EXAMINING OXIDATION PHOTOCHEMISTRY IN BAKERSFIELD, CALIFORNIA AND COMPARISON TO OTHER METROPOLITAN AREAS

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ABSTRACT

Poor air quality is a major problem that affects many metropolitan areas in the United States due to an increase in population and industrialization. Bakersfield, CA suffers from this problem. An extensive field campaign was conducted during the summer of 2010 to measure the reactive gases hydroxyl (OH) and hydroperoxyl (HO\textsubscript{2}) along with OH reactivity (the inverse of the OH lifetime). The goals of this field campaign were to better understand the underlying pollution problems and to provide a comparison with other metropolitan areas.

The field campaign was composed of two distinct periods: a cool period (May 16 – May 30) and a warm period (June 21 – June 28). During the cool period, OH was measured to be $\sim 0.5 \times 10^7$ molecules cm\textsuperscript{-3} and during the warm period around $0.75 \times 10^7$ molecules cm\textsuperscript{-3}, values that are fairly typical for many urban areas. These measurements are substantially lower than the modeled output using the Regional Atmospheric Chemistry Mechanism 2 (RACM2), particularly for OH. The outputs OH concentrations around $1.5 \times 10^7$ molecules cm\textsuperscript{-3} during the cool period and $\sim 2 \times 10^7$ molecules cm\textsuperscript{-3} during the warm period, values that are a little higher than those for many urban areas. HO\textsubscript{2} was $\sim 5$-10 pptv during the cool period and above 15 pptv during the warm period, which is generally lower than other urban areas. Generally measured and modeled OH is in better agreement in urban areas, so that Bakersfield is an anomaly that we cannot currently explain.

During the cool period OH reactivity was measured to be $\sim 5$ s\textsuperscript{-1} during the day, but rose to 15-25 s\textsuperscript{-1} at night. The measured OH reactivity remained lower than the modeled OH reactivity during the night, but rose to be above the modeled during the day. Throughout the warmer period, the OH reactivity was $\sim 10$ s\textsuperscript{-1} midday and 20-25 s\textsuperscript{-1}
at night. The measured OH reactivity remained higher than the modeled OH reactivity during the warmer period, indicating that some OH reactants were not measured.

These results provide insight to the complicated oxidation photochemistry in Bakersfield, CA and highlight areas where research can be improved on in order to better understand the underlying mechanics behind air pollution problems.
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CHAPTER 1: Introduction

Air quality in American urban areas is a problem that is estimated to adversely affect over 100 million individuals (EPA, 2003). Poor air quality exposes people to pollutant levels that exceed one or more health standards. A likely cause for these air pollution problems is increased population in urban areas and thus increased emissions of primary pollutants from factories, power plants, and transportation (Mayer, 1999).

The city of Bakersfield, located in the San Joaquin Valley of California, has the third worst air pollution in California (Ying et al., 2008). In order to regulate emissions effectively and improve air quality in Bakersfield and similar cities, the mechanisms underlying pollution problems in this region must first be fully understood.

To understand and predict this impact of increased population and industrialization on air quality, it is necessary to understand the underlying processes that control ozone (O$_3$), aerosols, and the atmospheric oxidation capacity (Martinez et al., 2003). The hydroxyl radical (OH) and hydroperoxyl radical (HO$_2$), together referred to as HO$_x$, are central players in almost all the atmosphere’s chemical reactions leading to these pollution problems (Logan et al., 1981). OH initiates many oxidation reaction sequences and HO$_2$ is an important precursor of ozone when in the presence of nitrogen oxides. In metropolitan regions, atmospheric chemistry is complex because emissions of pollutants are large, diverse, variable and poorly categorized (Martinez et al., 2003). To test the understanding of these complex oxidation reactions in these regions, measurements of OH and HO$_2$ abundances and analysis of loss rates and cycling are critical (Mao et al., 2010).

OH and HO$_2$ are produced in just a few ways. During the daytime, main HO$_x$ sources include the reactions of ozone, formaldehyde (HCHO) and HONO with sunlight,
which is called photolysis (Martinez et al., 2003). The photolysis of ozone produces an excited oxygen atom when then reacts with water in the atmosphere to produce two OH radicals. Similarly, one molecule of formaldehyde produces one HO$_2$ radical. HONO builds up overnight and is easily photolyzed, resulting in enhanced OH production in the early morning (Mao et al., 2010). In addition to purely daytime sources, small amounts of OH can be produced during the day or night through the reaction between ozone and alkenes (Donahue et al., 1998). This reaction is the dominant HO$_x$ source during the night when formation of HO$_x$ due to photolysis is necessarily small. These HO$_x$ sources are thought to be well known for urban environments.

