sealed shut with twenty-three 1 mm holes radially drilled into the rod approximately 1.25 cm from the end, the other end has a Swagelok tee fitting attached, through which the water-nitrogen mixture is added. Inside the injector, a mercury (Hg) lamp (PenRay model 90-0012-01) sits approximately 7.5 cm from the drilled holes. The lamp photolyses a water-nitrogen mixture producing OH. The Hg lamp is held in place by a 0.95 cm OD Teflon tubing which also carries the water-nitrogen mixture down the
injector tube. The power cord of the Hg lamp feeds out through the 90° connection in the tee to the lamp power supply.

2.2.3 Mounting System

To use the CIMS as the detection system, a method had to be developed to couple the flow tube to the sampling inlet as they are of different diameters. This coupling was accomplished by use of a 1.5” to 0.75” Swagelok reducing union bored through to allow the 0.75” sampling inlet to pass through. The reducing union is welded to a plate which is mounted to the faceplate of the CIMS inlet using two threaded rods with the sampling inlet sitting inside the 0.75” opening of the reducing union as close to the terminus of the flow tube as possible. This connection is made using a Teflon ferrule to prevent damage to the inlet and avoiding permanently affixing a ferrule to it.\footnote{The flow tube is affixed by reversing the ferrule and using an o-ring to seal the connection, as with the injector rod, to ensure that the seal is airtight and only air in the flow tube is entering the sampling tube.} Additionally, two 3/8” ports are drilled into the neck of the reducing union on the 1.5” side. These ports allow a diaphragm pump to pull air down the flow tube, which is regulated by a flow controller (MKS 1559A).

Initially two 122 cm long threaded rods, attached to the faceplate of the CIMS, were used to support the flow tube while it was connected to the CIMS since the sampling inlet is 91.44 cm above the ground and the tube could not free float from the reducing union. Glass clamps where attached to the threaded rod to hold the flow tube and the injector rod in place. Unfortunately, due to the weight of the flow tube, and the
shallow thread holes that the rods were screwed into, the entire system deflected as the injector distance from the instrument increased, particularly at the o-ring joints. This deflection led to the injector rod deviating from the ‘center’ position in the flow tube even for small changes in position of only a few centimeters.

To ensure that the flow tube was properly supported, a small wheeled cart was built of extruded aluminum to hold the flow tube (Figure 2.4). The cart was built to a height of 87.6 cm with wheels, below the height of the sampling inlet. A 122.9 cm long piece of double wide extruded aluminum extends from the cart underneath the injector rod supported by a leg was attached to the end of the arm. The flow tube was supported by three glass clamps attached to the cart. One supported the main flow tube, a second supported the tee section with the third supporting the end cap by gripping the Swagelok through which the injector rod slides.
2.2.4 System Automation

During the summer of 2008 the injector positioning system was automated with the goal of reducing the time it took to complete a decay run and improve the precision of the measurement. The extension arm of the cart provided a stable surface on which a motor and rod system could be mounted. The automation system was composed of a threaded rod driven by a bipolar stepper motor, two pillow blocks that supported the threaded rod and allowed it to rotate freely, and a platform and mast system that connected the threaded rod to the injector rod.

Figure 2.4 Schematic of flow tube cart with injector rod automation setup.
The threaded rod used was 111.8 cm long with a 2.54 mm per revolution thread distance. It was attached to the cart using two semi-open pillow block bearings coated with Teflon located at either end of the rod. Movement of the injector rod was accomplished by using a bipolar stepper motor with control/drive and encoder built in from Lin Engineering (SilverPak 23CE) to turn the threaded rod. The motor was powered by a DC power supply with the running current set at 2.7 amps and a holding current of 1.5 amps. These settings provided the necessary power to efficiently turn the rod with the mast and injector rod attached. The motor communicated with a computer via a USB-to-serial converter. As the platform approached the pillow block near the flow tube, a small tab of metal on the underside of the platform slipped into an opto-sensor to signal the motor that the injector rod was at the home position. To further ensure that the injector rod stayed centered in the flow tube, a small Teflon collar was placed on the injector rod approximately 17.8 cm behind the holes in the injector rod. The collar has a three spoke design connecting the ring around the injector rod to a ring that fits up against the interior of the flow tube and was designed to minimize flow disruption. The collar is kept in place by wrapping a small amount of Teflon tape around the injector rod in front and behind the collar.

A shelf was added to the cart to support the mercury lamp power supply, motor power supply and the serial to USB converter used to communicate with the motor. A plate was also added to attach the mass flow controllers needed to control the flow tube pump, the bubbler flow, the nitrogen dilute flow and the zero air flow used to quantify the wall loss of the system.
2.3 Flow Tube Operation

OH is produced for the measurements by flowing a small amount of nitrogen gas, between 80 and 400 sccm, through a glass bubbler containing deionized water. This humidified flow then merges with a dry nitrogen flow, referred to as a diluent flow, before entering the injector. The mixture flows over the mercury lamp, water is photolyzed, and OH is produced via reaction 2.1. The OH is then added to the main flow in the flow tube via the radial holes in the injector rod. As the OH travels down the flow tube towards the detection system it can interact with the main flow. At the end of the flow tube, the OH enters the detection system where its relative concentration is measured by CIMS. After the OH concentration has be determined for a given position, or reaction time, the injector is then moved to a new position, either manually or via the motorized system, and the OH concentration again determined. A decay run is typically comprised of nine OH concentrations measurements at varying distance, or reaction times, from the CIMS sampling inlet with usually two positions repeated to account for any drift.

2.4 CIMS Detection Technique

Detection of OH radicals by CIMS requires the OH to be converted to a species that the system can detect, in this case HSO$_4^\cdot$. OH radicals are first converted to sulfuric acid by the addition of isotopically labeled sulfur dioxide. The $^{34}$SO$_2$ is then
converted to $\text{H}_2\text{SO}_4^{34}$ via reactions 2.3-2.5. The $\text{H}_2\text{SO}_4^{34}$ is then ionized via chemical ionization (reaction 2.12) and detected with the mass spectrometer.

2.3) $\text{OH} + \text{SO}_2^{34} + \text{M} \rightarrow \text{H}_3\text{SO}_3^{34} + \text{M}$

2.4) $\text{H}_3\text{SO}_3^{34} + \text{O}_2 \rightarrow \text{H}_3\text{SO}_3^{34} + \text{HO}_2$

2.5) $\text{H}_3\text{SO}_3^{34} + \text{H}_2\text{O} + \text{M} \rightarrow \text{H}_2\text{SO}_4^{34} + \text{M}$

The ion NO$_3^\cdot$ (HNO$_3$) used in reaction 2.12 is created via reaction 2.6 – 2.11. The ions created in 2.6 were produced by emission of $\alpha$-particles from $^{241}$Am into the sheath flow region. The negative charge is transferred to a more acidic species (shown in reactions 2.7-2.10) before ultimately forming the NO$_3^\cdot$·(HNO$_3$) cluster in 2.11. While the ions pass from the sheath flow into the sample flow, the two flows themselves never mix.

2.6) $\text{O}_2 + e^- \rightarrow \text{O}_2^\cdot$

2.7) $\text{O}_2^\cdot + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{HO}_2$

2.8) $\text{OH}^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{H}_2\text{O}$

2.9) $\text{HNO}_3 + e^- \rightarrow \text{NO}_2^- + \text{OH}$

2.10) $\text{HNO}_3 + \text{NO}_2^- \rightarrow \text{NO}_3^- + \text{HONO}$

2.11) $\text{HNO}_3 + \text{NO}_3^- \rightarrow \text{NO}_3^\cdot(\text{HNO}_3) + \text{M}$

2.12) $\text{H}_2\text{SO}_4 + \text{NO}_3^-·(\text{HNO}_3) \rightarrow \text{HSO}_4^-·(\text{HNO}_3) + \text{HNO}_3$
2.5 CIMS Operation

The measurement of hydroxyl radical concentrations for reactivity measurements was conducted with the NCAR Sulfuric, OH and MSA Instrument (SUOMI) chemical ionization mass spectrometer (CIMS). A schematic of the system can be found in figure 2.1. The instrument consists of a sampling inlet, the ionization and ion reaction region and a vacuum region, containing the mass spectrometer and detector.

Ambient air is drawn into the sampling inlet at a rate of approximately 10 L min⁻¹. The sample flow is determined by the difference between the total flow, the total volume of air drawn through the sampling inlet and drift tube, and the sheath flow, the air introduced into the drift tube containing the regent ions. The sampling tube is a thin-walled (0.03”) stainless steel tube with an inner diameter of 1.9 cm. The sampled air is then modified by the use of two pairs of opposed injectors separated by ~5cm. The front pair of injectors introduces sulfur dioxide containing the sulfur-34 isotope to the sample flow. Enough sulfur dioxide is added to ensure > 99% of the hydroxyl radicals present are converted to H₂^{34}SO₄. The second pair of injectors adds propane continuously during this time to remove any hydroxyl radicals formed by peroxy radical reactions with ambient NO.

The sampled air then enters the ionization region of the instrument. Here a flow of air, referred to as the sheath flow, which has been filtered to remove any sulfur dioxide and spiked with a small amount of nitric acid and propane, is passed through some screens to laminarize the flow. The flow then passes over the ionization source. Propane is added to the sheath to eliminate any OH that may have formed during the
Figure 2.5 Schematic of the NCAR Sulfuric Acid, OH and MSA Instrument (SUOMI) Chemical Ionization Mass Spectrometer (CIMS)
ionization process. The Sheath flow is maintained at 33 slpm by use of a diaphragm pump (KNF N838) connected to a 50 L min$^{-1}$ mass flow controller (MKS 1559A). The ionization region is evacuated via the total flow which pulls out 43 slpm by use of another diaphragm pump and mass flow controller. Ionizing is achieved by use of a foil of $^{241}$Am attached to the outside of a 3.8 cm inner diameter stainless steel tube centered on the sampling tube. This arrangement allows only the outer sheath flow to be ionized. The ionization then follows reactions as described in the previous section. To reduce instrumental background, nitric acid is also added to the sample flow through the rear pair of injectors.

After formation, the NO$_3^-$HNO$_3$ (here after referred to by the core ion, NO$_3^-$) ions are then guided to the center of the sample flow via electrostatic lenses. It is important to note that only the ions, and not the gas they were formed in, enter the sample flow. The ions are then directed towards the detection instrument by means of series of voltages that increase from -155 V near the ion source to -145 V in the drift tube. Once in the sample flow, the NO$_3^-$ ions react with the sulfuric acid producing HSO$_4^-$. The average time for this reaction to occur is 0.15s (Tanner et al., 1997).

Signal optimization of both the core ion at mass 62 and the hydroxyl radical proxy ion at mass 99 is achieved by adjusting the various voltages applied to the system front end summarized as in table 2.1.
**Table 2.1** Electrostatic Lens Voltages.

<table>
<thead>
<tr>
<th>Ion Source</th>
<th>-155 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drift tube</td>
<td>-140 V</td>
</tr>
<tr>
<td>Buffer</td>
<td>-100 V</td>
</tr>
<tr>
<td>Collision Dissociation Chamber</td>
<td>-55 V</td>
</tr>
</tbody>
</table>

At the end of the ion reaction region, both reagent and product ions are moved by electrostatic fields towards the pinhole that separates the ambient pressure ionization and reaction region from the vacuum system. Just prior to passing through the pinhole, the ions are directed through a flow of dry nitrogen gas, dehydrating the ions from any water which they may have clustered. The pinhole consists of a thin (0.006”) metal disk with a 0.003” hole in the center. After passing through the pinhole, the ions enter the first chamber of the two chamber vacuum system.

Upon entering the vacuum system, where pressure has been reduced to ~ 0.2 Torr, the ions are in the collisional dissociation chamber (CDC). This pressure is maintained by the use of 2 turbomolecular pumps (Varian 301), one for each chamber backed by a scroll pump (Anest Iwata). The CDC consists of five rings that are linked by resistors with a voltage of -55 V applied to the first ring. Here, as the name implies, the clusters are collisionally dissociated by the potential applied such that only the core ions of the clusters remain.

\[
2.13) \text{M} + \text{HSO}_4^- \cdot (\text{HNO}_3) \rightarrow \text{HSO}_4^- + \text{HNO}_3 + \text{M}
\]

Upon exiting the CDC, the ions are guided by a set of conical octopoles into a second chamber where the quadrupole mass spectrometer is situated. The quadrupole
acts as a mass filter determining which ions can reach the detector. This filtering is accomplished by varying the field intensity and R.F. creating stable paths for ions with a specific mass-to-charge ratio. The quadrupoles on this system are powered by an Extrel RF power supply. At the end of the quadrupole mass filter is the detector. The mass selected output of the quadrupole was detected by a channeltron ion multiplier (CeraMAX 7550M). The multiplier works by impacting ions into the wall, which is essentially a continuous dynode, of the cone shaped detector, thus knocking off electrons. The electrons cascade down the channeltron until eventually reaching the detector at the base. A current pulse from the detector is then sent to a capacitor. The capacitor, which isolates the high voltage from the low voltage TTL electronics, then sends a current pulse to a pre-amp which then sends a TTL pulse to a counter (Measurement Computing). These counts are then recorded by the computer.

2.5.1 Calibration

Generally when calibrating a system for a particular compound, a standard gas is used; however the high reactivity of OH prohibits the use of a gas standard. Instead, calibrations were achieved by the in situ production of OH via photolysis of water (reaction 2.1 and 2.2). A 12 cm outer diameter stainless steel inlet is attached to the front plate of the CIMS (Figure 2.2). A small window is cut from the inlet and filled with a quartz window. A housing is attached that contains a mercury (Hg) lamp, two coated reflected mirrors to preferential reflect the 184.9 nm wavelength and a heater to maintain the lamp and housing at constant temperature.
After attaching the inlet, the CIMS operates in normal OH measurement mode, with the lamp being cycled on and off in 5 minute intervals, generally over a 30 minute period. The lamp cycling results in two distinct OH concentrations, the ambient OH from when the lamp is off and the ambient and created OH from when the lamp was on, which is generally 2-3 orders of magnitude larger. Subtracting the average ambient [OH] from the average lamp on [OH] gives the average [OH] created by the lamp from atmospheric water which is then used to determine the calibration coefficient.

Calculation of OH production by this method requires the absorption cross section of H$_2$O at 184.9 nm, the photon fluence from the Hg lamp, the quantum efficiency for OH production, flow velocity, and ambient water concentration.

\[
A) \quad [OH] = \phi_{184.9 \text{ nm}} \sigma_{H_2O}[H_2O]
\]

The absorption cross section for water at 184.9 nm is $7.2 \times 10^{-20}$ cm$^2$ photon$^{-1}$ (Cantrell et al., 1997). The photon flux of the mercury lamp ($\phi_{184.9 \text{ nm}}$) was determined by mapping the output of the lamp through the quartz window using a photodiode (Hamamatsu), which yields the number of photons emitted by the lamp that are transmitted through the quartz window. These diodes are calibrated against a NIST Si photodiode to determine their quantum efficiency.

Since the measured OH concentration is a result of a conversion to H$_2^{34}$SO$_4$, and then subsequent detection of the H$^{34}$SO$_4$ ion after reaction with NO$_3^-$, the ratio of H$^{34}$SO$_4^-$ ions to NO$_3^-$ ions is also needed for the calibration. Making the assumption
that the reaction is pseudo-first order (since $[\text{H}_2\text{OSO}_4]$ doesn’t change appreciably), the concentration of isotopically labeled sulfuric acid can be calculated as,

$$B) \ [\text{H}_2\text{OSO}_4] = C \cdot \frac{H_2\text{OSO}_4}{\text{NO}_3^-}$$

where $C$ is a directly measured calibration coefficient. This coefficient is a combination of the rate constant of the reaction and the time the ions have to react in the ion reaction region, and the detection sensitivities ions measured (Mauldin et al., 1998). The natural occurrence of the isotope Sulphur-34 is about 4% of the total sulphur abundance; therefore we can assume $[\text{H}_2\text{OSO}_4] \approx [\text{OH}]$. Equation C can be rewritten as,

$$C) \ [\text{HSO}_4^-] = k \ [\text{NO}_3^-][\text{H}_2\text{SO}_4]t$$

$$D) \ [\text{H}_2\text{SO}_4] = \frac{1}{kt} \cdot \frac{[\text{HSO}_4^-]}{[\text{NO}_3^-]}$$

$$E) \ [\text{H}_2\text{SO}_4] = C \cdot \frac{[\text{HSO}_4^-]}{[\text{NO}_3^-]}$$

For OH, $[OH] = [H^{34}\text{SO}_4^-]$

Setting equations A and E equal to each other yields,

$$F) \ C = \varphi_{184.9 \text{ nm}} \sigma_{\text{H}_2\text{O}}[\text{H}_2\text{O}] \left(\frac{\text{NO}_3^-}{H^{34}\text{SO}_4^-}\right)$$

To account for the presence of other compounds which can oxidize $\text{SO}_2$ into $\text{H}_2\text{SO}_4$, a background OH measurement is performed. During this OH background determination,
propane is added through the front injector pair in sufficient quantities to remove >98% of the hydroxyl radicals (Tanner et al., 1997; Mauldin et al., 1998). This switching is carried out by a 4 port valco valve. As discussed in chapter 3, this background is subtracted from the OH signal measurement, the signal obtained with no propane added, to obtain the “true” OH signal.

CIMS measurement accuracy is dependent on the inherent uncertainty in the calibration process. The overall uncertainty in the calibration arises from the uncertainty of the absorption cross section of water at 184.9 nm, the accuracy of the diodes in measuring the photon output of the mercury lamp, the uncertainty in measurement of the inlet flow velocity, and the concentration of water for photolysis as determined by the dew point. The absorption cross section has a quoted uncertainty of 5% (Cantrell et al., 1997). The accuracy of the dew point temperature is stated to be ±1º C of the actual value and the relative humidity uncertainty is ±5% from 0-100% (Mannix Model CMM880 spec sheet). The uncertainty in the hot wire anemometer is 10% of the measured value. Photon output as measured by the photodiodes is estimated to add an additional 10% if the average value of the three diodes is used, higher if only a single diode value is used. Combination of these uncertainties leads to a total uncertainty of about 36% in the measured hydroxyl radical concentration.