Sinks of HO$_x$ include reactions that remove OH or HO$_2$ from the atmosphere and do not cause OH and HO$_2$ to react to form each other. The primary sink for HO$_x$ in the polluted boundary layer is the reaction between OH and NO$_2$, which results in the production of nitric acid (HNO$_3$). In air with less abundant NO$_2$, the reactions between HO$_2$ + HO$_2$, HO$_2$ + RO$_2$ and HO$_2$ + OH are especially important (Martinez et al., 2003).

OH and HO$_2$ react with other compounds to cycle HO$_x$ between OH and HO$_2$. This cycling is much faster than either the production or loss of HO$_x$. OH can react with many chemical compounds including carbon monoxide (CO), methane (CH$_4$), ozone or volatile organic compounds (VOCs) to produce HO$_2$. HO$_2$ reacts with NO or ozone to produce OH. The cycling activity and rates are primarily determined by the abundances of these compounds and weather conditions (Mao et al., 2010).

OH reactivity is defined as the reciprocal of the OH lifetime. It can be calculated from the sum of the reaction rate coefficients multiplied by the concentrations of reactants with OH as shown by the following equation:

\[
\frac{1}{k_{OH}} = k_{OH + VOC[VOC]} + k_{OH + CO[CO]} + k_{OH + NO[NO]} + k_{OH + NO_2[NO_2]} + k_{OH + HNO_3[HNO_3]} + \ldots
\] (1)
This sum includes the reactions of atmospheric constituents that react with OH both in cycling processes as well as production/destruction processes. Calculated OH reactivity using the concentrations of the atmospheric constituents is typically between 5-25 s\(^{-1}\) at midday in United States metropolitan areas (Kleinman et al., 2002; Mao et al., 2010). Through using direct measurements of OH reactivity, the calculation method can be tested and better understood (Kovacs and Brune, 2001).

Because the OH lifetime is so short, typically less than 1s, the OH production and loss rates should be in balance for atmospheric conditions that occur on longer time scales. Therefore, the OH reactivity multiplied by the OH concentration should give a value equal to the OH production. Because both these values are measured, this technique can be used to test the understanding of OH production (Mao et al., 2010).

In order to create emission regulations to efficiently improve the air quality in Bakersfield, California, these underlying mechanisms must be well understood and measurement techniques must be tested. Measurements of OH, HO\(_2\) and OH reactivity are used here to test the understanding of the oxidation photochemistry in Bakersfield by comparing the measurements to a regional atmospheric chemistry model (RACM2). These measurements are also compared to previous metropolitan studies to gain an understanding of how air pollution in Bakersfield compares to cities with similar populations, transportation, and industry.
CHAPTER 2: Method

Intensive field campaigns are critical for understanding the chemical mechanisms that drive air pollution and to make informed decisions regarding emissions regulations. They also provide the opportunity to test and perfect measurement techniques in environmental conditions. In order to test and understand the air quality conditions in Bakersfield, California, a 6-week field campaign was conducted at a site that resided southeast of the city center at the University of California Cooperative Extension office of Kern County (Figure 1).

2.1 Description of HO\textsubscript{x} Measurements:

The OH and HO\textsubscript{2} radicals were measured using GTHOS (Ground-based Tropospheric Hydrogen Oxides Sensor); a Penn State crafted HO\textsubscript{x} detection instrument that uses laser-induced fluorescence (LIF) of the OH molecule to detect both OH and HO\textsubscript{2} (Faloona et al., 2004; Ren et al., 2003).