2.6 Summary

After careful consideration of the methods being used to perform OH reactivity measurements, it was decided to adapt an existing method to use with the CIMS rather
than to develop an entirely new method. The Penn State design was chosen for its simpler OH production mechanism and ability to be more readily adapted to the CIMS system. Initial lab and field work showed that the system had promise but that improvements would be necessary to improve overall performance. The flow tube was redesigned to eliminate an extraneous access port and to shorten the length slightly. A collar was developed to ensure the injector rod stayed centered in the flow tube. Also the system was automated to increase the speed at which measurements could be performed and eliminates the human error inherent in positioning the injector rod during decays.
Chapter 3

Measurement Theory and Data Analysis

3.1 Measurement Kinetics

Most reactions involving the OH radical are second order and follow the form:

\[
\text{OH} + \text{X} \rightarrow \text{Products}
\]

The rate law for this reaction can be written as:

\[
- \frac{d[OH]}{dt} = k[X][OH]
\]

where \( k \) is the rate constant for the reaction. In most instances however, the \([OH] \ll [X]\) such that the overall \([X]\) remains essentially constant. In this case, the above equation reduces to the first order form:

\[
- \frac{d[OH]}{dt} = (k[X])[OH] = k_{app}[OH]
\]

where \( k_{app} \) is the pseudo-first order rate coefficient, usually given in \( \text{sec}^{-1} \). Integration of this equation yields

\[
[OH] = [OH]_0 e^{-kt}
\]

Thus a plot of \( \ln([OH]) \) versus \( t \), where \( t \) for conditions of the OH reactivity flow tube is proportional to the ratio of distance to flow velocity, should result in a straight line with the slope equal to the pseudo-first order rate constant of the reaction. If first order kinetics are obeyed, it is not necessary to know the absolute concentration of OH.
If two compounds, A and B were reacting with OH, with rate constants $k_a$ and $k_b$, then the change in [OH] is a function of both A and B, which can be described by

3.1) $\ln \frac{[OH]}{[OH]_0} = -k_a[A]t$

3.2) $\ln \frac{[OH]}{[OH]_0} = -(k_a[A] + k_b[B])t$

Therefore, determining the lifetime of OH for a group of compounds requires only adding the compound concentration and rate constant to the parentheses of equation 3.2 for each reaction, so long as the concentration of the compound can be assumed constant. Applying the above equations to the OH reactivity system, the change in OH between the initial concentration produced, $[OH]_0$, and some point downstream, [OH], can be quantified by the equation:

3.3) $\ln \frac{[OH]}{[OH]_0} = -(k_{CO}[CO] + k_{CH_4}[CH_4] + k_{O_3}[O_3] + k_{NO}[NO] + k_{NO_2}[NO_2] + \sum k_{VOC_i}[VOC_i] + k_{unk}[unknown])t$

where $t$ is the reaction time determined by dividing the position distance by the flow speed, $k_x$ is the rate coefficient for compound X with OH, and $[OH]_0$ is the OH concentration at $t=0$. $k_{unk}[unknown]$ represents the non-measured and/or unknown sinks of OH attributing to the decay.
To account for OH loss that can be attributed to the surfaces of the flow tube as well as any possible self reactions, zero or wall loss decay measurements are carried out. These measurements involve filling the flow tube with zero air that is hydrocarbon free and proceeding to carry out the measurement as if measuring ambient air. The decay measured under these conditions is therefore just of the form:

$$3.4) \frac{\ln [\text{OH}]}{t} = k_{wall}$$

The measured decay, $k_{meas}$, is therefore the value $k_{wall} + k_{compounds}$. Subtracting $k_{wall}$ from $k_{meas}$ gives the actual decay rate of OH in ambient air and therefore its actual lifetime.

### 3.2 Measurement Uncertainty

As previously discussed in Chapter 2, the CIMS has a measurement uncertainty of 36%. The uncertainty though is with regards to an absolute OH concentration, which is not relevant to the OH reactivity system which is based on a relative measurement. When determining OH reactivity it is the change in concentration with time that matters not the absolute concentration, therefore the uncertainty in the OH reactivity measurement exists within the flow tube system and the 36% uncertainty in the detection system can be ignored.\(^3\) Sources of uncertainty for the flow tube system include water purity, lamp output and the effect of injector rod center.

---

\(^3\) What matters for the reactivity measurement is that the difference between two measured concentrations is consistent. If one measured concentration is 50 arbitrary units and the next is 35 arbitrary units, so long as a difference of 15 arbitrary units is always the same, the absolute value of the arbitrary units are of no concern.
position upon measured OH concentration. There are also error estimates with regards to the decay rate calculation, involving the reaction time and the fitting function.

The errors involving water purity can have two effects on the system. First, impurities can coat the mercury lamp thereby reducing the amount of the 184.9 nm light being emitted. Further, impurities in the water can react with the OH reducing the measured OH concentration. Impurities are estimated to add approximately 5% to the variability in the OH concentration at a given position. The mercury lamp has slight temperature dependence with respect to output stability. No method of temperature control on the lamp is used, so any changes in output are unknown. Efforts were made to ensure stability by allowing the lamp to warm up for 30 minutes and waiting until a stable OH output was measured. An additional 5% error uncertainty is added to the calculated decay rates when using a manually positioned injector because of the large interval of time (30-45 min) during which lamp efficiency could vary.

The position of the tip of the injector rod with relation to the center of the flow tube has a considerable impact on the measured OH concentration at a given position. While every effort was made to ensure that the injector rod was located at the same point of the y-z plane for each reaction distance, this positioning could not be guaranteed when manually moving the injector rod. When the tip is positioned closer to the wall in one direction compared to the opposite direction, the top of the flow tube versus the bottom for example, the concentration for the position can be effected greatly because \( k_{wall} \) can be much larger for that position than all the contributing terms in Eq. 3.3. There is wide variability for measurement to measurement when this effect occurs due to the OH no longer being introduced uniformly into the flow and the flow behavior
being altered. The OH concentration can vary by as much as 30% from point to point if the injector rod is not properly centered simply due to changes in OH gradients that are not related to reactions with compounds in the flow. Typically, though, this variation could be managed to around 10% by carefully recentering the injector rod was re-centered for each position. For each position, 3-4 measurements would be performed, with each measurement lasting 30 s. These measurements were than averaged together to account for a bad switch in the injector flows and any rapid changes, such as car exhaust, in the air mass during the 30 sec measurement. Combining these error estimates results in an 18% uncertainty to the measured OH concentration at a given position.

The reaction time used in calculating the decay rate is determined by dividing the injector rod position by the flow velocity. The velocity of the flow in the flow tube is measured using a hot wire anemometer with a stated uncertainty of 10%. The injector rod position in the x direction has an average uncertainty of approximately 3% over the range of positions used. These two factors combine to give an error of 10% in the calculated reaction time. Combining the uncertainty here with that of the previous paragraph works out to an uncertainty in the Indiana measurements of about 30%. With the addition of the Teflon ring to the injector rod and automation of injector positioning, the measurement uncertainty was reduced for the OASIS campaign. The Teflon ring fit snugly in the flow tube leading to minimal y-z plane displacement of the injector rod. The error associated to this effect was reduced from 10% to 1% for the OASIS data. Testing of the motorized injector rod found the system to be accurate and only deviated from its proper position by one thread of the rod. Averaging over the
distances used for decay measurements found distance deviation to contribute a 1% uncertainty to the calculated decay rate. The overall uncertainty for the OH decay rates from the OASIS study was calculated to be 25%.

3.3 Data Processing and Quality Control

Analysis of the data begins by formatting the raw data files for importation into Igor Pro software. Once imported the data is time normalized to account for differences in measurement time due to internal computer processes, waiting for a response from the stepper motor, or instrument components communicating with their control programs. While measurements are usually completed within a few hundredths of a second of the programmed times, they can sometimes differ by as much as half a second. Once the data have been normalized to frequency, average values for OH background, reagent ion, and electronic background are calculated.

As shown in equation 3.5, the OH concentration is calculated by dividing the difference of the OH signal and background by the difference of the reagent ion and electronic background and then multiplying by the calibration coefficient as discussed in Chapter 2. As stated above, it is not necessary to know the absolute OH concentration, just its relative change over time. Thus calibrations were not performed as they would have been if the instrument were used to measure ambient OH. The
calibration coefficient used for this study was $5 \times 10^9$ molecules cm$^{-3}$ and is the average of calibrations performed over the span of this work.

$$3.5) \ [\text{OH}] = (\text{OH}_{\text{Sig}} - \text{OH}_{\text{Bkgd}}) / (\text{mass} \ 62 - e^{-\text{Bkgd}}) \times 5 \times 10^9$$

Once the concentrations have been calculated, a series of filters are applied to ensure that any compromised data is flagged for inspection and possible removal. These filters check the flow values, the ion source voltages, the reagent ion signal and the electronic background. The flow filter flags any time stamps where the total flow is not between 42 and 48 slpm, the sheath flow is not between 30 and 36 slpm, the rear propane flow falls below 35 sccm, the SO$_2$ flow is not between 14 and 19 sccm or the pinhole flow falls below 380 sccm. The ion source voltages get flagged if they are not between -160 and -140 volts. Finally if either the reagent ion count falls below 6000 Hz or the electronic background is above 10 Hz, those timestamps are flagged. The compromised data can then be removed from the final dataset.

Initial concentrations of OH produced during decay runs ranged between $5 \times 10^6$ and $3 \times 10^9$ molecules cm$^{-3}$. While the low end of the measured OH concentrations in the decay runs are within the range of ambient OH concentrations, testing of the flow tube system showed the system was at its detection limit with regards to ambient OH, therefore it is assumed that ambient OH did not contribute to the measured OH during decay runs.

The next step is to calculate the decay rate of the OH concentrations. To do this, the OH concentration data set is exported as a text file for analysis in Excel. The decay rates can be calculated by either fitting an exponential curve to the data, or by
transforming the concentration via a natural log and using a linear fit. For the projects, the natural log of the concentrations was calculated. This method was chosen because it allowed for easier visual interpretation of the data once plotted.

### 3.3.1 Additional Analysis for Alaska

While certain trends can be picked out from the raw data plots, the quality of the fit to the data and the fact that the wall loss contribution varies as a function of flow velocity in the flow tube, further analysis was required. This analysis was not applied to the data from Indiana due to the large time interval over which those decay runs were measured. The first step in the process was to identify high quality decay measurements using the coefficient of determination of each fit as a filter. The decays were classified as one of three categories: 1) high quality fit \( r^2 > 0.7499 \), 2) moderate quality fit \( 0.4999 < r^2 < 0.75 \), and 3) poor quality fit \( r^2 < 0.50 \). Using this classification led to 983 high quality fits, 670 moderate quality fits and 600 poor quality fits being identified. The decays in the moderate and poor quality fits were compared to the high quality fits to determine the cause of the lesser quality decays, and determine if anything could be done via post processing to improve the fits. The following subsections discuss the primary causes identified as leading to poorer quality fits. Examples of what such decays look like are presented as well as the attempts made to try to improve them when possible.

Examination of the decays showed that in a fair number of cases the poor quality in the decay correlation was due to high variability in the OH concentrations measured.
These cases suggested a rapid change in the composition of the air being measured. Figure 3.1 shows an example of such a scenario with the \( \ln ([OH]) \) on the y-axis and the calculated reaction time for each injector position on the x-axis. This decay has two branches to it. The upper branch, in black, consists of measurements conducted with the injector rod moving away and the lower branch, in red, as the injector rod moved towards the sampling inlet. Examining decays before and after this decay run, showed that this decay occurred during a transition period in the composition of the air. The preceding decay runs had \( \ln ([OH]) \) values comparable to the upper branch, while the lower branch is consistent with decay runs following this run. A linear fit of these types of data yield basically no correlation, \( r^2 = 0.0003 \). In these types of situations, there is no way to correct the data to gain a meaningful decay rate and such instances were removed from the overall data file.

These situations have no obvious systematic cause, rather are the result of short term changes in the composition of the air from local point sources or from longer term changes due to changes in air mass. The most probable local point source was pollution from vehicle exhaust which could be attributed to diesel engines in most cases. (A smaller number of cases could probably be attributed to snow mobile use in the vicinity of the modules or vehicular traffic in the parking lot east of the modules.) As mentioned earlier, high winds were common during the study resulting in large amounts of snow drifting on the ice road to the modules. On low wind, fair weather days after such events the front end loader would clear the road of these snow drifts.
In many other cases, however, an apparently systematic issue was the cause of a low quality fit. These systematic issues could be classified into one of four categories: 1) low OH concentrations at the second measurement position, 2) split in OH concentration at a twice measured position, 3) split decay, where a series of sequential decay runs have OH concentrations higher with the injector rod moving in one direction vs. another, and 4) single point OH concentration inconsistent with the rest of the decay run. This last category can be divided between 2 situations: a) an elevated OH concentration at the longest reaction time, and b) a position with an OH concentration lower than surrounding measurements. When these issues occurred they generally were
not isolated, rather they would happen for several decays in a row with normal decay runs on either side. Determination of when a data point should be maintained or removed was done using the Cook’s Distance measure.

### 3.3.1.1 Low OH Concentrations at the Second Measurement Position

An example of low OH concentrations at the second measurement position is presented in Figure 3.2. Here it can be seen that the relative OH concentration measured at 0.06 s reaction time is considerably lower than would be expected from the decay the other points seem to follow. The OH concentration was determined twice at this injector rod position, once while the injector rod is moving away from home position and once moving towards the home position. On both occasions, the measured OH is lower than measurements on either side of it and is even lower than a measurement two positions farther away from the inlet. The reproducibility suggests that these apparent low measurements are not due to instrument instabilities as other points were measured during the minimum of 90 seconds between these two points. Initially, it was thought this effect was due to something in the vicinity of this location of the flow tube. However, decays from 7 April 2009 using different distances show this same peculiarity at the second measurement position (Figure 3.3) while it is not present in any decay from 6 April 2009. At this point, the cause of this effect has not been determined.
Figure 3.2 April 5, 2009 Decay Run

The majority of values fall along a straight line except for those with a reaction time of 0.6 s. The reason for this appears to be something systematic but not constant day to day.
Figure 3.3 April 7, 2009 Decay Run

Decay run on a second day with different distances and flow tube velocities exhibiting the same behavior with the second measurement position.

The next step was to determine if these data points were outliers that unduly influencing the regression. This was done by using the Cook’s distance, which looks at the influence of a point on the regression by applying the regression to the data with the point removed. The equation for the calculation is:

$$ C = \frac{\sum_{j=1}^{n} (Y_j - Y_{j(i)})^2}{p \times MSE} \quad (3.10) $$

Where:
- $Y_j$ represents the predicted value from the regression with all points for observation $j$
- $Y_{j(i)}$ represents the predicted value for $j$ from the regression with observation $i$ removed
P is the number of parameters in the model
MSE is the mean square error of the regression

Once $C$ has been calculated, it can be compared to an F distribution. For these calculations the threshold was set at a cumulative probability of 50%, producing an F value of 0.77 for $F(2, 7)$, 0.78 for $F(2, 6)$ and 0.80 for $F(2, 5)$. Therefore if $C$ is larger than 0.80 the value can be considered an outlier and removed.

In Figure 3.4, the plot from Figure 3.2 is again displayed this time with the data point of initial interest colored red. When the initial regression was calculated while including this point, the linear fit, identified with the red line, had a slope of 1.629. The red data point at (0.06, 18.98) was removed and a linear regression performed again on the remaining data points. The Cook’s Distance for this case was 7.84, which is larger than 0.77 and therefore should be removed. The new linear fit, shown as the black line, has a slope of 1.79 with an $r^2$ of 0.79, making it a marginally high quality fit.

The data point at (0.06, 19.0) was then considered. Calculating the Cook’s distance using the linear fit for the plot displayed in Figure 3.4 for $Y_j$ and the linear fit with data point (0.06, 19.0) removed yielded $C=0.18$ which is less than 0.78 and is thus kept in the plot. A majority of plots that had a data point deleted fell in this category.
The red data point is tested via Cook’s Distance to determine if it is an outlier. According to Cook’s distance it is an outlier and so a new fit, in black, is performed on the remaining data points.

The decay run from April 7, 2009 presented in Figure 3.3 presents a slightly different scenario. While both points at the second position are below the fit line, only the lower of the two data points, plotted in red, is lower than data points with longer reaction times. Further it also could be categorized as a Type 4b systematic issue. In this case it is kept within this category because it does occur at the second measurement position and both points are below the initial fit line. It is therefore possible that once a stronger fit is made that both points will be considered inconsistent with the other data points.
Following the procedure to determine Cook’s Distance, the point corresponding to $y=19.2$ is kept for the moment and the point at $y=19.1$ is removed for the second linear fit of the data. This results in a slightly steeper slope than for the line in Figure 3.4, along with a stronger correlation between the fit and data points. The amount of increase in the decay rate is smaller than for the 5 April decay (only 0.134 vs. 0.381), but the decay goes from a marginally high quality fit to a solidly high quality fit, $r^2=0.7947$ vs. $r^2=0.9253$. The Cook’s Distance calculation, however, results in a value of 0.06, well below the cutoff of 0.77 requiring removal of the data point. Therefore the data point is added back into the plot since it is not an outlier and the original linear regression is used.

Therefore the guidelines for dealing with these types of data are:

1) Identify if the data points at the second measurement position are both below the best fit line. If not, classify in another category.

2) Remove the data point farthest from the regression line to low side first. Calculate the Cook’s Distance and determine if removal is required.

3) Remove the second point, perform another linear fit and calculate the Cook’s Distance again.

4) If the Cook’s Distance shows that the point is not an outlier, add it back into plot and use the linear regression including that point.
3.3.1.2 Split in OH Concentration at a Twice Measured Position

This scenario is a variation on the previously described issue. Instead of the data points being inconsistent with the other data points because they have low relative concentrations, in this instance, one data point stands out for having a smaller concentration than the second measurement at the same position. This problem was common to the second measurement position since it was frequently measured twice and like the previous issue occurred with different positions and velocity speeds used during the measurements. This problem generally resulted in a data point below the linear regression line by a few tenths and a data point above the regression line by a few tenths. A special case was one in which the high and low point were perfectly symmetrical about the regression line, and their removal would only change the coefficient of determination. They were further verified as being symmetrical by averaging the two points and performing the fit with the averaged point resulting in the same decay rate.

A plot exhibiting this phenomenon is presented in Figure 3.5. As can be seen, at $x=0.07$ sec, one point has $y=19.48$ and the other $y=19.18$. The value of 19.48 is larger than any surrounding values and $y=19.18$ is the furthest below the fit line of any of the values plotted. While point (0.07, 19.48) appears to be an outlier because its $y$-value is larger than any other, it’s not clear that point (0.07, 19.18) is not also an outlier. To determine which point(s) if any are an outlier(s), the Cook’s distance was calculated once with point (0.07, 19.49) removed and once with point (0.07, 19.18) removed. The result was that $C=0.11$ with point (0.07, 19.48) removed and $C=0.05$ with point (0.07,
19.18) removed. Therefore neither point is an outlier and the initial regression is used for the decay rate. This lack of change was a consistent occurrence with this category. The difference between the observation and predicted value from the regression was similar in magnitude for the suspect data points and therefore balanced one another’s pull with regard to the fit. Eliminating both values lead to a similar regression, just with a higher coefficient of determination value.

![Graph](image-url)

**Figure 3.5 Decay Run 109 from 10 April 2009**

Example of a high/low split in measured concentrations for a twice measured point.
The guidelines for analyzing issues of these types are:

1) Carry out Cook’s Distance calculation one with the higher value removed and once with the lower value removed.

2) If a point is removed due to Cook’s Distance calculation, recalculate Cook’s Distance with both points removed to determine if second point needs removal as well.

3) If both points are to be kept according to Cook’s Distance Calculation, remove them both and refit regression with only 7 points just to ensure that there is not significant change in slope in absence of the points.

3.3.1.3 Value Dependence on Directional Motion of Injector Rod

This is a situation that, the OH concentration varies with change in injector position in a manner (e.g., increases or decreases) that is opposite to the behavior when the injector is moved in the opposite direction. Small variations are to be expected in concentrations since at least a minute of time has passed between some positions being measured as the injector rod moves. These cases though were situations where a definitive decay could be seen among the points with a set of data points set apart from the definitive decay. Figure 3.6 presents a prime example of an extreme case where the set of positions measured as the injector rod moves away from the sampling inlet shows a decay and then the points measured moving towards the sampling show another definitive decay. Additionally the issue of having the second position concentrations lower than surrounding measurements as discussed in section 3.3.1.1 is present.
Figure 3.6 Extreme Case of OH Concentration Dependence on Injector Rod Direction

The measurements in black are as the injector rod moves towards the sampling inlet. The bottom set in red is as the injector rod moves away from the sampling inlet.

The plot in figure 3.6 looks similar to the plot in figure 3.1, however this was not a case of a change in air mass being measured since decay runs preceding and following exhibit the same behavior and the ln([OH]) values stay in the same range. A simple method of fixing this would be if the slope of the top set of measurements and the bottom set were the same or very near the same. Doing that though would require the deletion of the point (0.047, 18.00) leaving only 3 data points for a fit since the point at x=0.141 fits better with the measurements when the injector rod is moving towards the sampling inlet. Another option is just to use the data points measured as the injector rod was moving towards the inlet providing five points for the linear fit. Unfortunately this
would ignore what was happening with the beginning of the run and produce a result that is not necessarily representative of what was actually happening at the time. Further a test like Cook’s Distance cannot be used on the data so there would be no justification for the removal of points other than trying to get a strong correlation between the data points and the linear. Therefore, decay runs such as these were removed from the data set.

Not all decays fitting this category were discarded, however. Sometimes the measurement set up was such that only 2 to 3 points were measured with the injector rod moving in a particular direction. Further they did not have the issue with second position measurements described in section 3.3.1.1. Figure 3.7 shows a decay run from 10 April 2009 that suffered from the issues described in this section that could be worked with to obtain a decay. Inspection of the plot reveals that the points (0.128, 19.46) and (0.231, 19.28) are possibly outliers since they are both above the linear fit line while all the other points are below it with the exception of (0.026, 19.49). Performing a Cook’s Distance calculation with the questionable data points removed separately provides C values just below the threshold of 0.77 that would recommend their removal. Since both points are about equidistance from what the fit says their values should be it is possible that removal of one point is only removing about half the contribution of pulling the fit upward. To test this, Cook’s Distance was calculated with both points removed resulting in a C>1. This implies that the two points combined have a large influence on the linear fit which is expected since they make up 22% of the data points. To further test whether or not these points should be removed and the resulting fit used, data points were removed two at a time, sometimes including one of
the questionable points and sometimes not. The Cook’s Distance was then calculated with these combinations of points. When one of the suspect points was not included, the C value was never greater than 0.15. When a suspect point was considered in the calculation, the majority of the C value was contributed by the suspect value. This change in C increased confidence that the suspect points should be removed from the data set and the slope of the resulting linear fit should be used for the decay. Doing so resulted in the decay increasing from $1.77 \, s^{-1}$ to $2.31 \, s^{-1}$ and changing from a poor quality fit ($r^2=0.484$) to a high quality fit ($r^2=0.893$).

**Figure 3.7 Decay Run from 10 April 2009**

The red line is the linear fit for all nine data points. The black line is the linear fit when the points for $x=0.128$ and $x=0.231$ are removed.
The guidelines for analyzing these decays are:

1) First identify that the points that are questionable occurred for the injector rod moving in a direction opposite the direction that the majority of the measurements were measured.

2) If the majority of the data falls on a straight line, begin Cook’s Distance calculations for the questionable points and follow the guidelines for section 3.3.1.2.

3) If the majority of the points don’t fall on a line, like in Figure 3.7, determine if there are two groups of data points that can have separate fits with similar slopes. If so, average the slopes and use that as the decay for the run if it meets the definition of a high quality fit.

4) If fits cannot be done to subsets of the data or if the slopes are not similar, then remove that decay run from the dataset.

3.3.1.4 Single Point Inconsistency

Having a single questionable data point during a decay run was a fairly common occurrence and the easiest problem to rectify. Generally calculating the Cook’s Distance was sufficient in determining whether a point should be removed; however, there were certain scenarios under which Cook’s Distance suggested the data point was valid for the dataset. An example of decay runs where a data point was in question and passed Cook’s Distance but was subsequently removed will be examined.
Figure 3.8 presents a scenario where the data point at the third measurement distance (x=0.07 sec) is as low as the value measured at the longest reaction time. This example also points out a shortcoming of using the Cook’s Distance to determine whether a value should stay in the dataset. The data point (0.07, 19.29) is the lowest point of the entire plot even though its reaction time is about a third of the time of the longest reaction time. C was calculated to be 0.15, below the 0.77 threshold for removal, yet examination of the plot shows that the data point appears to be highly questionable. Comparing this decay to others measured at about the same time, reveals a consistently low point at this position with the injector rod moving away from the inlet suggesting that some additional turbulence was possibly occurring in the flow tube. Under these conditions, the wall loss of OH was most likely higher than normal leading to the depressed measured OH concentration. Therefore the data point was removed from this decay. Removing this questionable point modestly increased the slope but reclassified it as a high quality fit ($r^2=0.918$).

Finally the last common issue that arose during data processing was that of the last point measured being elevated above the fit line as also shown in Figure 3.8. This effect was generally attributed to be the result of the final position being too close to the access port used for measuring the flow velocity of the flow tube. These points always had a Cook’s Distance value of less than 0.01 since they were low concentrations and always close to the linear fit. Generally this issue occurred on high quality decays so removal of the point would not lead to an additional acceptable decay run for the final dataset and lead to a minimal improvement in $r^2$. Its removal did,
however, result in slight increases in the slope of the fit and was therefore left out of the linear fit.

![Graph](image)

**Figure 3.8 Decay Run 176 from 24 March 2009**

Example of a decay run with a single suspect point (black) that passes Cook’s Distance calculation. The repetition at this position under the same conditions suggests an issue within the flow tube under the correct conditions. Points like this are removed and a refit is performed.
3.3.2 HO$_2$ + NO Conversion Chemistry Correction

During the course of data processing several decay runs were flagged for more in-depth analysis because of suspected OH production via HO$_2$ reacting with NO (Reaction 1.5). The primary criteria for flagging for possible NO contamination was elevated OH background and signal. OH signal was seen to increase from a few kHz to upwards of 30kHz when the ambient NO$_x$ levels increased. It is assumed that there is a one to one production rate of HO$_2$ to OH within the flow tube. Since produced OH concentrations are quite large, typically 6-8 $\times$ 10$^8$ molecules cm$^{-3}$ in zero air and occasionally up to 2 $\times$ 10$^9$ molecules cm$^{-3}$, there was concern that the measured decays were less than the actual decay rate of the ambient air. To determine the possible influence of HO$_2$ conversion to OH, calculations were made to see what amount of OH might be produced and what percentage of the measured OH concentration this might represent. Table 3.1 presents the results of these calculations at different temperatures, and concentrations of NO and HO$_2$. The rate constant used for Reaction 1.5 was $k = 3.45 \times 10^{-12} \times \text{exp}(270/T)$ with temperature in Kelvin. Ambient concentrations of HO$_2$ were taken into consideration with the peak concentration measured being 5 $\times$ 10$^8$ and maximum NO of 40 ppb. Temperatures ranged between 240 K and 273 K while OH reactivity measurements were being performed. The peak NO concentration during an OH reactivity measurement was 15 ppb.

At the maximum concentration of NO measured, half of all HO$_2$ is converted into OH, which significantly impacts the decay runs. At the maximum [NO] measured while OH reactivity measurements were being performed, about 20% of HO$_2$ was converted.
into OH. The maximum distance between first measurement position and last position was 35.6 cm. Assuming that one of the slower flow velocities was used, around 86 cm/s, this means the HO$_2$+NO reaction has 0.413 seconds to react. This leads to a production of $2.47 \times 10^8$ molecules cm$^{-3}$ of OH. Therefore when using a large measurement range at low flow velocities in the presence of high NO levels, corrections to the data points will be required. For NO mixing ratios below 1 ppbv, OH production is less than 1% of the HO$_2$ present and therefore can be ignored.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>HO$_2$ (molec cm$^{-3}$)</th>
<th>NO</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40 ppb</td>
<td>15 ppb</td>
<td>1 ppb</td>
</tr>
<tr>
<td>240</td>
<td>$3 \times 10^9$</td>
<td>1.59 x $10^9$</td>
<td>5.98 x $10^8$</td>
<td>3.99 x $10^7$</td>
</tr>
<tr>
<td></td>
<td>$7 \times 10^8$</td>
<td>3.72 x $10^8$</td>
<td>1.4 x $10^8$</td>
<td>9.3 x $10^6$</td>
</tr>
<tr>
<td></td>
<td>$5 \times 10^7$</td>
<td>2.66 x $10^7$</td>
<td>9.97 x $10^6$</td>
<td>6.45 x $10^5$</td>
</tr>
<tr>
<td>255</td>
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<td>1.40 x $10^9$</td>
<td>5.72 x $10^8$</td>
<td>3.51 x $10^7$</td>
</tr>
<tr>
<td></td>
<td>$7 \times 10^8$</td>
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<td>1.23 x $10^8$</td>
<td>8.2 x $10^6$</td>
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<tr>
<td></td>
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<td>8.78 x $10^6$</td>
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<tr>
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<td>1.30 x $10^9$</td>
<td>4.88 x $10^8$</td>
<td>3.25 x $10^7$</td>
</tr>
<tr>
<td></td>
<td>$7 \times 10^8$</td>
<td>3.03 x $10^8$</td>
<td>1.14 x $10^8$</td>
<td>7.58 x $10^6$</td>
</tr>
<tr>
<td></td>
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<td>8.12 x $10^6$</td>
<td>5.41 x $10^5$</td>
</tr>
<tr>
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<td>4.52 x $10^8$</td>
<td>3.02 x $10^7$</td>
</tr>
<tr>
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<td>$7 \times 10^8$</td>
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<td>1.06 x $10^8$</td>
<td>7.04 x $10^6$</td>
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<tr>
<td></td>
<td>$5 \times 10^7$</td>
<td>2.01 x $10^7$</td>
<td>7.54 x $10^6$</td>
<td>5.03 x $10^5$</td>
</tr>
</tbody>
</table>
With this knowledge, the flagged decays can be revisited and corrected as needed to account for the production of OH from HO₂ in the flow tube. Upon closer examination only a small number of the flagged decay runs did line up with NO concentrations above 1 ppb, and were generally self excluding from the data sets due to the quality of the decay run. One reason that few runs required correction due to high NO concentrations, was that when such situations did present themselves and showed to be more than brief events, measurements were stopped and the pump on the flow tube turned off to conserve SO₂ gas and limit the amount of NO that could adhere to flow tube surfaces. For decay runs that were measured in these elevated NO timeframes, the decay runs suffered from wide variability in the first measurement position making it difficult to determine the initial OH concentration needed for the calculation of production of OH during the run. Several more decay runs looked like the plot in Figure 3.1 with wide variability from point to point so subtraction of produced OH was impossible. Finally, several cases showed an increase in OH concentration as reaction time increased leading to a positive slope. The increase in OH from point to point however could not be accounted for solely from OH produced from ambient NO and available HO₂. The plot presented in Figure 3.9 displays this phenomenon nicely with ambient NO not exceeding 2 ppb and the maximum OH concentration measured at 4.6 x 10⁸ molecules cm⁻³. The plotted data has a V shape, resulting from increasing OH concentrations at longer reaction times. The reason for this behavior is unknown at this time.

After data processing was completed and final fits were calculated, the decay runs were re-categorized to determine which ones would make the final data set. In the
end, 1263 decay runs were categorized as high quality fits. Any data points not considered high quality fits were removed and kept for future evaluation as more ancillary data becomes available to further understand the behavior of the system and chemistry of the environment. To obtain the ambient OH reactivity from the remaining decays, the wall loss or loss of OH to the flow tube wall needed to be subtracted. The wall loss or $k_{\text{wall}}$ was determined by obtaining decays in zero air.

![Figure 3.9 Suspected OH Production from NO+HO₂](image)

Production of OH from NO+HO₂ was suspected during this decay but ambient NO levels never exceeded 2 ppb. The V shape suggests OH production occurring in the flow tube.
3.4 Zero Air Data Processing

The zero air decays consisted of 6 to 10 decay runs at a time to develop an average loss rate attributable to the surfaces of the flow tube at various flow velocities. These average decay rates were then plotted against their corresponding flow velocities so that loss rates could be interpolated if a particular flow velocity was not measured with zero air. Upon plotting this data and fitting a linear regression to it, it was discovered that the loss rates attributed to surfaces of the flow tube were higher than in previous studies. These high loss rates were the result of the zero air used in Alaska. Unfortunately, the zero air that was provided for the study was only ultra high purity, and not hydrocarbon free, total hydrocarbon concentrations less than 100 ppb. A comparison of measured loss rates from lab and field work is presented in Figure 3.10. Zero decays in Indiana were only done at one flow velocity. For the lab decays, multiple decays were run at flow velocities of 1 m/s, 2 m/s and 2.54 m/s using the same automated set up as used in Barrow, Alaska. These decays were then averaged together to derive the average wall loss at the 3 flow velocities. Comparing the linear fits, the Alaska decays are twice as steep as the lab measurements. While it is not unexpected that zero decays done in the field would be higher (Kovacs and Brune, 2001), the fact they are more than double strongly suggesting that hydrocarbons and/or CO were present in the zero air. Therefore, the decays measured in the zero air are an over estimation or upper limit of the flow tube’s contribution to the overall decay rate. Subtracting these loss rates from the decay rates measured in the ambient air at Barrow will result in reactivities which are lower limits for the Alaskan values.
Of further note is the fact that for both the lab and Alaska zero decays, the wall loss contribution increases with faster flow velocities, or shorter reaction times. At first glance this seems counterintuitive that shorter reaction times have greater wall loss, but this is due to the increasing turbulence in the flow tube. At the slower flow velocities, the flow tube is laminar with a Reynolds number of 1082 at 1 m s$^{-1}$. At the high end of flow velocities used in the flow tube, the flow is considered transitional with a Reynolds number of 2700 at 2.5 m s$^{-1}$. Figure 3.11 shows the relationship for flow velocity in the flow tube and corresponding Reynolds number. The flow never reaches a turbulent regime, Reynolds number $> 4000$, for the range of velocities used.

**Figure 3.10 Comparisons of Zero Air Decay Values**

This is a plot of measured decays in zero air for Alaska (red), Indiana (black) and lab experiments (blue).
Relationship of Reynolds number to flow velocity of the flow tube. Flow is laminar to about 2.25 m s\(^{-1}\), where it becomes transitional. Under current operating parameters, the turbulent regime, Re > 4000, is never met.