GTHOS is comprised of four main systems including the detection module, the laser system, the electronics and the vacuum system. The detection module, consisting of two detection axes, was mounted on top of a scaffolding tower that was 12 m tall. Air samples were pulled by a vacuum pump through an inlet 1 mm in diameter and down a 20-cm-long, 5-cm-diameter sampling tube into the low-pressure first detection axis, where OH was measured, and then into the second detection axis, where HO\textsubscript{2} was measured. In both detection axes, a pulsed laser beam probed the air stream with a wavelength corresponding to an $\text{A}^2\Sigma (\nu' = 0) \rightarrow \text{X}^2\Pi (\nu'' = 0)$ transition for OH, near 308 nm. An electronically gated microchannel plate (MCP) detector detected the weak OH
fluorescence (Faloona et al., 2004). The total collection efficiency is estimated to be between 5-8% (Brune et al., 2005) resulting in an accurate measurement of OH.

In order to detect HO₂, NO was added to the low-pressure air stream in the second detection axis (20 cm downstream from the first detection axis) to convert HO₂ into detectable OH:

\[ \text{NO} + \text{HO}_2 \rightarrow \text{OH} + \text{NO}_2. \]  
(R1)

The second measurement, therefore, yields the total HOₓ of the sample. The difference between the HOₓ measurement and the OH measurement from the first detection axis is used to calculate the HO₂. The NO flow rate is controlled by a series of stainless steel flow restrictors to be 5 standard cubic centimeters (sccm). Hourly calibrations were performed to ensure maximum HO₂ conversion at flow rates of 3 and 8 sccm (Faloona et al., 2004). By combining the converted HO₂ measurement with OH measurement from the first detection axis, a measurement for the total amount of HOₓ can be obtained.

The 308 nm UV source was created by a dye laser that was intracavity doubled and was pumped by a diode-pumped Nd:YAG laser. The laser light was delivered to the top of the detection system through fiber optic cables (200 µm diameter, Thor Labs) where the power is split so that 80% goes to the OH detection axis, 10% to the HO₂ axis, and 10% goes to the OH reactivity detection axis. The laser beams were focused into multipass White cells at each detection axis.

### 2.2 Calibration of HOₓ Instrument

GTHOS was calibrated before, during and after the field measurements. In order to determine the instrument's sensitivity, known equal amounts of OH and HO₂ were generated by the vacuum-UV photolysis of water vapor at 184.9 nm with the subsequent reaction with O₂.
\[ \text{H}_2\text{O} + \text{hv} (\lambda = 184.9 \text{ nm}) \rightarrow \text{OH} + \text{H} \quad (\text{R2}) \]

\[ \text{H} + \text{O}_2 (\text{M}) \rightarrow \text{HO}_2. \quad (\text{R3}) \]

The M in R3 represents mostly nitrogen (N\(_2\)) and (O\(_2\)) and the rest of ambient air that acts to remove the excess internal energy. OH and HO\(_2\) are produced outside of the instrument with concentrations given by:

\[ [\text{OH}] = [\text{HO}_2] = F_{185} \sigma_{\text{H}_2\text{O}} [\text{H}_2\text{O}] \varphi \Delta t \quad (2) \]

where \(F_{185}\) is the actinic flux of 184.9 nm, \(\sigma_{\text{H}_2\text{O}}\) is the photolysis cross section of water vapor in the air, \(\varphi\) is the quantum yield of the photolysis, and \(\Delta t\) is the exposure time of the water vapor to the light source. From the above expression, a calibration factor is obtained,

\[ C = \frac{\Delta S}{\chi_{\text{OH}}} P \quad (3) \]

where \(\Delta S\) is the difference in signal between the on-line and off-line signals (counts per second) and \(\chi_{\text{OH}}\) is the calculated volume mixing ratio from Eq. (1) divided by \([\text{M}]\) (pptv\(^{-1}\)), \(P\) is the laser power monitored at the output of the white cell (mW\(^{-1}\)) and \(C\) is the sensitivity per mW of laser UV power.

The calibration was performed by running ultra-zero air at a flow rate of 50 SPLM, almost ten times that needed for GTHOS. A small portion of the stream was passed through a water bubbler to humidify the air. By adjusting the fraction of air that passes through the bubbler, a variety of mixing ratios (between 0\% and 20\%) were obtained. The water concentration was detected with solid-state water vapor sensor (Vaisaila) that was calibrated against National Institutes of Standards and Technology (NIST) standards. The bulk of the calibration air was sent into the wand, a 1.27 x 1.27 x 30cm square aluminum tube, which is manufactured with three 3.8 cm long Suprasil\textsuperscript{TM} windows.
A low-pressure Hg lamp was used to generate the 184.9 nm actinic flux. The Hg lamp was housed in an aluminum cartridge mounted over one of the Suprasil™ windows on the wand. The housing was continually purged with dry N₂. Through varying the water vapor mixing ratio, Hg lamp supply current, and flow speed of the calibrator, the amount of OH and equivalent HO₂ can be varied from 1.5 pptv to 100pptv (Faloona et al., 2004)(Ren et al., 2003). The absolute uncertainty is estimated to be ±40% (2σ confidence level) for both OH and HO₂ and the limits of detection are 0.01 pptv (2x10⁵ OH cm⁻³) for OH and 0.1 pptv for HO₂.

2.3 Description of OH reactivity measurements

The OH reactivity (kₐOH) can be measured by measuring the OH decay rate:

\[
\frac{d[OH]}{dt} = -k_{OH}[OH]
\]

(4)

Assuming that \(k_{OH}\) is constant during the decay, the OH reactivity can be determined by using the following equation:

\[
k_{OH} = -\frac{\ln\left(\frac{[OH]}{[OH]₀}\right)}{\Delta t}
\]

(5)

(Mao et al., 2009)

The OH reactivity was measured by adding OH to the flow of ambient air (0.5 m s⁻¹) and measuring the OH signal with laser induced fluorescence. The OH added to the ambient airflow was generated through photolyzing water vapor with an ultraviolet light (185 nm) in a moveable wand. The flow occurred in a 40cm long, 7.5 cm diameter aluminum tube that was attached to the inlet at one end and an aluminum block that attached to the OH detection system at the other. The aforementioned moveable wand was 2.0 cm in diameter and was attached through a slot in the aluminum flow tube to a
dead screw, which was turned by a stepper motor. The moveable wand could then by pulled back and the OH signal decay could be recorded. For each complete decay, nine steps of 1.0 cm were used. The wand would stay at each step for approximately 20 s before moving to its new location. Measuring the entire decay would take about 3.5 min (Mao et al., 2009).

2.4 Calibration of the OH Reactivity Instrument

The OH reactivity instrument was calibrated by running zero air through the instrument with four different calibration gases. The measured OH reactivity was then compared to the calculated OH reactivity from well-known reaction rate coefficients and the known gas concentrations (Mao et al., 2009).

One important consideration in the OH reactivity measurement is the wall loss. It is inevitable that OH will get lost due to the walls resulting in an increase in the effective decay. This wall loss thus must be determined by measuring the OH decay when only ultrapure zero air is added to the instrument. This method gives a median wall loss of 2.5 ± 0.3 s⁻¹. Because this measurement can be affected by impurities in the carrier gas, a third method involves measuring OH reactivity in clean ambient air and subtracting the calculated OH reactivity due to measured atmospheric constituents.

The absolute uncertainty primarily depends on three factors: the uncertainty in the anemometer, the uncertainty of the regression coefficients, the statistical precision of the fluorescence signals and the uncertainty of the measured position of the wand. The uncertainty of the anemometer is 2% of readings from manufacture specification for Model 8455-03 Air Velocity Transduction and 10% for the temperature and pressure correction. The uncertainty of the regression coefficients is 15% when the decay is less than 2 s⁻¹. The uncertainty due to the statistical precision of the
fluorescence signals is about 4% and the uncertainty of the measured position of the wand is less than 1% (Mao et al., 2009).

About a dozen other research groups contributed measurements of essentially all atmospheric chemical constituents and environmental variables that are necessary to understand the atmospheric chemistry in Bakersfield. The instruments or instrument inlets were placed on the same tower as GTHOS so that all measurements were made within five meters of each other. These measurements included the chemical species nitric oxide (NO), nitrogen oxide (NO₂), ozone (O₃), and hundreds of volatile organic compounds and the products of their reactions with OH. This fairly complete suite of measurements is essential for the modeling of OH and HO₂.