3.5 Summary

The theory behind OH reactivity measurements is mathematically simple, given that the relationship between OH and the compounds it reacts with is easily described by a differential equation where the slope of the plotted equation gives the OH reactivity. The implementation and analysis, unfortunately, is not as simple as just solving for the slope. During the data processing stage of the OASIS project, several issues were discovered within the decay runs. First, the existence of in congruencies within the measurements themselves was discovered. For instance a particular measurement position would consistently produce values that did not line up with the rest of the measurements done during a decay run. Also, there were issues where the system
behaved differently depending on whether the injector rod was moving towards or away from the sampling inlet. Careful attention also had to be paid to the NO concentrations during the experiment to identify OH was being produced from the HO_2 radicals present in the system. After such analysis was done and any necessary corrections were made for OH recycling, contributions to the overall decay from the flow tube system had to be removed; otherwise the OH reactivity value was artificially inflated. Complications arose when the uncertainty in the flow tube contribution increased due to contaminants in the gases used to quantify the instrumental contribution yielding results greater than those previously established in lab work and at times above those measured in the ambient air.
Chapter 4

OH Reactivity Measurements from the NIFTy Study in Morgan Monroe State Forest, Indiana

4.1 Overview

In May 2008, the NCAR SUOMI CIMS was deployed to participate in the Nucleation in Forest (NIFTy) Study in central Indiana. The goal of this study was to examine nucleation in a forested region and identify the temporal and spatial extent of such events, the vertical location of the forest in which they are strongest/most prevalent, composition of the aerosols and what the main chemical controls of these events are. In relation to these goals, the CIMS was primarily employed to measure sulfuric acid concentration on the forest floor. The measurement of hydroxyl radical concentrations would be performed by a group from Indiana University using the laser-induced fluorescence technique (LIF). At the time of this study, methods of OH reactivity measurements had been developed for each system. Therefore this study provided an excellent opportunity not only to obtain reactivity values in the field with supporting measurements but also to intercompare results between the instruments. This chapter will describe the experiment site, the operating parameters for the CIMS while conducting OH reactivity measurements and the results of OH reactivity measurements with regards to literature and to the LIF OH reactivity system.
4.2 Experimental Setup

The study was conducted within Morgan Monroe State Forest (MMSF), located in central Indiana, between Bloomington and Martinsville. The study was based at the AmeriFlux tower site located in MMSF and operated by the Department of Geography at Indiana University – Bloomington. An in depth description of the site can be found in Schmid et al. (2000), but a brief description of the area follows.

![Figure 4.1 Spatial Arrangement of Instruments at Ameriflux Tower In Morgan Monroe State Forest](image)

The vast majority of the tree species, upwards of 75 per cent, in the area surrounding the footprint of the tower site were comprised of sugar maple (*Acer saccharum*), white oak (*Liriodendron tulipifera*), sassafras (*Sassafras albidum*), tulip poplar (*Liriodendron tulipifera*),
and black oak (*Quercus nigra*). The tower site is at an elevation of ~275 m and is located approximately 325 m down a gated dirt and gravel access road presented in Figure 4.1 with a linear distance of 250 m due west to the nearest paved public road. The tower and its support trailer are located approximately 30 m into the forest off the gated dirt and gravel access road via a dirt and gravel driveway. Approximately 20 m to the east of the tower, scaffolding was erected for the measurement of VOCs. As shown in Figure 4.1, the LIF and CIMS systems were housed in a 2 m x 3 m plastic shed located on the dirt and gravel driveway approximately 20 m north of the tower.

### 4.3 Measurement Methodology

The shed was set-up so the SUOMI CIMS was measuring out the south face and the LIF was measuring out the west face. Operation of the CIMS for this location required adjustment to the flows and lens voltages to obtain the best OH signal, which can be found in Appendix A.1. The flow tube for the CIMS protruded out the wall such that the open arm of the tee was approximately a foot from the wall exterior. The injector rod was manually set at predetermined distances by one person outside while another inside the shed directed the centering of the injector rod. The injector rod was held in place with a glass clamp. Between 4 and 6 OH concentration measurements were then made before moving the injector rod to the next position. The positions were randomized to avoid the systematic errors of constantly moving the injector in or out as discussed previously in chapter 3. Each OH concentration measurements lasted 30 s.

involved single 30 s measurement consisted of a 8 s OH background signal measurement, a 2 s core ion measurement, a 4 s H₂SO₄ measurement, a 1 s determination of the electronic
background, a 8 s OH signal measurement, another 2 s core ion measurement, a 1 s scan measurement and another 4 s H$_2$SO$_4$ measurement. This led to an overall decay measurement time of between 30 and 45 minutes depending on the number of positions, measurements per position, and positioning of the injector rod. Flow tube velocity measurements were conducted at the completion of each decay run.

4.4 OH Reactivity Expected from Literature

As discussed in Chapter 1, two previous studies on measured OH reactivity had been conducted in a forested environment. These two studies provide a good starting point for what type of OH reactivity values could be observed as part of NIFTy. Measurements from PROPHET (Di Carlo et al., 2004) and PMTACS-NY (Ren et al., 2006b) found that peak reactivities should be in the mid-teens per sec with average reactivities in the mid-single digits per sec for forested regions. Both of these studies, however, were carried out in the forest canopy rather than ground level and therefore ground level pollution and biogenic emissions may not mix up to those heights. The Southern Oxidants Study (SOS) provided ground level measurements near a forest with anthropogenic influence due to a nearby airport and adjacent urban environments (Kovacs et al., 2003). This study found average reactivities of around 11 s$^{-1}$ with maximum measured reactivities of 25 s$^{-1}$. Therefore reactivities between 8 s$^{-1}$ and 15 s$^{-1}$ seem a reasonable range to expect for measured OH reactivity during NIFTy if ground level pollution was present.
4.5 Measurements

Reactivity measurements were performed from 25 May to 29 May 2009, inclusively, between the hours of 1800 and 2400 Central Standard Time. On 26 May and 28 May, OH reactivity measurements were performed with both instruments allowing an intercomparison between the techniques. In addition zero air measurements to quantify OH decay due to wall effects were also made on these dates. On 25 May and 27 May, select atmospheric species were measured during the times the CIMS was conducting OH reactivity measurements.

4.5.1 Zero Air Measurements

Zero air measurements were performed in conjunction with the intercomparison measurements of the LIF system. For these decays, between seven and nine positions were used to determine the wall loss decay of OH. The dynamic range for the measurements was between 0 and 150 ms of reaction time for the flow rate of 2.3 m s$^{-1}$ used in the flow tube. For determination of the decay rate, the concentrations are transformed by taking their natural log. These are then plotted against OH reaction time. The slope of a fit of $\ln([\text{OH}])$ versus reaction time then yields the decay rate. The average of the three zero decays carried out was 2.3 s$^{-1}$.

4.5.2 OH Reactivity Expected from Trace Species

A limited number of trace species were measured during the evening hours, but are still useful in developing a lower limit for what the OH reactivity can be. Seven VOCs were
measured using a bulk filter method for 2 hour intervals. In addition SO₂ was measured using a TECO SO₂ analyzer. Compounds and the concentrations measured are presented in Table 4.1. Even though methane was not measured during the study, the atmospheric background concentration of 1800 ppb₉ is used in the calculations for a lower bound since it is ubiquitous in the atmosphere. Carbon monoxide concentrations are estimated for the purpose of this calculation since it is the compound that generally has the largest contribution to overall OH loss. For these calculations a value of 200 ppb₉ was used. The rate equations used for these calculations can be found in Appendix A.2.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprene</td>
<td>48-238 ppt</td>
</tr>
<tr>
<td>α-pinene</td>
<td>8-149 ppt</td>
</tr>
<tr>
<td>cumene</td>
<td>48-77 ppt</td>
</tr>
<tr>
<td>limonene</td>
<td>9-60 ppt</td>
</tr>
<tr>
<td>Benzene</td>
<td>64-469 ppt</td>
</tr>
<tr>
<td>Toluene</td>
<td>61-2770 ppt</td>
</tr>
<tr>
<td>m,p-xylene</td>
<td>71-455 ppt</td>
</tr>
<tr>
<td>o-xylene</td>
<td>43-142 ppt</td>
</tr>
<tr>
<td>SO₂</td>
<td>0-10 ppt</td>
</tr>
</tbody>
</table>

For the 25 May, the calculated OH reactivity minimum is 1.52 s⁻¹ compared to a measured value of 5.1 s⁻¹. A minimum value of 1.76 s⁻¹ was calculated for May 27, compared to the measured value of 6.4 s⁻¹. The difference between measured and calculated values is what one would expect from the literature discussed in Section 1.4 given the large numbers of compounds present in a forested environment. While inferences cannot be made as to the identity
of the compounds which heavily influence OH lifetime in this environment, it is comforting to see that the measured OH reactivity is not less than the calculated values. Comparing the two OH reactivity measurements gives a better idea of how well the instrument is behaving in this environment and will be explored in the following section.

### 4.5.3 OH Reactivity Intercomparison

The intercomparison of the two systems offers some insight into the instruments ability to measure OH reactivity when compared to an established technique, as well as a few things about the atmospheric chemistry of the site. Figure 4.2 shows the time series of reactivity measurements with the CIMS measurements in red and the LIF measurements in black. Since the LIF system was automated and could complete a decay run in 30 s, it was necessary to average the LIF values over a 30 minute period to compare the two systems. As can be seen, measurements from the two systems agree in general both with regards to the magnitude of OH lifetime as well as the undulating pattern seen in the measurements. The level of agreement is particularly surprising given that the CIMS system has such a large measurement window. The LIF system generally has slightly higher OH reactivities which can be attributed to the much shorter measurement window. The automation of the LIF system kept its injector rod y-z axis consistent throughout the measurement whereas the CIMS had some variability in its y-z axis due to manual positioning.

The majority of the values fall between 5 and 15 s\(^{-1}\), which are slightly higher than average reactivities reported in other forest environments (Di Carlo et al., 2004; Ren et al., 2006) but similar to those found during the Southern Oxidants Study in Nashville, Tennessee.
(Kovacs et al., 2003; Martinez et al., 2003). MMSF has several roads surrounding and going through it, fairly large towns close by and coal burning power plants in the surrounding area; all of which can add strong anthropogenic sources with proper wind direction. The addition of these more urban type sources make the area more chemically similar to the Nashville study, and could explain observed values higher than other reported forest measurements.

Figure 4.2 Intercomparison of OH Reactivity Measurements

Performed during the NIFTy Study
Two main concerns for getting an accurate OH loss rate measurement are interferences within the detection system and the cycling of HO\(_2\) to OH. Since both systems use photolysis of water to produce OH, there is an equal concentration of HO\(_2\) produced (R 2.1-2.2) which can artificially increase OH lifetime in elevated NO environments (R 1.5). Though NO measurements are not available during the time of the intercomparison, CIMS measurements can help to determine that NO levels were low enough not to be a concern. The CIMS is sensitive to elevated NO, such that both the background and signal modes of the system show very elevated values. Examination of the data files reveal that this telltale sign is not present, with both background and signal values appearing as expected between the ambient air and zero air decays, i.e. higher signal and background values under zero air conditions.

Interferences could be harder to eliminate as a possibility, if not for the fact that two different detection methods are used that have unique interference issues. As the CIMS system works by measuring the mass to charge (m/z) ratio, interferences of primary concern are other compounds with the same m/z being present in the ambient air or being formed in the flow tube. As mentioned before, mass 99 is the mass used to detect OH after its conversion into sulfuric acid. If another compound was present at this m/z the first indicator would be an elevated background. Generally the background during OH reactivity measurements is about 10 per cent of signal for ambient air, and slightly more for zero air. This ratio also held true for this intercomparison. Furthermore, since the LIF method is based on the excitation at a particular wavelength, it would not be affected by an additional compound at mass 99 as the CIMS would. Since the decays are similar between instruments given the errors within the measurements, it is highly unlikely that these reported values of OH reactivity for the MMSF site are an error.
4.6 Summary

During deployment for the NIFTy Study, two OH reactivity measurement systems ran simultaneously to evaluate the functionality and determine the OH lifetime for a forest with anthropogenic intrusion in central Indiana. Both instruments were of the injector and flow tube technique developed by William Brune at Penn State, while one method also incorporated an LIF OH detection system the second employed the CIMS technique. For the time period analyzed, there is good agreement between the two systems. They both capture the variability in the measured OH reactivity as well as the magnitude of the OH reactivity. OH reactivity rates were measured to be between 5 and 15 s\(^{-1}\) for the late evening to middle of night on this particular day. While the high end values measured are larger than values reported for other forest studies, they are similar to average values measured in mixed use landscapes, such as in the Nashville SOS study. While interferences in the detection of OH are always a concern, the use of two different detection regimes with different known inference issues agreeing so well strongly suggests that both systems operate as designed and add new capabilities to each group.
Chapter 5

OH Reactivity Measurements from the OASIS 2009 Study
in Barrow, Alaska

5.1 Introduction

The Ocean Atmosphere Sea Ice Snowpack (OASIS) campaign at Barrow, Alaska, as a part of International Polar Year (IPY) activities, took place between February and April 2009. As mentioned in Chapter 1, there were several hypotheses to test during the OASIS project which will be briefly reviewed here:

Is the instrument sensitive enough to measure OH reactivity in what is expected to be a chemically clean environment? If so, is it sensitive enough to pick up changes in OH reactivity?

How is measured OH reactivity of the Arctic different from what one would expect from the known chemistry of the Arctic and how well does it compare with calculated OH reactivity from the species measured during the study?

How does OH reactivity vary with increasing incoming solar radiation since OH is present for longer and there is a reduction in the amount of dark time for species to build up?

Does OH reactivity show a discernable difference between ozone depletion events (ODEs) and non ozone depletion event periods?
These hypotheses were tested via OH reactivity measurements carried out from late March through the study’s conclusion in April to identify the oxidative capacity of the atmosphere with regards to OH, under various conditions, both meteorological (temperature, wind speed and direction) and chemical (predominantly anthropogenic vs. natural sources, changes in ozone concentration). In total, 2315 OH reactivity measurements were made during the study.

This chapter will discuss in detail the measurement site and instrument setup, ancillary measurements and their location in relation to the OH reactivity system. Measurement procedures for performing OH reactivity measurements and zero air decays; and an analysis of the data itself and comparison to other compounds measured during this study will also be shown.

**5.2 Expected OH Reactivity**

Unlike the study in Indiana, where previous measurements of OH reactivity in forested environments can serve as a guide, there have been no previous measurements of OH reactivity in the Arctic. In this environment, one would expect OH reactivity to be low, as reduced biologic activity this time of year should limit the atmospheric emissions of reactive compounds. Oceanic biogenic sources are only available when ice opens later in the year. There are a limited number of anthropogenic sources easily identifiable to the south-southwest of the research site, which can raise OH reactivity.
Ren et al. (2005 and 2006b) give an idea of how low measured OH reactivity values can be under relatively clean rural conditions. Table 1.1 shows that averaged measured reactivities as low as the 5.5 to 6.5 s\(^{-1}\) range are realistic for non-urban locales. Still, even these low OH reactivities were observed in biologically active environments and are more than likely higher than the reactivities that would be observed in Barrow, Alaska during late winter and early spring. Using an aggregate of studies in the Arctic, calculating a realistic OH reactivity range is possible assuming that the largest contributors can be identified particularly for the time of year that the measurements were undertaken. Calculations of OH loss were performed for a variety of species that have been measured in the Arctic to determine the compounds that most contributed to OH loss in the Arctic environment. All concentrations for sink compounds were based on measurements in the Arctic and for the months of February through May. In all the calculations, a temperature of 248 K was used in the rate constants as a representative average temperature for Barrow, Alaska during the late winter to early spring time period. The rate constants used for the calculations can be found in Appendix A.4.

The top six compounds for OH loss were found to be carbon monoxide (CO), nitrogen dioxide (NO\(_2\)), ethene (CH\(_2\)CH\(_2\)), propene (CH\(_2\)CHCH\(_3\)), methane (CH\(_4\)), and formaldehyde (HCHO) with these last two being equal in contribution. The value used for CO, 155 ppb, was the average from Bottenheim et al. (2002) and Evans et al. (2003) measured at Alert, Canada and as a part of TOPSE for locations north of 50\(^\circ\) N and at an average altitude of 500 m, respectively, in 2000. An average value of 33 ppt of NO\(_2\) was used in the calculation, derived from measurements performed for four different
studies (Bottenheim et al., 1986; Beine et al., 2001; Beine et al., 2002; Evans et al., 2003). The propene and ethene measurements used in the calculation were performed in 1989 at the NOAA/GMCC observatory located a short distance from the site for the OASIS 2009 campaign. The average values measured during the course of the study were 230 ppt of propene and 640 ppt of ethene (Doskey and Gaffney, 1992). The contribution from methane assumed a concentration of 1.84 ppm measured at Alert in 1995 (Ariya et al., 1999). A formaldehyde concentration of 370 ppt was based the work of Sumner and Shepson (1999) at Alert, Canada. These six compounds contributed an OH loss of 1.93 s\(^{-1}\) in the order of CO (1.16 s\(^{-1}\)), propene (0.25 s\(^{-1}\)), ethene (0.19 s\(^{-1}\)), NO\(_2\) (0.13 s\(^{-1}\)), and methane and formaldehyde (0.10 s\(^{-1}\) each). The next five compounds of importance, n-butane, propane, ozone, isopentane and n-pentane, contributed a combined 0.14 s\(^{-1}\) to OH reactivity. Based on the loss of OH to CO and methane alone, the two long-lived gases, OH reactivity in the arctic should be no lower than about 1.2-1.3 s\(^{-1}\).