The model used in this study is based on the chemical mechanism called the Regional Atmospheric Chemistry Mechanism (RACM2) and is commonly used in air quality models. This mechanism has explicit reactions for the nitrogen oxide chemicals like NO but has the VOC reactions lumped into chemical groups to improve model computational speed. The model is constrained by all the measurements except OH, HO₂, and OH reactivity in order to calculate OH and HO₂. Because the lifetimes of OH and HO₂ are so short, the RACM2 mechanism can be used as a box model without considering the transport of chemicals by the wind.
CHAPTER 3: Results and Discussion

3.1 HO\textsubscript{x} Measurements and Model Comparison

Data were collected for 6 weeks (May 18-June 29, 2012) in Bakersfield, California. During this time, the campaign was broken into two distinct periods, an unusual cool period (May 18-May 30, 2010) where the high temperature was less than 30\(^\circ\)C and a more typical warm period (June 24-29) where the high temperature was greater than 40\(^\circ\)C. Figures 2 and 3 displays the measured and modeled OH and HO\textsubscript{2} values throughout the entire campaign respectively. Early on in the campaign, between May 18 and May 30, the OH and HO\textsubscript{2} observed values are lower due to the lower temperatures. After June 14 both the OH and HO\textsubscript{2} observed values increase considerably.

The campaign measurements are diurnally averaged and separated into the cool and warm periods in Figure 4. The diurnal variations of both OH and HO\textsubscript{2} observations and model output show a maxima value midday and a minima at night during both the cool and warm period. This midday peak in OH and HO\textsubscript{2} is due to the solar intensity maximum. During the cool period, the observed OH and HO\textsubscript{2} values are much lower than expected for the area and indicate a possible cool marine air mass over the region. The modeled OH is significantly higher than the observed values during this time period; however, the modeled HO\textsubscript{2} values correlate well with the observed values. During the warm period, the observed OH and HO\textsubscript{2} values increased compared to the previous cool period. While the HO\textsubscript{2} model output agrees well with the observed values, the modeled OH is much greater than measured OH. The modeled OH is far higher than the measured OH for this region, suggesting a possible error in the modeled OH because
The measured OH is consistent with OH measurements from other urban areas (Mao et al., 2010).

The ratio of the observed and modeled OH depends on both on the NO mixing ratio and HO\textsubscript{x} production rate (Ren et al., 2003). This ratio is plotted as a function of NO in Figure 5(a). During the night (blue points) when the NO mixing ratio is low, the ratio of the observed to modeled OH is well above 1 indicating that the model underestimated the amount of OH. During the day (green points) however, the ratio drops to below 1 suggesting that the model is overestimating the OH concentration at these higher NO mixing ratios.

Similar to the ratio of the observed and modeled OH, the ratio of the observed to modeled HO\textsubscript{2} also depends on the NO mixing ratio and HO\textsubscript{x} production rate (Ren et al., 2003). As with the OH ratio, the observed to modeled HO\textsubscript{2} ratio is plotted against the NO mixing ratio in Figure 5(b). During the night (blue points), the NO mixing ratio generally remained below 0.3 ppbv and the ratio between the observed and modeled HO\textsubscript{2} remained close to 1. During the day (green points) when the NO mixing ratio was below about 2 ppbv, the ratio was slightly less than 1 indicating an overestimation of the HO\textsubscript{2} mixing ratio by the model. At NO values above 2 ppbv however, the ratio climbs to be slightly over 1 indicating an underestimation of the HO\textsubscript{2} concentration by the model. This behavior has been observed in other urban areas including New York City (Ren et al., 2003) and La Porte, Texas (Martinez et al., 2002). The reason for this behavior is unknown, however it may be due to unknown HO\textsubscript{x} sources (Ren et al., 2003).

The HO\textsubscript{2} to OH ratio plotted in figure 5(c) tests the understanding of the cycling between OH and HO\textsubscript{2}. This cycling is very fast and the photochemical equilibrium between the two radicals is very closely related to the cycling on NO and NO\textsubscript{2} in the
troposphere (Ren et al., 2003). As expected, both the measured and modeled HO₂ to OH ratios decrease with increasing NO. This behavior is due to the shift of HOₓ towards OH because of the reaction between HO₂ and NO. At NO mixing ratios below 0.07 ppbv, the modeled HO₂ to OH ratio is substantially higher than the measured ratio. The agreement between the modeled and measured ratio is good at NO mixing ratios 0.2-0.3 ppbv. This agreement occurs at lower NO values than what has been seen in previous studies in urban areas during the summer such as New York City and Houston (Ren et al., 2003; Chen et al., 2010).