### 5.3 Site Description and Meteorology

The study was based at the Barrow Arctic Research Center (BARC), on the grounds of Ilisagvik College. The college is located approximately 7 km northeast of Barrow, Alaska. Figure 4.1 is an image from Google Maps showing Barrow, Alaska and the surrounding infrastructure. The Chukchi Sea is located 500 m to the west and north of the college and the Beaufort Sea a few kilometers to the northeast and east. The SUOMI CIMS used for the OH reactivity measurements was housed in one of two
wooden modules located on the southwest shore of Imikpuk Lake, identified by the red dot in Figure 4.1. Approximately 1 km to the southwest of the modules is Middle Salt Lagoon. During the duration of the study both bodies of water were frozen and covered with snow. The surrounding land is permafrost tundra with no appreciable change in local topography. During the latter part of the campaign, open ocean water was present in the Chukchi Sea within 2 km of the shore. The complex on the eastern shore of Imikpuk Lake in Figure 4.1 is a Department of Energy Atmospheric Radiation Measurement (ARM) site. Just southwest of that location is the Barrow Observatory for NOAA’s Global Monitoring Division. The college grounds can be seen just to the northwest of the modules.

Climatologically, the predominant wind direction is north-northeast for this time of year, meaning the air is marine polar that is modified by the sea ice of the Arctic Ocean. Multiple wind directions influenced the site during the study introducing different air masses to the site. Southerly winds brought a mixture of air that was continental and marine polar modified by the city of Barrow. When easterly winds were present, the air mass was one that had been modified by Prudhoe Bay and the vast expanse of tundra between Barrow and Prudhoe Bay. Westerly winds brought a marine polar air mass modified by the arctic sea and possibly Asian outflow. Wind speeds ranged from near-zero on calm, still days, to up to nearly 18 m/s, constituting gale force winds, that could last for xxx hours (or days). While there was very little precipitation, there were periods of blowing snow when winds were strong. These blowing snow events not only reduced visibility, but also reduced the amount of incoming solar radiation reaching the ground. The temperature remained firmly below freezing during
the entire study, ranging between -46º C and -3.2º C. A more in-depth discussion of the meteorological conditions pertaining to wind behavior during the OH reactivity measurements is presented later.

![Google Map Satellite Image of Barrow, Alaska and Surrounding Infrastructure](image)

**Figure 5.1 Google Map Satellite Image of Barrow, Alaska and Surrounding Infrastructure**

Red dot represents location of wooden modules housing instrumentation.
5.4 Instrument Housing

Most of the instruments were housed in two wooden modules sitting on top of approximately 30 cm x 30 cm wooden blocks. The modules’ external dimensions were 10 m long by 3 meters wide and 3 m high built on a framework of steel I-beams. A 1 m wide door existed at each end of the trailer. Both the interior and exterior were paneled with sheets of plywood. The walls were about 20.3 cm thick consisting of 17.1 cm of fiberglass insulation sandwich between clear plastic, 1.3 cm thick plywood for the interior walls and 1.9 cm thick plywood for the exterior walls. The north end of the modules housed the heater and three phase transformers that provided the power for the trailers. The south end had the exhaust fan that removed the air from the module and kept them negatively pressurized.

The trailers were positioned in a V shape facing north with the space between the trailers increasing in the south direction as shown in Figure 5.2. The space between the north ends was about 2.5 m, increasing to around 5 m at the south ends. The trailers were arranged such that when the wind was coming for the predominant direction of north/north-east, the sampled air would not be influenced by the walls of the modules.

Thirteen instruments were housed in the two modules. The interior layout of the two modules can be found in Figure 5.3. Module 1 housed NCAR’s formaldehyde instrument, TOGA, PAN and NO$_x$/O$_3$ instruments. The University of Toronto PTR-MS was also in this module. The data acquisition system for the NCAR sonic wind measurement (sonics) tower was also housed here. TOGA and the PTR-MS both were measuring VOCs. The instruments in Module 1 were profile sampling at 3 different
heights, 0.6 m, 1.8 m and 5.5 m, from the sonics tower. On some days these instruments also sampled at heights of 150 m, 300 m and 450 m when a tethered balloon was deployed. Additional VOC measurements were performed using canisters sampling generally from the 5.5 m sample line 3 times a day. Module 2 housed NCAR’s atmospheric radiation instrument in addition to the radical instruments: HO$_2$+RO$_2$, SUOMI CIMS, OH reactivity. Also in module 2 were the Georgia Tech CIMS measuring halogens as well as a TECO measuring carbon monoxide, the INSTAAR fast ozone and the University of Wuppertal LOPAP HONO instrument. The instruments, method of detection and compounds each measured can be found in Table 5.1.
Figure 5.2 Layout of Modules and Related Structures
Figure 5.3 Module layout
<table>
<thead>
<tr>
<th>Instrument</th>
<th>Detection Technique</th>
<th>Compounds Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCAR Formaldehyde</td>
<td>Difference Frequency Generation</td>
<td>Formaldehyde</td>
</tr>
<tr>
<td>Total Organic Gas Assay - TOGA</td>
<td>GC-MS</td>
<td>2-pentanone, acetaldehyde, acetone, benzene, bromomethane, butanal, butane, chloroform, chloromethane, dichloromethane, ethylbenzene+m,p-xylene, isobutane, isopentane, isoprene, o-xylene, methyl ethyl ketone, methanol, propanal, tetrachloromethane, toluene</td>
</tr>
<tr>
<td>U. of Toronto PTR-MS</td>
<td>PTR-MS</td>
<td>Acetaldehyde, acetic acid, acetone (poss. glyoxal), benzene, dms, formic acid, methanol, methyl ethyl ketone, toluene, xylenes</td>
</tr>
<tr>
<td>NCAR NO₂,O₃</td>
<td>chemiluminescence</td>
<td>NOₓ, NOᵧ, NO, NO₂, O₃</td>
</tr>
<tr>
<td>NCAR PAN</td>
<td>Thermal Dissociation CIMS</td>
<td>PAN, PPN</td>
</tr>
<tr>
<td>OH Reactivity</td>
<td>CIMS</td>
<td>OH</td>
</tr>
<tr>
<td>INSTAAR Ozone</td>
<td></td>
<td>O₃</td>
</tr>
<tr>
<td>Georgia Tech CIMS</td>
<td>CIMS</td>
<td>Br₂, BrCl, BrO, Cl₂, ClNO₂</td>
</tr>
<tr>
<td>CO Monitor</td>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>NCAR HO₂+RO₂</td>
<td>CIMS</td>
<td>HO₂, HO₂+RO₂</td>
</tr>
<tr>
<td>NCAR SUOMI CIMS</td>
<td>CIMS</td>
<td>OH, MSA, H₂SO₄</td>
</tr>
<tr>
<td>U. of Wuppertal HONO</td>
<td>LOPAP</td>
<td>HONO</td>
</tr>
<tr>
<td>NCAR Radiation</td>
<td>Scanning Actinic Flux Spectroradiometers</td>
<td>Actinic Fluxes</td>
</tr>
</tbody>
</table>
5.5 Instrument Setup

As mentioned in Chapter 2, refinements were made to the OH reactivity instrument since its deployment in Indiana. These changes led to changes in the method of operation while in Barrow. The first change was that the entire system was kept inside the module, instead of having the flow tube penetrating the wall. This arrangement required a new method for sampling of ambient air. A glass extension with a bend in the arm was fabricated to attach to the tee in the flow tube and penetrate through the wall. Unfortunately, due to the thickness of the wall, the arm was not long enough to extend out past the exterior of the module. As a work-around, 1.27 cm OD Teflon tubing was used in place of the arm. This tubing extended 38 cm from the exterior of the module.

The mass flow controllers and lens voltages were set to optimize OH signal for the reactivity flow tube (Appendix A.3). Adjustments of the lens and flow settings were done by first optimizing the reagent ion signal, mass 62, with the flow tube attached but with the total and sheath flow pumps running and the flow tube pump off. Flow and voltage adjustments were carried out without the flow tube pump because the reagent ion signal decreases 15-25 KHz when the flow tube pump is on. Once optimized for the reagent ion, the flow tube pump was turned on along with the mercury lamp and diluent flow. The system was allowed to warm up for 30 minutes before turning on the bubbler flow and adjusting the flows and lenses to optimize the OH signal. The flows and lenses were set to produce a high signal while minimizing the OH background.
5.6 Measurements

Measurements were carried out at various times of day on a total of 19 days from 23 March to 13 April 2009, inclusive. The only times of day for which there are no observations are between 0515 and 0900 Alaska Standard Time. OH decay measurements in zero air were carried out periodically during the study. These were done in the middle of a series of ambient air decays and at the end of the day’s runs to quantify the contribution of the flow tube system to the overall measured OH reactivity.

A different measurement sequence was used for this study because of the automation of the position of the injector rod. Instead of using an average of 4 to 6 30 s OH measurements per injector rod position as in Indiana, a new program was developed that allowed for a complete decay to be done in approximately 150 s. The measurement sequence was such that 2 OH background measurements were performed, with 9 OH signal measurements. Additionally, 3 reagent ion measurements were carried out, along with 2 electronic background and 2 mass scan measurements. The measurement sequence and time per measurement are presented in Table 5.2.

Initially an OH background, reagent ion, electronic background, mass scan and OH signal measurement were all done at an initial position; however, because of an issue with the injector flows balancing, the SO₂ flow was not always consistent for the OH signal measurement. To resolve this, after the mass scan measurement was completed, the injector rod was moved to a new position for the first OH signal measurement. The travel time provide sufficient time to ensure the SO₂ flow was
Table 5.2 Measurement Sequence used during OASIS

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Length of Measurement (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH Background (mass 99 w/ propane)</td>
<td>8</td>
</tr>
<tr>
<td>Reagent Ion (mass 62)</td>
<td>2</td>
</tr>
<tr>
<td>Electronic Background</td>
<td>2</td>
</tr>
<tr>
<td>Mass Scan</td>
<td>5</td>
</tr>
<tr>
<td>OH Signal 1 (mass 99 w/ $^{35}$SO$_2$)</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 2</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 3</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 4</td>
<td>8</td>
</tr>
<tr>
<td>Reagent Ion</td>
<td>2</td>
</tr>
<tr>
<td>OH Signal 5</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 6</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 7</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 8</td>
<td>8</td>
</tr>
<tr>
<td>OH Signal 9</td>
<td>8</td>
</tr>
<tr>
<td>Reagent Ion</td>
<td>2</td>
</tr>
<tr>
<td>Electronic Background</td>
<td>2</td>
</tr>
<tr>
<td>Mass Scan</td>
<td>4</td>
</tr>
<tr>
<td>OH Background</td>
<td>8</td>
</tr>
</tbody>
</table>

equilibrated. The injector rod would subsequently be moved to the initial position to perform and OH signal measurement for that position. To ensure that the OH output of the injector system was being consistent during a run, seven positions of the injector rod were measured with the extra two OH signal measurements in the program used to measure two positions twice, once while increasing the reaction time of OH in ambient air and once while decreasing the reaction of OH in ambient air. Surreptitiously, this also allowed for identification of system influence on the measurements which will be discussed in the subsequent section. Additionally the flow through the flow tube was varied to assess the response of the measured decays to contact time with the walls of
the flow tube. In general, faster flow rates were used at the start of the study compared to the end of the study. Eventually, lower flow velocities, 0.90 to 1.27 m s\(^{-1}\), were used because of frost accumulation occurring on the Teflon tube and blocking the intake. In total 2315 OH reactivity measurements were conducted during this study.

5.6.1 1-Minute Averaging

To be able to perform correlation plots with other measured species, the OH reactivity measurements needed to be averaged onto the same time scale, which for this study meant 1 min averages. A chart of the process is shown in Figure 5.4. OH reactivity measurements were not synchronized to start at a full minute or half minute timestamp, therefore the timestamp needed to be rounded to the nearest minute. This rounding resulted in a measurement every two to three minutes with no values for the intervening timestamps as shown in Figure 5.4 under the expanded timestamp and value headings. These measurements were then all offset by 1 minute to account for the fact that while the measurement timestamp identified when the measurement began, the first full minute for which the measured value is valid is the minute following the rounded timestamp for the measurement. A detailed example of the averaging shown in Figure 5.4 can be found in the footnote below.\(^4\)

\(^4\) Using the timestamp 17:32:16 from Figure 5.4 as an example, it is first rounded to timestamp 17:32:00, followed by its value being offset to timestamp 17:33:00, the first full minute occurring during the measurement. Next the one minute timestamps without values are calculated. For a single timestamp without a value between two filled timestamps, a weighted average of the two is used. Again looking at time stamp 17:32:00, the measurement done at 17:29:46 extends into the minute starting 17:32:00 by 15 seconds. Therefore the value measured at 17:29:46 is multiplied by 16/60. The remainder of the 17:32:00 timestamp is comprised of the measurement beginning at 17:32:16. The
Next a complete timestamp index had to be built from 00:00:00 23 March 2009 to 23:59:00 12 April 2009 for the OH reactivity values to be merged into the existing data. This merging was done by creating a time series in Excel and omitting the dates 3 April, 4 April and 9 April since files from those days were not added to the data merge used for this analysis since OH reactivity measurements were not performed on those days. Next the 1 minute averaged timestamps were appended to the end of the built time series with the OH reactivity values in the adjoining column. The two columns were then sorted with a primary sort on the time column of oldest to newest, and a secondary sort on the OH reactivity column from largest value to smallest value. Sorting was done so that the duplicate timestamps would have a blank cell in the OH measured value for 17:32:16 is therefore multiplied by 44/60, the remainder of the 17:32:00 minute. These two values are then summed to provide a decay rate for that minute. If there are two timestamps without a value following a timestamp with a measured value, the first timestamp is given the measured value and the second timestamp is calculated as previously stated. This can be seen in Figure 5.4 for the timestamps from 17:34:00 to 17:36:00.
reactivity column for the second time. Finally Excel’s Remove Duplicates command was performed on the time column to remove the duplicate timestamps in the build. As a result of filtering and analysis discussed in chapter 3 and averaging the OH reactivity measurements to 1 minute, a total of 3059 data points were available for analysis.

5.7 Instrument Performance

The instrument performed well during the study with only minor mechanical issues. Decays were well grouped with a precision of approximately 0.8 s\(^{-1}\). When noticeable spikes were observed in the data they correlated well with increases in reactive species. A more detailed discussion of measured OH reactivity and measured trace species occurs in the following section.

One of the main concerns going into the study was how well the glass flow tube would hold up over the course of the study due to its prolonged exposure to cold air while being housed in a heated module. The flow tube and some of the attached metal fittings became quite cold during extend use but the silicon o-rings which maintained the seals of the glass joints and fittings did not leak or show signs of stress. Only one o-ring failure occurred during the study; that sealing the Teflon inlet tube in the Ultra Torr fitting. Whether this failure was due to prolonged exposure to the cold temperatures or just due to use is unknown. As mentioned previously, the flow velocity
had to be moderated to alleviate snow and frost build up on the inlet, reducing the air intake and occasionally getting into the flow tube itself where it would melt.\textsuperscript{5}

5.8 Results

A time series of the OH reactivity measurements is shown in Figure 5.5. The median of the 1 minute average of OH reactivity measured during the study was 0.12 s\(^{-1}\) (mean = 0.49 s\(^{-1}\)) for the measurement period with a standard deviation of 1.96 s\(^{-1}\). Measured reactivities in April were lower and had less variability than the measurements during March. When broken down by month, March has a median OH reactivity of 0.25 s\(^{-1}\) (mean = 0.86 s\(^{-1}\)) versus a median of 0.10 s\(^{-1}\) (mean = 0.24 s\(^{-1}\)) for April. The standard deviations for March and April are 2.71 and 1.18, respectively. These median and average values are lower than the expected values calculated in Section 5.3. It is possible that the concentrations of primary sinks of OH were quite low during the study but not very likely given the expected contribution from CO and

\textsuperscript{5} The only major mechanical issue was the stepper motor stalling or resetting the home position after receiving a static shock. The low water vapor mixing ratios, generally less than 0.6 g of water per kg of air, prevented the rapid neutralization of electric build up on motor, threaded rod and cart. Therefore when a discharging source such as a person or hand tool was close enough to the instrument for the breakdown potential to be achieved, the buildup would discharge and short-circuit the motor. When the motor did stall, it had to be shut down and reset to the zero position as well as restarting the measurement program which would freeze up since it could no longer communicate with the motor. While inconvenient this was not as serious an issue as when the zero position reset. When the zero was reset during a measurement, zero became the spot where the injector was when the shock occurred. This reset could lead to the distances set by the program to be beyond the end of the threaded rod, causing the platform moving the injector rod to run into the pillow block at the end of the threaded rod. The end effect was the threaded rod pulling the motor and flow tube towards the far pillow block, which could have damaged either the injector rod or the glass flow tube. Attempts were made to insulate the motor by wrapping the end of the threaded rod in Teflon tape and place a small sheet of Teflon under the motor. Both efforts met with little success though.
CH₄. One way to determine what occurred with these measurements is to see how they compare with the calculated OH reactivity.