3.2 OH Reactivity Measurements and Model Comparison

The diurnally averaged measured and modeled OH reactivity during the cool and warm periods are given in Figure 7. During the cool period (Figure 5(a)), the measured daytime OH reactivity (black line) is about 5 s⁻¹ and the nighttime OH reactivity is between 15-25 s⁻¹. The modeled OH reactivity (blue line) is larger than the measured OH reactivity during the nighttime, however it is lower than the measured OH reactivity during the day. The calculated OH reactivity (red line) correlates well with the modeled output, showing values higher than the measured OH reactivity during the night, but lower during the day. During the warmer period (Figure 7(b)), the measured OH reactivity (black line) is ~10 s⁻¹ during the day and between 20-25 s⁻¹ during the night. The modeled (blue line) and the calculated (red line) OH reactivity remain lower than the measured OH reactivity throughout both the daytime and nighttime. In both the cool and warm periods, there is a morning peak in the OH reactivity shortly before 6am local time.

Compared to previous field studies in other urban areas, the measured OH reactivity values during the cool period are lower than has been seen in any other urban
area. Kovacs et al. (2003) reported the measured daytime OH reactivity to be about 11.3 ± 4.8 s⁻¹ in Nashville, TX in 1999 and Ren et al. (2003) reported the measured OH reactivity to be about 19 ± 3 s⁻¹ during the summer in New York City in 2001. These daytime OH reactivity values of ~5 s⁻¹ are much closer to the values observed over the Pacific Ocean during the INTEX B aircraft study, about 4 s⁻¹ (Mao et al., 2009). This similarity suggests that air in the cool period came from the Pacific Ocean with little influence from pollution on land.

During both the cool and warm periods in Bakersfield, there is a substantial nighttime increase in the OH reactivity that is not seen to the same degree in Nashville or New York City. This increase in OH reactivity indicates the continued emission and buildup of OH reactants during the nighttime hours when the boundary layer has decreased.

### 3.3 OH Production and Loss

Since OH has such a short lifetime, the production and loss of OH should always come into balance in less than a second. The OH loss can be calculated by multiplying the measured OH reactivity by the measured OH concentration. OH production can be calculated from the reaction between the measured HO₂ and NO, although OH is also produced by photolysis as described in Chapter 1 and this primary production can account for up to about 20% of the total OH production (Martinez et al., 2003). By comparing the OH loss with this calculated OH production, one can test for the presence of additional sources (Ren et al., 2003). The diurnal average of this OH production and loss is displayed in Figure 8. The measured OH loss was greater than the OH production during the night but less than the OH production during the day. The typical OH loss values were about 2x10⁷ and 5x10⁷ cm⁻³ s⁻¹ during the night and day respectively. The
typical OH production values were near zero at night and about $7 \times 10^7$ cm$^{-3}$ s$^{-1}$ during the day. OH production, in theory, should not exceed the OH loss, indicating a problem with one or more of the measurements.

Figure 9 shows a few days during the campaign where the OH production also exceeded the OH loss along with the NO measurements. Where the NO mixing ratio (green line) is high, the OH production exceeds the OH loss. One possibility for this occurrence is that with a high NO concentration in the atmosphere, the reaction between HO$_2$ and NO dominates the OH production. According to Ren et al. (2003) however, no laboratory or field tests have shown problems with the HO$_2$ measurements at high NO. A suggested alternate possibility is that the under-correction of the OH reactivity for NO, which affects the OH reactivity measurement by reacting with HO$_2$ to produce OH in the OH reactivity instrument (Shirley et al., 2006). Under-correcting the OH loss rate would result in a higher calculated OH loss rate and would bring the OH loss and production values closer. Additionally, errors in the OH measurement could result in errors in the OH loss-rate calculation. Further work on the calibrations of both the OH and OH reactivity measurement should be conducted to further understand the OH production and loss balance.
Figure 1: Map of Bakersfield, CA with field site labeled “A”

Figure 2: Time series of measured OH concentration (molecules cm\(^{-3}\)) from May 15-June 30, 2010.
Figure 3: Time series of measured HO₂ mixing ratio (pptv) from May 15-June 30, 2010.

Figure 4: (Top left and right) Median diurnal OH concentration during the cool period (May 18-May 30, 2010) and the warm period (June 24-29, 2010) respectively. (Bottom left and right) Median diurnal HO₂ mixing ratio during the cool period (May 18-May 30, 2010) and the warm period (June 24-29, 2010) respectively.
Figure 5: (Top) observed to modeled OH concentration plotted against NO mixing ratio. (Middle) observed to modeled HO$_2$ mixing ratio plotted against NO mixing ratio. (Bottom) Observed (red) and modeled (blue) HO$_2$ to OH ratio plotted against NO mixing ratio.