OH reactivity was calculated using the chemical reactions and rate constants in Appendix A.4. The temperature used in the calculations was taken from the NCAR sonic data at 2 m. Calculations were done for data from 23 March through midday on 8 April, because temperature and CO measurements stopped at that point. Additionally, OH reactivities were only calculated for timestamps when hydrocarbon measurements were available. TOGA hydrocarbon data was generally available every 10 or 20 minutes. These values were used for calculated OH reactivities for intervening time periods if OH reactivity measurements were conducted. The resulting 1704 calculated OH reactivities are presented in Figure 5.6 for March and April with their statistical values found in table 5.3.
Figure 5.5 Measured OH Reactivity Time Series for OASIS
Figure 5.6 Calculated OH Reactivity Time Series for OASIS
Table 5.3 Statistics for Measured and Calculated OH Reactivity by Month

<table>
<thead>
<tr>
<th></th>
<th>Average (s⁻¹)</th>
<th>Standard Deviation (s⁻¹)</th>
<th>Median (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>March Measured OH</td>
<td>3.55</td>
<td>2.11</td>
<td>2.89</td>
</tr>
<tr>
<td>(n=757)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>March Calculated OH</td>
<td>1.88</td>
<td>1.90</td>
<td>1.37</td>
</tr>
<tr>
<td>(n=757)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April Measured OH</td>
<td>1.63</td>
<td>1.43</td>
<td>0.93</td>
</tr>
<tr>
<td>(n=582)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>April Calculated OH</td>
<td>1.45</td>
<td>0.19</td>
<td>1.39</td>
</tr>
<tr>
<td>(n=582)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Examining Table 5.3 the first item of interest that stands out is how much better the April averages agree compared to the March averages. However the averages for March measured and calculated as well as April measured and calculated agree within 1 standard deviation. The comparison between the April measured and calculated OH reactivities do not provide as strong a comparison as the March numbers since only a subset of April measurements were used due to a large number of the April measurements occurring after CO measurements had stopped. That said the mean values are significantly lower for the measured reactivities than the calculated reactivities for both months. This discrepancy can be attributed to the contamination of the zero air used to quantify wall loss as discussed in Chapter 3.
Looking at a frequency distribution of the measured and calculated OH reactivities can provide information about whether the values are just shifted or if there is more involved in the difference between the statistics of the measured and calculated datasets. Figure 5.7 shows two histograms of OH reactivity values for March. The calculated OH reactivity histogram shows that the vast majority of the values, close to 900, are between 1 and 3 s\(^{-1}\). The measured values are more distributed with the peak frequency containing more than 350 data points, being between -2 and -0.25 s\(^{-1}\) closely followed by the -0.25 to 1.5 s\(^{-1}\) bin with about 325 data points. The reactivity bins from 3.2 to 6.6 s\(^{-1}\) contain about 200 data points each, much more than the data points in bins 2.6 s\(^{-1}\) through 14.2 s\(^{-1}\) for the calculated reactivity. This difference suggests the presence of reactive species within the arctic environment that were not specifically measured during the study. While the calculated OH reactivity has several values larger than those measured, they do fall within the uncertainty of the measurements.
Figure 5.7 Histograms of Measured and Calculated OH Reactivity for March
Histograms of measured OH reactivity (left) and calculated OH reactivity (right).
Figure 5.8 Pie Charts of March Calculated OH Reactivity from Measured Species

The top pie chart shows the distribution of OH loss for calculated reactivities less than 2.6 s\(^{-1}\). The bottom chart is for calculated reactivities above 5.6 s\(^{-1}\).
Most of the calculated OH reactivities are located in the 1.2 to 2.6 s\(^{-1}\). This is attributed to the fact that the main sources of OH loss, CO and methane, do not vary significantly and NO\(_x\) remains low. For the calculated OH reactivities above 5.4 s\(^{-1}\), the main sources of OH loss are NO, NO\(_2\), Toluene, and CO. The pie charts in Figure 5.8 show the relative contribution of OH sinks in the calculated OH reactivity for the two scenarios. In both scenarios, CO is a major contributor to OH loss, contributing approximately 1 s\(^{-1}\) to the overall calculated OH reactivity. This provides a good first run filter to identify within the data set times when there may have been issues with the measurement, i.e. measured OH reactivity is much less than 1 s\(^{-1}\). Also, if the measured OH reactivity is large and the [CO] is such that it is contributing an approximately 1 s\(^{-1}\) loss, this may be a time when there are unknown sinks at work.\(^6\) In addition, if the wall loss values from lab work are compared to the values from Alaska, the measured reactivities would increase by 0.6 s\(^{-1}\) at a 0.8 m s\(^{-1}\) flow velocity and 2.6 s\(^{-1}\) at a 2.1 m s\(^{-1}\) flow velocity.

Before deciding how to filter the measured reactivity values, seeing if similar relationships are present in the April data is prudent. Figure 5.9 shows the histograms for measured and calculated OH reactivity for April. Different bin sizes were used for these two histograms to give better resolution to the calculated OH reactivity, which otherwise would have comprised one bin clustered around 1.38 s\(^{-1}\). These low reactivity values with a tight distribution suggest that hydrocarbon and other trace species concentrations were low and not too variable. The measured OH reactivity

\(^6\) If the measured OH reactivity increases, without a corresponding increase in [CO], this tends to rule out a pollution plume. During the study there were few times when increases in NO\(_x\) occurred driving up OH loss, without a corresponding increase in [CO].
suggests more variability in the concentration of reactive species with approximately 200 measured OH reactivities above 2.2 s⁻¹, the highest calculated OH reactivities, though these values are still within the instrumental uncertainty of the measurement. These larger measured reactivities could be an indication of unmeasured OH reactive species. Additionally, they could be due to the higher time resolution of the reactivity measurement more closely tracking changes in the conditions as compared to the VOC measurements. The main sources of the calculated OH loss in April are very similar to March with CO, CH₄, HCHO and NO₂ being four of the largest sinks. The contribution of Toluene’s to the calculated OH reactivity is larger in April than acetaldehyde, due to the average acetaldehyde concentration in April being about a third of its March value, while toluene’s remained about the same. A pie chart showing the general contributions to the calculated OH reactivities is given in Figure 5.10. As in March, CO contributes about 1 s⁻¹ to OH loss.
Figure 5.9 Histograms of Measured and Calculated OH Reactivity for April

Histograms of measured OH reactivity (left) and calculated OH reactivity (right).

Figure 5.10 Pie Chart of April Calculated OH Reactivity from Measured Species

April Sources of OH Loss for Calculated Reactivites

- CO: 78%
- CH4: 10%
- HCHO: 5%
- NO2: 4%
- Toluene: 3%
The next step was to subtract wall losses determined from lab measurements using zero air to determine what impact the suspect zero air used in Alaska had on the final measured OH reactivities. Figure 5.11 below shows the data if the zero decays used from lab experiments were used, providing an upper limit for what the decays in measured in Alaska could be. Using the lab measured wall loss still results in measurements not only below the expected OH reactivity but also below 0 s$^{-1}$. Therefore an additional filter should be applied to the data to develop a subset in which there is higher confidence than there is in the whole of the data set.

Figure 5.12 shows the correlation between measured OH reactivity and [CO] for March (red) and April (blue) with the expected OH loss from CO at -24º C given as the solid black line. -24º C was used as it was the average temperature during the OH reactivity measurements. The plot shows that a significant number of the measured OH reactivities are below what should be expected from just the OH + CO reaction. This is partly attributable to the quality of the zero air used in Alaska. If it is assumed that the wall losses quantified in the lab are closer to the true influence of the flow tube on the measurement, than for April, the measured reactivities around zero would fall along the line for OH loss due to CO. It would also mean that all the values below -0.4 s$^{-1}$ should be considered suspect and could be excluded for the time being since the most that could be added back into the measured reactivities if lab wall losses were used is about 1.2 s$^{-1}$. This can be seen in Figure 5.13 which shows the same plot as in Figure 5.12 but using the lab wall loss values. The values that were at about 0.4 s$^{-1}$ now sit clustered right below the OH loss from CO line. Given the uncertainty in the measurements, those points fit well to that loss line. Still a significant number of measurements are
below the OH loss from CO line. Therefore anything below 0.7 s\(^{-1}\) will be filtered out to form a subset of measurements for further analysis.

**Figure 5.11 Measured OH Reactivity Using Lab Measured \(K_{\text{wall}}\)**
Figure 5.12 Measured OH Reactivity vs. [CO]
Figure 5.13 Measured OH with Lab Quantified Wall Loss Removed vs. [CO]

Measurements kept for the data subset denoted with +. Measurements removed denoted with an elongated diamond.
Running a statistical analysis on the subset data that was filtered using a minimum loss from CO, the new averages are closer to that of the calculated OH reactivities. The March subset data has a mean of 3.55 s\(^{-1}\) with a standard deviation of 2.11. This mean is more realistic for the OH reactivities given the CO and CH\(_4\) concentrations. The April subset now has a mean of 1.63 s\(^{-1}\) with a standard deviation of 1.43. The fact that the mean for April is now very similar to March is surprising given the percentage of measurements in April that have values below 1 s\(^{-1}\) compared to March. Comparing this to the calculated reactivities, the subset means are now slightly higher than the calculated reactivities.

**Figure 5.14 Comparison of March Calculated OH Reactivities**

Note the change in bin size between the two histograms. The subset data (right) almost entirely consists of points in the first bin of the complete data set (left).
Examining the frequency of the calculated reactivities for the subset of measured reactivities reveals something interesting for the March values. The measured reactivities that were removed correspond with the high end of calculated reactivities as demonstrated by the histograms in Figure 5.14. Whereas previously there had been about 70 calculated OH reactivities greater than $2.6 \text{ s}^{-1}$, there are only a handful in the bin containing $2.6 \text{ s}^{-1}$. Examination of the removed measured OH reactivities show that the change in [OH] was small from reaction time to reaction time and their average value was about $1 \text{ s}^{-1}$ before wall loss was subtracted. These measurements were performed with flow velocities of $1.5 \text{ m s}^{-1}$ or higher, resulting in $k_{\text{wall}}$ values of $3 \text{ s}^{-1}$ and greater. Looking through the measurements of chemical compounds corresponding to those measurements, [NO] were between 1 and 7 ppb. Therefore cycling of HO$_2$ to OH is occurring but only 10% of the HO$_2$ is cycling back to OH and is less than the instrument uncertainty for a single OH measurement. This strongly suggests that two things could be occurring in the flow tube; there is a source of OH production in the flow tube that is not being accounted for during these elevated NO events, or a compound is being produced under these conditions that show up a $m/z$ 99 in the negative ion spectra. It is possible that the amount of OH being produced in the flow tube is being underestimated and there is more conversion of HO$_2$ to OH occurring, but the decay runs do not bear that out. At the [NO] present, the decay rate should be about $3 \text{ s}^{-1}$ from NO alone, with an additional $1 \text{ s}^{-1}$ from CO. Therefore, the production of OH from NO+HO$_2$ would have to completely offset the loss of OH from NO and the loss of OH to any other compounds present. This seems highly unlikely since NO$_2$ forms along with OH, and OH will react with NO$_2$ partially counteracting the OH
production mechanism. Further examination of the data is required to determine what is happening in the flow tube under these conditions and modeling of the flow tube chemistry could be valuable in identifying the cause.

In addition to the statistical comparisons between measured and calculated reactivities, these measurements allow for the identification of possible missing OH chemistry. This analysis is complicated slightly by the number of measured decays below the loss expected from just CO. Only measured decays of 0.7 s\(^{-1}\) were used in the following analysis because of that. Also, measurements were ignored if CO observations were not available. Doing so provides 973 measurements for comparison. Dividing the calculated reactivity by the measured reactivity provides a measure of missing chemistry. Table 5.4 shows the breakdown of how much of the measured reactivity can be accounted for by the calculated reactivity.

\[
\begin{array}{|c|c|}
\hline
\text{Ratio of Calculated Reactivity to Measured Reactivity} & \text{Percentage of Measurements} \\
\hline
\geq 1.55 & 3.9 \\
1 \leq r < 1.55 & 6.5 \\
0.75 \leq r < 1 & 6.2 \\
0.50 \leq r < 0.75 & 22.3 \\
0.25 \leq r < 0.50 & 40.3 \\
r < 0.25 & 20.5 \\
\hline
\end{array}
\]

Allowing for a 55% uncertainty for any single measurement, 38 of the 973 points have a ratio greater than 1.55 and an additional 35% are within the instrument
uncertain. That leaves more than half the measurements not being accounted for in the calculated reactivity, which is significant for a region with limited sources of reactive compounds. Of these slightly over 60% occurred on 23 March and 2 April and during light and variable winds. These cases will be discussed below. Of the remaining points, the average unaccounted for reactivity is 69% of the measurement with the difference between calculated and measured 2.72 s\(^{-1}\), which is a similar contribution from NO and NO\(_2\) when calculated OH reactivities get above 6 s\(^{-1}\). While there is missing data for NO and NO\(_2\) for low ratios of calculated to measured, most of the time there are NO and NO\(_2\) measurements 30 minutes earlier or later and those concentrations are too low to be the cause of the discrepancy. Gaps in the hydrocarbon data also would not account for the missing reactivity. One case was the first run of the day having a measured reactivity of 22.6 s\(^{-1}\), and probably can be attributed to something coming off the injector rod when it was first repositioned. The subsequent measurements were around 1.2 s\(^{-1}\). Several other situations had one or two measurements that were elevated above measurements before and after and may have been the result of something briefly contaminating the measurement. On 26 March in the afternoon there is a very interesting 2 hour period. Initially the measurements were between -0.8 and -1.4 s\(^{-1}\) for about twenty measurements, then after two measurements started averaging about 5.5 s\(^{-1}\) for about 15 minutes before going back to negative values. For about the next hour the values hovered around 0 before increasing to about 2.5 s\(^{-1}\) on average for twenty minutes then returning to the lower measured values. Both times these episodes were preceded by an increase in the [CO] that lasted about 10 minutes. The first time the [CO] increased by 20 ppb, and approximately 4 minutes after this peak, the measured
OH reactivities jumped. The second time the increase was a more modest 10 ppb and about 5 minutes later the OH reactivities increased. The increase in CO suggests an anthropogenic source and other compounds may have been present that were not being measured. NO and NO$_2$ showed no change at the time but were measuring off the 18 m line the first time and the 6 m line the second. It is possibly that a plume had passed through but not mixed up to the height of the inlets and was missed by those measurements.

Next is an examination of the influence of wind direction and speed on OH reactivity using wall losses quantified in Alaska. The measurement site was chosen in part because the predominant wind direction for that time of year is from the north and the air should be relatively free of anthropogenic influence since it would be coming in off the Arctic Ocean. Therefore, the measured reactivities should be lower with a northerly wind direction than with a southerly one that passes over the town of Barrow. Figure 5.15 shows the measured OH reactivity as a function of wind direction as measured at the NOAA observatory at 10 m. This includes days after 8 April with the data filtered as for the histograms. NOAA meteorological data was used for this analysis because meteorological measurements at the measurement site ended midday on 8 April in addition to gaps in the data record prior to that date.

For March there is no statistically significant change in measured reactivity with wind direction. This is partly due to a low number of measurements at wind directions outside of 30° to 110°. There is also a large variability in the measured reactivities between 30° and 110° obscuring any trend in the measured reactivities. The one
noticeable difference is that the reactivities measured when winds were outside the 30° to 110° direction generally remain above 0 s⁻¹. For measurements in April however, there is a clear trend in the measured reactivity with changing wind direction. Measurements performed with an easterly wind have reactivities between 0 and 1 s⁻¹, increasing to between 2 and 4 s⁻¹ when the wind is south-southeasterly. This increase in OH reactivity is likely a signature of Barrow, Alaska.

**Figure 5.15 Measured OH Reactivity as a Function of Wind Direction**
The OH reactivities measured on 2 April 2009 between 1:30 and 4:30 AST, corresponded to wind directions of 140° to 170°. The measured reactivities for wind directions 65° to 110° were measured from 7 April to 12 April. For 2 April, the mean of the measured reactivities was 3 s⁻¹ compared to 0.26 s⁻¹ for the other days in April. This is unlike the calculated reactivities which are very similar for the two wind direction segments, 1.48 s⁻¹ for the south-southeasterly winds and 1.39 s⁻¹ for easterly winds. Further examination of the measurements of individual chemical species showed only small gaps in the data, so lack of measurement coverage does not explain the discrepancy between measured and calculated OH reactivities. It is possible that unknown OH sinks were present, but this would require a concentration of 1 ppb with a rate constant of 10⁻¹¹ to account for such a loss. One other option is the dependence is on wind speed rather than wind direction.

Figure 5.16 is a plot of the OH reactivity data in Figure 5.12 but plotted against wind speed colored by direction, again using the NOAA 10 m data. Immediately apparent is the elevated reactivity values corresponding to the lowest wind speeds, from about 2 to 4.5 m s⁻¹. There are lower measured reactivities between 3 and 5 m s⁻¹ from an easterly wind direction. This suggests that the measured reactivities on the morning of 2 April were dependent on both wind speed and direction. The hypothesis is that this particular wind direction at those speeds allowed the air to stagnate in the space between the trailers building up concentrations which were not picked up by the measurements on the nearby mast.
Wind speeds of 2-4 m s\(^{-1}\) are fairly fast and should not lead to stagnation of air. These wind speeds, though, were recorded at a height of 10 m, away from surface friction and turbulent drag which would slow the wind down. Wind speed measurements were being made at a lower height of 2 m near the site by NCAR using sonics. While wind speeds were not measured during the entirety of this particular time frame there are sufficient measurements during the whole study with which to compare the two data sets to get an estimate of what the winds on 2 April.

Figure 5.16 OH Reactivity vs. Wind Speed for April
Figure 5.17 Correlating 10 m Height Wind Speeds to 2 m Height Wind Speeds

Figure 5.17 shows the relationship between the two wind speed data sets. The 1:1 line is in black with the linear fit in red. A wind speed of 0 m s\(^{-1}\) at 2 m corresponds to about 3 m s\(^{-1}\) at 10 m. While this means a 2 m s\(^{-1}\) wind speed at 10 m would have a negative value, an estimate of the near surface winds can still be made. On the morning of 2 April, the winds were most likely calm, between 0-1 m s\(^{-1}\), sufficient to keep the air from advecting.
To further support the idea that stagnation of air led to a buildup of unmeasured species between the trailers a local source of reactive compounds needs to be identified. Since winds are minimal a source close to the sampling inlet would be most likely. This would point to the wooden modules that housed the instruments. Figure 5.18 is a picture showing the module with the sampling tube (indicated by the black arrow) protruding through the wall. The exterior of the module as noted earlier was plywood. The plywood could have been emitting reactive species that built up under the light wind conditions.
Table 5.5 Table of Mass 99/Mass 62 Ratios with Different Air Sources

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
<td>0.138</td>
<td>0.201</td>
<td>0.162</td>
<td>0.112</td>
</tr>
<tr>
<td>Zero</td>
<td>0.186</td>
<td>0.309</td>
<td>0.196</td>
<td>0.115</td>
</tr>
<tr>
<td>Zero</td>
<td>0.132</td>
<td>0.225</td>
<td>0.194</td>
<td>0.124</td>
</tr>
<tr>
<td>Ambient with Leak</td>
<td>0.003</td>
<td>0.003</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>Ambient with Leak</td>
<td>0.0007</td>
<td>0.001</td>
<td>0.001</td>
<td>0.0003</td>
</tr>
<tr>
<td>Ambient</td>
<td>0.024</td>
<td>0.029</td>
<td>0.026</td>
<td>0.021</td>
</tr>
<tr>
<td>Ambient</td>
<td>0.019</td>
<td>0.025</td>
<td>0.021</td>
<td>0.020</td>
</tr>
</tbody>
</table>

To add further support to the notion of the modules being a local source for species that are reactive to OH, Table 5.5 above shows some raw counts data of mass 99 normalized to mass 62 for zero air and for room air. The first three lines show mass 99 ratio while measuring zero air. These values are about 15 percent of the measured mass 62 signal. The lines following were decays for ambient air that also had room air being sampled inadvertently because a cap had not been replaced during the switch back to measuring ambient air. As can be seen the mass 99 ratios are less than 1 percent of the mass 62 signal. The final two lines are after the cap had been replaced and about 2 to 2.5 percent of the mass 62 signal. This supports the idea that the wood used to build the modules emits reactive compounds.