Figure 6: Time series of the measured OH reactivity (s$^{-1}$) from May 15 – June 30, 2010.
Figure 7: Averaged diurnal OH Reactivity during the cool period, May 18-30, 2010 (top) and during the warm period, June 24-29, 2010 (bottom). The observed values are shown in black, the modeled values are in blue, and calculated values are in red.

Figure 8: Averaged diurnal OH production (green) and OH loss (blue).
Figure 9: Measured OH loss (blue), OH production (red) and NO mixing ratio (ppbv) during one day where high NO values result in OH production exceeding OH loss.
CHAPTER 4: Conclusion

This extensive field campaign provided the opportunity to test the knowledge of oxidation photochemistry in an urban environment. The measurements of OH, HO\textsubscript{2} and OH reactivity provided expected values for Bakersfield, California during the warmer period. The model comparison to the RACM2 output provided a good simulation of the HO\textsubscript{2} behavior during both the cool and warm period. The modeled OH was slightly higher than the measured OH during the cool period and much higher than measured OH during the warm period. This difference suggests an error in either the OH measurement calibration or in the model chemistry itself. One difference between this study in Bakersfield and all previous studies were the almost constant “spikes” of NO from local traffic, both day and night. All previous studies were at locations where the daytime NO dropped to values below 1 ppbv and had few “spikes”. Initial attempts to de-spike the measurements did not change the results, but perhaps a more sophisticated method will be needed to examine this possibility for the discrepancy between the measured and modeled OH. Likely most of the discrepancy can be resolved with closer examination at the OH calibration and the effects of the persistent NO “spikes” on the modeling.

The OH reactivity measurements collected during this field campaign are lower than observed during other studies, however are still reasonable for the location. The RACM2 model output agrees well with the observed OH reactivity during both the cool and warm periods.

The OH production and loss balance provides a peculiar problem with the data. The OH loss should always be equal to the OH production. However, when the NO mixing ratio was observed to be high, this balance was not observed. This may indicate
a possible source not accounted for in the OH production calculation or a calibration error in the OH reactivity measurement. Further investigation into the problem is recommended to fully understand the reason behind the effect of NO on the OH loss and production balance.

The field campaign in Bakersfield, California provided insights into oxidation photochemistry and its role in air quality problems in urban areas. The research highlighted potential gaps in understanding and problems in both measurements and modeling. Further investigation into air quality models and measurements will provide a good basis to make important regulation decisions in the future.
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ACADEMIC VITA

Jordan Leigh Thomas

Education

The Pennsylvania State University, University Park, PA
The College of Earth and Mineral Sciences
The Schreyer Honors College
  ▪ Bachelors of Sciences in Meteorology, Expected May 2012

The University of Southampton, Southampton, England
The National Oceanographic Centre
  ▪ Minor in Marine Science

Publications & Presentations

AGU Fall 2010 Meeting (December 2010)
  OH, HO2, and OH Reactivity Behavior in the Southern San Joaquin Valley during CalNex 2010

AGU Fall 2011 Meeting (December 2011)
  Oxidation photochemistry in the Southern San Joaquin Valley during CalNex 2010

Research Experience

CalNex 2010 (May 2010 – May 2012)
  Participated in a two-month field study in Bakersfield, CA studying oxidation photochemistry and preformed analysis and model comparison of collected data under the direction of Dr. William Brune.

Falmouth (July 2011)
  Participated in a two-week marine science field study through the University of Southampton in Falmouth, UK.
Award and Honors

Freshman Scholarship (August 2008 - May 2009)

John and Elizabeth Holmes Teas Scholarship (August 2009 - May 2012)

Kruhoeffer Endowed Scholarship in Meteorology (August 2010 - May 2011)

Robert A. Case Scholarship in Meteorology (August 2011 - May 2012)

Other Activities

Marine Science Society

Treasurer (August 2009 - May 2011)
Vice President (August 2011 - May 2012)

Student Red Cross Club

On-Site Coordinator Chair (August 2010-January 2011)

Vice President (August 2011 – May 2012)