Since higher OH reactivities were correlated with low wind speed in April, does the same hold true for March? Figure 5.19 shows the March measured OH reactivities versus wind speed and colored for direction again using the NOAA 10 m data. There is an observable decrease in measured reactivity with increased wind speed, though not as
distinct as the April data. Also wind direction appears to be immaterial for March. The assumption that wind direction is important could be wrong and be isolated to that one event in April. It also may be the result of sampling chemical exhaust or the off gassing of compounds from the wooden trailers. All instruments where hooked up to a shared exhaust system that vented into the snowpack 300 meters from the module. The pump used to pull air through the exhaust system was located near module 1, and on several occasions it stopped running, allowing the exhaust to build up in the vicinity of the module. This was the case a few hours after the measurements were conducted on 2 April, when the pump stopped completely. It is possible that the pump was not operating efficiently leading up to this failure, and exhaust-contaminated air was slowly building up near the trailers at that time. More measurements under those conditions, low wind speed with a south-southeasterly wind would clarify the situation.
As mentioned in the introduction to this chapter, the behavior of OH reactivity during ozone depletion events (ODEs) was the primary reason for conducting these measurements during OASIS. Figure 5.20 shows a time series of [O₃] during the period when OH reactivity measurements were made. Three well defined ODEs are present and labeled 1, 2 and 3. The first is in March and lasts about 3 days. The second lasts a little over a day, from noon to 6 pm the following day. The third also lasts about a day from about noon on 6 April to about noon on 7 April. The OH reactivities are plotted alongside ozone in Figure 5.20, and in general appear to track ozone abundances.
To determine if OH reactivity changed significantly between ODE and non-ODE measurements, the OH reactivity measurements were grouped together by ozone concentration. \([O_3]\) of 5 ppb or less were considered ODEs and those above 6 ppb were considered non-ODEs. This excluded only 20 points where ozone mixing ratios were between 5 and 6 ppb. During ODEs, the mean OH reactivity was 0.34 s\(^{-1}\) with a range of -1.67 to 6.36 s\(^{-1}\). The standard deviation was 1.39 for the 610 measurements. When \(O_3\) was above 6 ppb, the range of measured OH reactivities was -1.6 to 9.2 s\(^{-1}\) with a mean of 1.43 s\(^{-1}\) and standard deviation of 2.02 for 1175 measurements. The means are within 1 standard deviation of each other and therefore the difference between OH reactivity measurements for ODEs and non-ODEs is not statistically significant.
This behavior with regard to the mean OH reactivity, is somewhat expected. The sources of OH loss in the region are dominated by two species whose abundances do not vary greatly. With OH loss being dominated by CO, except in certain highly polluted situations, a 50 ppb change in the [CO] only results in a 0.3 s\(^{-1}\) change in OH reactivity at these temperatures, and well within the uncertainty of the reactivity measurement. With the second largest contributor to OH reactivity [CH\(_4\)] long lived, any significant change in reactivity would require a large influx of reactive compounds. While this does occasionally occur, it is due to anthropogenic sources and is generally short lived. During the ODEs, there were very low levels of NO\(_x\), which generally contribute a not insignificant amount to measured variability. Also acetaldehyde and HCHO, which combined contribute about 10% to calculated OH reactivity in low NO\(_x\) situations, were low as well during the ODEs. What can be said is that during ODEs, the measurement shows a reduction in mean reactivity which can be traced to a reduction in ozone precursors that OH would react with. Although OH would have reduced competition for reactions with hydrocarbons in the absence of O\(_3\) the concentrations available are small and contribute one or two per cent to the overall reactivity.

Where, though, is the variability coming from in the measurements, particularly during the first ODE? First, for the non-ODE measurements, a larger number of days are included, which in itself will add variability based on changing conditions in the atmosphere as well as in-flux of pollution, particular NO\(_x\). Also changes in the flow velocity are partly responsible, since different wall losses are subtracted out and these can vary by up to 1 s\(^{-1}\) between what was measured in Alaska and in the lab for the
various flow velocities that were used on consecutive measurements. Additionally, only 5 of the 610 measurements during ODEs were above 6 s$^{-1}$. If those points are ignored, the top end of the range is 4.3 s$^{-1}$, meaning the range is only 6 s$^{-1}$. Finally, the values being measured are small and are largely accounted for in the measurement uncertainty. Here however, the numbers being dealt with are usually below 5 s$^{-1}$ putting the system near its level of detection and the overall results are not inconsistent with what one would expect for a relatively clean environment.

5.9 Summary

Ground based measurements of OH reactivity were carried out in the Arctic for the first time. These measurements provided an opportunity to test how well the OH sinks are understood in the arctic during ozone depletion events in springtime. The system performed well in the conditions and only suffered minor operational impediment due mainly to build up of electrical charges on the support cart. Measurements were conducted under a variety of meteorological conditions and as well as during ozone depletion events.

After some additional filtering of the data, there was good agreement between the measured OH reactivity and that calculated from the other measurements performed at the site. The mean measured reactivities were within one standard deviation of the calculated overall and by month. Approximately 40% of the reactivity measurements could be accounted for from the calculated reactivity, within the OH reactivity instruments uncertainty. For the remaining 60% of measurements examined, the
discrepancy could be accounted for from missed chemical species. In these cases, chemical modeling of the arctic environment can be constrained by the OH reactivity measurements by adding reactive species common to the arctic that were not measured to the model equivalent to the missing OH reactivity. If such species are insufficient to account for the missing reactivity, it suggests that there may be unknown chemical mechanisms present which was a hypothesis put forth at the start of this chapter. A 2 hour period on 26 March showed an increase in CO and measured reactivity but not in other compounds of anthropogenic origin such as NO, NO₂ or hydrocarbons. This is attributed to the fact that the increase lasted between 10 and 20 minutes and the hydrocarbon and NOₓ systems were measuring off inlet liens at 6 and 18 m at the time. Under low wind speed conditions it seems possible that chemicals out gassing from the plywood used to build the modules can build up in the stagnant air and not mix vertically but instead just stay at low levels. These were then picked up by the OH reactivity system but not instruments measuring off the sampling mast.

Measurements of OH reactivity in and out of ozone depletion events showed no significant difference. Means were similar and within one standard deviation of each other, and the spread in measured values did not differ much either, being slightly higher for non ozone depletion events. This agrees with calculations of OH reactivity where CO and CH₄ are the primary loss mechanisms in the Arctic. CH₄ is long lived and therefore varies little unless a local source is nearby and hence should be very similar both during and in absence of an ODE. CH₄ is globally steady state and only varies if a source of it is nearby; its concentrations would not appreciably change during an ODE. CO saw large variations during the study but an 80 ppb change in
concentration only influences OH loss by about 0.3 s\(^{-1}\). Therefore even if \([\text{CO}]\) did change substantially during an ODE the measureable difference would be no more than natural variability in the measurement.
Chapter 6

Summary & Conclusions

6.1 Project Review

The goal of this research was to successfully undertaken with three main questions in mind: 1) Could the Laser Induced Fluorescence (LIF) OH reactivity flow tube system be successfully adapted to Chemical Ionization Mass Spectrometry (CIMS) detection method? 2) Would the CIMS OH reactivity system successfully intercompare with the more established LIF method and what insights could be gained about OH chemistry in the process? 3) What is the behavior of OH reactivity for a previously unstudied environment, specifically the springtime Arctic in the absence and presence of ozone depletion events?

6.2 Instrument Adaptation

A series of revisions and refinements were made to the CIMS OH reactivity system over the course of its development in response to operational needs and insights from field deployments. Field testing of the first design showed promise in the feasibility of adapting the system to the CIMS but also revealed several shortcomings. A major overhaul from the initial design led to the glass flow tube system described in this paper. This design resulted in a lighter though more delicate system that was much
more manageable for a single person. A field intercomparison of the new design showed good improvement to overall function as well as drawbacks to its manual operation and overall measurement time. A final refinement was made to the system, whereby the entire process was automated and computer controlled. This significantly reduced measurement time, from approximately 40 minutes to 2.5 minutes, as well as improving the precision of the instrument.

6.3 Conclusions from Indiana

The NIFTy study in Indiana provided an opportunity not only to do an intercomparison with an LIF OH reactivity system but also to measure OH reactivity in a forested environment and compare those results to results from other forested environments. The intercomparison (see figure 4.2) showed good agreement in the shape of the OH reactivities’ behavior though the CIMS generally had lower reactivity values. This is attributed to the CIMS measurements time of 30-45 minutes compared to the 30 s for the LIF system. The nighttime measurements ranged between 5 and 15 s$^{-1}$ for the CIMS and are similar to reported values for forests in Michigan and New York (see table 1.1). While a comparison of measured reactivities to calculated reactivities was not possible due to only a small number of VOCs having been measured during the study, the good agreement between the two systems and with previously reported values strongly suggests that the OH reactivity seen is real and that the systems do work as intended.
The length of time though that the CIMS system required to complete a single decay run, on average 40 minutes, was prohibitive for seeing the fine detailed behavior of OH reactivity. This led to a redesign of the injector system and measurement process. Positioning of the injector rod was automated to reduce the time and improve the accuracy of the positioning process. With the automated positioning process was instituted, the measurement process was refined to simplify the process and reduce the overall measurement time further. Instead of doing several 30 second measurements at a position involving a background and signal measurement and then repeating the process at a new distance, a background measurement would be performed at the start and end of each run and only measurements of OH signal would occur at the various injector positions. This sped up the process by eliminating the need to switch between background and signal flows in the sampling inlet of the CIMS at every position and waiting for the flows to balance. Also, multiple measurements at the same position would not be needed to determine an average to account for variation in the balancing of the flows.

6.4 Conclusions from Alaska

These are the first known ground based measurements of OH reactivity made this close to the Arctic Ocean and during ozone depletion events. The instrument performed exceedingly well under the conditions with only minor technical issues due to blowing snow clogging the inlet and static discharge affecting the motor. Data was recorded on 19 days under a variety of meteorological conditions, varying times of day and both in
the presence and absence of ozone depletion events. While complications arose in
determining the flow tube’s contribution to overall OH loss, conclusions could still be
drawn from the collected data. The average reactivity for the study had an upper limit
of 2.57 s⁻¹, which is larger than the expected value of 1.3 s⁻¹ from CO and CH₄ but is
within instrumental uncertainty. Examining a subset of data to determine how much
of the measured reactivity could be attributed to measured compounds, for
approximately 60% of the OH reactivity measurements less than half of the measured
reactivity could be accounted for from measured hydrocarbons and other compounds.
Approximately 60% of these cases occurred with calm to low wind speeds suggesting a
local source of reactive species. The likely source of these reactive species was either
the wooden modules housing the instruments or the chemical exhaust of the
instruments. In other cases, increases in CO were observed in relation to increases in
OH reactivity but no elevation was seen in hydrocarbons or NOₓ. This is possibly due
to those compounds being measured at height above the surface and the compounds not
mixing vertically. It does however suggest the instrument is sensitive to changes in the
environment. Therefore it is suggested that in future studies where stable air could be
quite frequent, OH reactivity measurements be co-located with hydrocarbon and/or NOₓ
measurements to ensure that the same air is being sampled and a stronger comparison
can be made between measured and calculated.

Examination of measurements during ozone depletion events versus non
depletion events shows lower average OH reactivity than during non depletion events
though part of that may be attributable to higher wall loss subtractions for earlier
measurements compared to measurements towards the end of the study. The top end
range during ODEs was about two thirds of that in non depletion events suggesting cleaner air during depletion events, but not dramatically more. Given the limited number of sources in the region, the difference in range can probably be attributed to advection of pollution from the town of Barrow to the measurement site which would be stronger during non events since ODEs generally had calm to light winds. Also, since CO and CH₄ seem to dominate OH loss the majority of the time it is not unexpected that the change in reactivity is small between the two conditions. Some of the lower measured OH reactivity could be attributed to less loss from CO since Cl reacts with CO at about 1/3 the rate of OH (Ramacher et al., 1999). If during the non ODE events, it was seen that a significant loss of OH came from ethanol, ethane, propane, propene or tetrachloromethane, then one would expect to see measured OH reactivity decrease since those compounds react with Br and Cl between 150 and 600 times faster than OH.

6.5 Comparison of Field Results

While it is difficult to draw many comparisons between Alaska and Indiana due to the small number of measurements performed in Indiana, some conclusions can be drawn. First, Indiana had higher OH loss rates at night than Alaska did during the majority of the study. The lowest measured reactivity in Indiana, 5 s⁻¹ was near the high end of the range for measurements ion ODEs and middle of the range for non ODEs. While these ranges may shift upward somewhat if a method of correction can be determined for the measured wall loss, reactivity in Alaska only approaches that of
Indiana when NO\(_x\) concentrations get to about 1 ppb. The dominant sinks between the two environments are different. While CO and CH\(_4\) would be present at both, the plant life in Indiana would contribute significantly to OH loss, particularly isoprene with a rate constant around \(10^{-10}\), while the compounds measured in Alaska had rate constants at least an order of magnitude slower. Some isoprene was measured in Alaska but not at high enough concentrations to significantly affect OH loss. Adding the results from Alaska and Indiana to Table 1.1, reproduced below as Table 6.1, Indiana looks very much like several of the other locations investigated while Alaska has the lowest averaged measured reactivity and lowest max reactivity of any study to date.

<table>
<thead>
<tr>
<th>Study / Location</th>
<th>Average reactivity (s(^{-1}))</th>
<th>Max Reactivity (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nashville SOS</td>
<td>11</td>
<td>25</td>
</tr>
<tr>
<td>PROPHET 2000</td>
<td>N/A</td>
<td>13</td>
</tr>
<tr>
<td>PMTACS-NY 2001</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>Agrarian Pennsylvania</td>
<td>6.1</td>
<td>15</td>
</tr>
<tr>
<td>PMTACS-NY Whiteface</td>
<td>5.6</td>
<td>12</td>
</tr>
<tr>
<td>Mexico City, Mexico</td>
<td>33</td>
<td>200</td>
</tr>
<tr>
<td>Tokyo, Japan</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>PMTACS-NY 2004</td>
<td>30</td>
<td>N/A</td>
</tr>
<tr>
<td>NIFTy Study, Indiana</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>OASIS 2009, Barrow, Alaska</td>
<td>3 upper limit</td>
<td>11 upper limit</td>
</tr>
</tbody>
</table>
6.6 Closing Conclusion

A second viable detection system for OH reactivity measurements provides the opportunity not only to verify the work done with LIF systems but also to add additional insight into the HO$_x$ (OH+HO$_2$) budget in new environments. Being able to close the HO$_x$ budget on the loss side provides valuable understanding of the chemical mechanisms occurring in different environments and can help identify the species of most interest for further measurement. For Alaska, at this time it appears that the major mechanisms of OH loss are understood. The average measured OH reactivity of 2.57 s$^{-1}$ is very similar to the calculated average of 1.67 s$^{-1}$ and the expected reactivity of 2 s$^{-1}$ from literature. Two compounds used to calculate the expected reactivity from literature, ethene and propene, were not measured during this study. The literature analysis suggests that those two compounds add about 0.4 s$^{-1}$ to OH loss. If this was true during the OASIS campaign, then the calculated average would be about 2.07 s$^{-1}$ and closer to the averaged measured value. This still leaves about 0.5 s$^{-1}$ though of the average measured reactivity unaccounted for during OASIS. That however is not that great of discrepancy under most cases of measured to calculated OH reactivity. In this environment, the values being measured are so small that the fact that any variation is able to be measured is significant in and of itself with regards to measuring OH reactivity. If this was an urban study where average reactivities are 30 – 40 s$^{-1}$, a discrepancy of only 0.5 s$^{-1}$would be considered ideal. Therefore as additional filtering of the data is done to remove measurements when the air was modified by the city of Barrow, the average measured reactivity will come down and the discrepancy between measured and modeled reduced. When that occurs it is expected that the OH loss side
of the HO\textsubscript{x} budget can be closed and any discrepancy still existing will be a result of instrumental uncertainty and/or the lack of measurements for species such as ethene and propene.

6.7 Further Work

While the CIMS OH reactivity system has been successfully utilized to measure OH reactivity in the field a few refinements need to be made to the system. First is a further reduction in measurement time. The current 2.5 min measurement time, while fast, still leaves the measurements susceptible to rapid changes in the air mass. While this was not a grave issue while in Alaska, application in a more polluted environment may not work as well. The time it takes to complete a measurement can be separated into two components, the time the injector rod spends traveling from one position to the next position and the time spent measuring at a given position. While the motor is already being used near its maximum speed to safely move the injector, it may be possible to reduce the distance it needs to travel to perform a decay measurement. In Alaska, because of the low expected reactivity rates, a 0.2 to 0.4 s change in reaction times was used. In a more reactive environment that span in reaction times could be reduced since the change in concentration should be faster. Another method of reducing measurement time is reducing the amount of time spent on the measurements themselves.

Table 5.2 presented the measurement cycle used during the Alaska study. Examining the data files showed that mass 62 did not change during appreciably during a measurement run, therefore one of these measurements could be eliminated,
particularly the second one, even though it is only 2 seconds gained. A second option, which will need testing, is to reduce the time spent measuring the OH signal. Since this is done 9 times for 8 seconds each, it accounts for nearly half of the measurement time. If testing shows that a 2 second reduction in measuring OH signal is just as accurate as a full 8 second measurement, then the total run could be reduced to about 2 minutes 10 seconds and gain an extra measurement run about every 6 measurements.

There is still analysis to do on the data itself from Alaska. Recently temperature and wind speed data that INSTAAR measured during the study has become available. This data was measured near the modules at a height of 2 m and has coverage through the end of the study. This data should provide a better understanding of how the measured OH reactivity responded to changes in wind speed and direction. Also an examination of the vertical structure of the boundary layer could prove useful in determining if in fact some of the discrepancies in the measured vs. calculated OH reactivity is due to a lack of vertical mixing when hydrocarbons were being measured at 6’ and 18’.
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from the international campaign HOx Comp. *Atmos. Chem. Phys.* 9 7923-7948.


Appendix

This appendix contains the voltage and lens settings along with the rate constants used to calculate OH loss for the NIFTy and OASIS field studies.

A.1 Optimized Flow and Voltage Setting for NIFTy

Table A.1 Gas flows used during the NIFTy Study

<table>
<thead>
<tr>
<th>Flow Name</th>
<th>Flow Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>45 slpm</td>
</tr>
<tr>
<td>Sheath</td>
<td>35 slpm</td>
</tr>
<tr>
<td>Pinhole Nitrogen</td>
<td>400 sccm</td>
</tr>
<tr>
<td>Rear Nitrogen</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Sheath Nitric Acid</td>
<td>1 sccm</td>
</tr>
<tr>
<td>Rear Nitric Acid</td>
<td>2 sccm</td>
</tr>
<tr>
<td>Pulsed Nitrogen</td>
<td>5 sccm</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>15 sccm</td>
</tr>
<tr>
<td>Pulsed Propane</td>
<td>18 sccm</td>
</tr>
<tr>
<td>Rear Propane</td>
<td>41 sccm</td>
</tr>
<tr>
<td>Front Nitrogen</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Sheath Propane</td>
<td>45 sccm</td>
</tr>
<tr>
<td>Bubbler</td>
<td>200 – 400 sccm</td>
</tr>
<tr>
<td>Dilute</td>
<td>3 slpm</td>
</tr>
<tr>
<td>Flow Tube Pump</td>
<td>45 slpm</td>
</tr>
<tr>
<td>Zero Air</td>
<td>45 slpm</td>
</tr>
</tbody>
</table>

Table A.2 Lens voltages used during the NIFTy Study

<table>
<thead>
<tr>
<th>Lens Name</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Source</td>
<td>-150</td>
</tr>
<tr>
<td>Drift Tube</td>
<td>-140</td>
</tr>
<tr>
<td>Pinhole</td>
<td>-90</td>
</tr>
<tr>
<td>CDC</td>
<td>-50</td>
</tr>
</tbody>
</table>
A.2 Rate Constants for NIFTy Measured Species

The table below lists the reaction and rate constant used in the calculation of OH loss. Rate constants were taken from the IUPAC Subcommittee on Gas Kinetic Data Evaluation website. Rate constants for some compounds were supplied by John Orlando from NCAR. The Bimolecular rate constants are presented in the Arrhenius form.

\[ k(T) = A \exp\left(\frac{-E}{RT}\right) \]

### Table A.3 Bimolecular Reactions with Known Temperature Dependence

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OH} + \text{Isoprene} \rightarrow \text{products}$</td>
<td>$k = 2.7 \times 10^{-11} \exp(390/T) \text{molec. cm}^{-3}$</td>
<td>IUPAC HOx_VOC8</td>
</tr>
<tr>
<td>$\text{OH} + \alpha-\text{pinene} \rightarrow \text{products}$</td>
<td>$k = 1.2 \times 10^{-11} \exp(440/T) \text{molec. cm}^{-3}$</td>
<td>IUPAC HOx_VOC9</td>
</tr>
<tr>
<td>$\text{OH} + \text{Benzene} \rightarrow \text{products}$</td>
<td>$k = 2.3 \times 10^{-12} \exp(-190/T) \text{molec. cm}^{-3}$</td>
<td>IUPAC HOX_AROM1</td>
</tr>
<tr>
<td>$\text{OH} + \text{Toluene} \rightarrow \text{products}$</td>
<td>$k = 1.8 \times 10^{-12} \exp(340/T) \text{molec. cm}^{-3}$</td>
<td>IUPAC HOX_AROM2</td>
</tr>
<tr>
<td>$\text{OH} + m\text{-xylene}$</td>
<td>$k = 1.66 \times 10^{-11} \exp(115/T) \text{molec. cm}^{-3}$</td>
<td>John Orlando</td>
</tr>
</tbody>
</table>

### Table A.4 Bimolecular Reactions with Unknown Temperature Dependence

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{OH} + \text{cumene}$</td>
<td>$k = 7 \times 10^{-12} \text{molec. cm}^{-3}$</td>
<td>John Orlando</td>
</tr>
<tr>
<td>$\text{OH} + \text{limonene}$</td>
<td>$k = 1.7 \times 10^{-10} \text{molec. cm}^{-3}$</td>
<td>John Orlando</td>
</tr>
<tr>
<td>$\text{OH} + p\text{-xylene}$</td>
<td>$k = 1.5 \times 10^{-11} \text{molec. cm}^{-3}$</td>
<td>John Orlando</td>
</tr>
<tr>
<td>$\text{OH} + o\text{-xylene}$</td>
<td>$k = 1.5 \times 10^{-11} \text{molec. cm}^{-3}$</td>
<td>John Orlando</td>
</tr>
</tbody>
</table>
A.2.1 Termolecular Reaction

The reaction of OH + SO$_2$ has a pressure and temperature dependence. Rate constants for association reactions have been determined for low and high pressure limits. The limits have been taken from Jet Propulsion Laboratory Evaluation of Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies.

\[
L.P.\ Limit = k_0(T) = k_0 \left( \frac{Temp}{300} \right)^{-n}
\]

\[
H.P.\ Limit = k_\infty(T) = k_\infty \left( \frac{Temp}{300} \right)^{-m}
\]

**Table A.5 Termolecular Reaction for NIFTy**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>L.P. Limit</th>
<th>H.P. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + SO$_2$ +M $\rightarrow$ HOSO + M</td>
<td>3.3e-31*(T/300)$^{-3}$</td>
<td>1.6e-12*(T/300)</td>
</tr>
</tbody>
</table>

To obtain the effective second order rate constant for OH + SO$_2$, the following equation was used, from Jet Propulsion Laboratory Evaluation of Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies:

\[
k_l ([M], 1) = \left( \frac{k_\alpha(T)[M]}{1 + \left( \frac{k_0(T)[M]}{k_\alpha(T)} \right)^{0.5}} \right)^{1+\left[ \log_0 \left( \frac{k_0(T)[M]}{k_\alpha(T)} \right) \right]}^{0.5}
\]
A.3 Optimized Flow and Voltage Setting for OASIS

Table A.6 Gas flows used during OASIS

<table>
<thead>
<tr>
<th>Flow Name</th>
<th>Flow Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>45 slpm</td>
</tr>
<tr>
<td>Sheath</td>
<td>33 slpm</td>
</tr>
<tr>
<td>Pinhole Nitrogen</td>
<td>405 sccm</td>
</tr>
<tr>
<td>Rear Nitrogen</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Sheath Nitric Acid</td>
<td>2 sccm</td>
</tr>
<tr>
<td>Rear Nitric Acid</td>
<td>2 sccm</td>
</tr>
<tr>
<td>Pulsed Nitrogen</td>
<td>3 sccm</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>15 sccm</td>
</tr>
<tr>
<td>Pulsed Propane</td>
<td>18 sccm</td>
</tr>
<tr>
<td>Rear Propane</td>
<td>41 sccm</td>
</tr>
<tr>
<td>Front Nitrogen</td>
<td>50 sccm</td>
</tr>
<tr>
<td>Sheath Propane</td>
<td>45 sccm</td>
</tr>
<tr>
<td>Bubbler</td>
<td>180-400 sccm</td>
</tr>
<tr>
<td>Dilute</td>
<td>3 slpm</td>
</tr>
<tr>
<td>Flow Tube Pump</td>
<td>20-55 slpm</td>
</tr>
<tr>
<td>Zero Air</td>
<td>35-55 slpm</td>
</tr>
</tbody>
</table>

Table A.7 Lens voltages used during OASIS

<table>
<thead>
<tr>
<th>Lens Name</th>
<th>Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion Source</td>
<td>-150</td>
</tr>
<tr>
<td>Drift Tube</td>
<td>-125</td>
</tr>
<tr>
<td>Pinhole</td>
<td>-85</td>
</tr>
<tr>
<td>CDC</td>
<td>-55</td>
</tr>
</tbody>
</table>
A.4 Rate Constants for OASIS Expected Reactivity and Measured Species

The table below lists the reaction and rate constant used in the calculation of OH loss. Rate constants were taken from the IUPAC Subcommittee on Gas Kinetic Data Evaluation website, the Jet Propulsion Laboratory (JPL) Evaluation of Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies and Atkinson 2003. Rate constants for some compounds were supplied by John Orlando from NCAR. The Bimolecular rate constants are generally presented in the Arrhenius form.

\[ k(T) = A \exp \left( \frac{-E}{RT} \right) \]
Table A.8 Bimolecular Reactions with Known Temperature Dependence

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + Isobutane → products</td>
<td>$k = 5.4e-12*\exp(-285/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC60</td>
</tr>
<tr>
<td>OH + chloromethane → H$_2$O + CH$_2$Cl</td>
<td>$k = 2.1e-12*\exp(-1210/T)$ molec. cm$^{-3}$</td>
<td>IUPAC oCLOx37</td>
</tr>
<tr>
<td>OH + Acetaldehyde → products</td>
<td>$k = 4.7e-12*\exp(345/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_VOC12</td>
</tr>
<tr>
<td>OH + Butane → products</td>
<td>$k = 9.8e-12*\exp(-425/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_VOC7</td>
</tr>
<tr>
<td>OH + Bromomethane → H$_2$O + CH$_2$Br</td>
<td>$k = 1.7e-12*\exp(-1215/T)$ molec. cm$^{-3}$</td>
<td>IUPAC oBrOx1</td>
</tr>
<tr>
<td>OH + Isopentane</td>
<td>$k = 1.01e-11*\exp(-296/T)$ molec. cm$^{-3}$</td>
<td>John Orlando</td>
</tr>
<tr>
<td>OH + Methanol → products</td>
<td>$k = 2.85e-12*\exp(-345/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_VOC23</td>
</tr>
<tr>
<td>OH + Pentane</td>
<td>$k = 2.52e-17<em>T^2</em>\exp(158/T)$ molec. cm$^{-3}$</td>
<td>Atkinson 2003</td>
</tr>
<tr>
<td>OH + Isoprene → products</td>
<td>$k = 2.7e-11*\exp(390/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC8</td>
</tr>
<tr>
<td>OH + Ethanol → products</td>
<td>$k = 3e-12*\exp(20/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC24</td>
</tr>
<tr>
<td>OH + Propanal → products</td>
<td>$k = 4.9e-12*\exp(405/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC13</td>
</tr>
<tr>
<td>OH + Acetone → H$_2$O + CH$_3$(O)CH$_2$</td>
<td>$k = 8.8e-12*\exp(-1320/T) + 1.7e-14*\exp(423/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC19</td>
</tr>
<tr>
<td>OH + Dichloromethane → H$_2$O + CHCl$_2$</td>
<td>$k = 1.8e-12*\exp(-860/T)$ molec. cm$^{-3}$</td>
<td>IUPAC oCLOx39</td>
</tr>
<tr>
<td>OH + Acetonitrile → products</td>
<td>$k = 8.1e-13*\exp(-1080/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC50</td>
</tr>
<tr>
<td>OH + Butanal → products</td>
<td>$k = 6e-12*\exp(410/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC14</td>
</tr>
<tr>
<td>OH + MEK → products</td>
<td>$k = 1.5e-12*\exp(-90/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_VOC20</td>
</tr>
<tr>
<td>OH + Chloroform → H$_2$O + CCl$_3$</td>
<td>$k = 1.8e-12*\exp(-850/T)$ molec. cm$^{-3}$</td>
<td>IUPAC oClOx42</td>
</tr>
<tr>
<td>OH + Tetrachloromethane → HOCL + CCL$_3$</td>
<td>$k = 1e-10*\exp(-6220/T)$ molec. cm$^{-3}$</td>
<td>IUPAC oClOx45</td>
</tr>
<tr>
<td>OH + Benzene → products</td>
<td>$k = 2.3e-12*\exp(-190/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_AROM1</td>
</tr>
<tr>
<td>OH + 2-pentanone</td>
<td>$k = 3.8e-13*\exp(705/T)$ molec. cm$^{-3}$</td>
<td>John Orlando</td>
</tr>
<tr>
<td>OH + Toluene → products</td>
<td>$k = 1.8e-12*\exp(340/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOX_AROM2</td>
</tr>
<tr>
<td>OH + HCHO → H$_2$O + HCO</td>
<td>$k = 5.4e-12*\exp(135/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC11</td>
</tr>
<tr>
<td>OH + CO → products</td>
<td>$k = 1.44e-13*(1+[N_2]/4.2e19)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx_VOC10</td>
</tr>
<tr>
<td>OH + O$_3$ → HO$_2$ + O$_2$</td>
<td>$k = 1.7e-12*\exp(-940/T)$ molec. cm$^{-3}$</td>
<td>IUPAC HOx13</td>
</tr>
<tr>
<td>OH + BrO → products</td>
<td>$k = 1.7e-11*\exp(250/T)$ molec. cm$^{-3}$</td>
<td>JPL</td>
</tr>
<tr>
<td>OH + Br$_2$ → HOBr + Br</td>
<td>$k = 2.1e-11*\exp(240/T)$ molec. cm$^{-3}$</td>
<td>JPL</td>
</tr>
<tr>
<td>OH + Cl$_2$ → HOCl + Cl</td>
<td>$k = 1.4e-12*\exp(-900/T)$ molec. cm$^{-3}$</td>
<td>JPL</td>
</tr>
<tr>
<td>OH + HCl → H$_2$O + Cl</td>
<td>$k = 2.6e-12*\exp(-350/T)$ molec. cm$^{-3}$</td>
<td>JPL</td>
</tr>
</tbody>
</table>
\[
\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad k = 4.8\text{e}-11\times\exp(250/T) \text{ molec. cm}^{-3} \quad \text{IUPAC HOx11}
\]

\[
\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O} \quad k = 6.2\text{e}-14\times\left(\frac{T}{298}\right)^{2.6}\times\exp(945/T) \text{ molec. cm}^{-3} \quad \text{IUPAC HOx9}
\]

\[
\text{OH} + \text{HONO} \rightarrow \text{H}_2\text{O} + \text{NO}_2 \quad k = 2.5\text{e}-12\times\exp(260/T) \text{ molec. cm}^{-3} \quad \text{IUPAC NOx9}
\]

\[
\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3 \quad k = 1.85\text{e}-12\times\exp(-1690/T) \text{ molec. cm}^{-3} \quad \text{IUPAC HOx_VOC1}
\]

**Table A.9 Bimolecular Reactions with Unknown Temperature Dependence**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate Constant</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + o-xylene</td>
<td>( k = 1.5\text{e}-11 \text{ molec. cm}^{-3} )</td>
<td>John Orlando</td>
</tr>
<tr>
<td>OH + PAN ( \rightarrow ) products</td>
<td>( k &lt; 3\text{e}-14 \text{ molec. cm}^{-3} )</td>
<td>IUPAC HOx_VOC44</td>
</tr>
<tr>
<td>OH + PPN ( \rightarrow ) products</td>
<td>( k &lt; 1\text{e}-12 \text{ molec. cm}^{-3} )</td>
<td>IUPAC HOx_VOC45</td>
</tr>
</tbody>
</table>

**A.4.1 Termolecular Reactions**

The reaction of \( \text{OH} + \text{SO}_2 \) has a pressure and temperature dependence. Rate constants for association reactions have been determined for low and high pressure limits. The limits have been taken from Jet Propulsion Laboratory Evaluation of Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies.

\[
\text{L.P. Limit } = k_\theta(T) = k_\theta \left( \frac{\text{Temp}}{300} \right)^{-n}
\]

\[
\text{H.P. Limit } = k_\alpha(T) = k_\alpha \left( \frac{\text{Temp}}{300} \right)^{-m}
\]
Table A.10 Termolecular Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>L.P. Limit</th>
<th>H.P. Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH + NO + M → HONO + M</td>
<td>7.0e-31*(T/300)^-2.6</td>
<td>3.6e-11*(T/300)^-0.1</td>
</tr>
<tr>
<td>OH + NO₂ + M → HONO₂ + M</td>
<td>1.8e-30*(T/300)^-3</td>
<td>2.8e-11</td>
</tr>
</tbody>
</table>

To obtain the effective second order rate constant for OH + SO₂, the following equation was used, from Jet Propulsion Laboratory Evaluation of Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies:

\[
k_f([M],1) = \left( \frac{k_a(T)[M]}{1 + \frac{k_a(T)[M]}{k_x(T)}} \right)^{0.5}[1 + \log_{10}\left( \frac{k_0(T)[M]}{k_x(T)} \right)]^2^{1}
\]