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MEASUREMENT OF OZONE PRODUCTION SENSOR

A Dissertation in
Meteorology

by

Maria del Carmen Cazorla Andrade

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The dissertation of Maria del Carmen Cazorla Andrade was reviewed and approved* by the following:

William H. Brune  
Distinguished Professor of Meteorology  
Head of the Department of Meteorology  
Dissertation Advisor  
Chair of Committee

Anne M. Thompson  
Professor of Meteorology

Scott J. Richardson  
Research Associate

James F. Kasting  
Professor of Geosciences

*Signatures are on file in the Graduate School
ABSTRACT

The Measurement of Ozone Production Sensor (MOPS) is a new ambient air monitor that measures directly the rate of ozone production in the atmosphere. The sensor consists of two environmental chambers made of UV-transmitting Teflon film continuously exposed to the solar radiation, a unit to convert NO$_2$ to O$_3$, and a modified ozone monitor. In the sample chamber, photolysis processes and radical chemistry produce ozone just as it happens in the atmosphere. In the second chamber, called the reference chamber, a UV-blocking film prevents radical formation in a way that only the photostationary state component of ozone formation is retained. High-efficiency conversion of NO$_2$ to O$_3$ accounts for differences in the NO$_x$ photostationary state between both chambers. An ozone monitor operating without its ozone scrubber detects the ozone differential between the sample and the reference chamber. By doing so, the photostationary state component of ozone formation is canceled out and the ozone produced via radical chemistry is detected. The ozone differential is divided by the exposure time of the air in the chambers to find the rate of ozone production. Radical abundance measurements, wall loss tests and radiometric measurements demonstrate the feasibility of the technique.

The MOPS was deployed in a rural environment, on the campus of Penn State University (September 2008), and in an urban environment, in Houston during the Study of Houston Atmospheric Radical Precursors SHARP (15 Apr to 31 May, 2009). The MOPS retrieved the first experimental plots of ambient P(O$_3$) vs. NO in both locations. In addition, the sensitivity of ozone production in these two environments was studied by adding NO$_x$ mixtures to the ambient air and looking at the response in the production of ozone. The results presented in this work demonstrate how an extended use of the MOPS can contribute to the improvement of air quality regulations by quantifying ozone production and ozone transport at a regional scale. Another practical benefit is to be able to improve and validate chemical box models. Finally, our current understanding of the chemistry of ozone production can be verified or revisited as additional experimental evidence is retrieved in future field campaigns with the MOPS.
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Chapter 1

Introduction

1.1 Ozone Production and Air Quality Control

Ground level ozone (O$_3$) is one of the main constituents of smog. Ozone causes respiratory discomfort, reduces lung functioning, and worsens conditions such as chronic bronchitis, emphysema, and asthma. The development and aggravation of respiratory diseases in humans caused by ozone (O$_3$) in the ambient air is currently a serious health concern (Ho et al., 2007). The oxidative nature of ozone also affects foliage of croplands and woods (Madden and Hogsett, 2001). On a regional-to-global scale, ground-level ozone contributes to climate change by acting as a greenhouse gas (Foster et al., 2007). The Environmental Protection Agency, EPA, monitors continuously the levels of ozone across the country through a network of commercial ozone analyzers. Currently, the 8-hour average national air quality standard, NAAQS, for ozone is 75 ppbv (US EPA, 2010). This standard is now under review and EPA will issue the new standard by August 2010 between 60 and 70 ppbv (Broder, 2010).

Ozone is not emitted directly from pollution sources but is instead formed in the atmosphere when nitrogen oxides and volatile organic compounds react in the presence of sunlight. Ozone production is sensitive to the concentration of nitrogen oxides (NO$_x$) and volatile organic compounds (VOC$_x$), and it is different for rural and urban environments (Kleinmann et al., 1997). To protect public health, EPA has mandated limits on VOCs and NO$_x$ emissions. The complexity of ozone chemistry, however, depends on local conditions of pollution and meteorology, which makes the effectiveness of applying a universal method for controlling either NO$_x$ or VOCs uncertain.
EPA pollution control strategies to attain the NAAQS have failed several times in the past (NRC, 1991). For example, in the early stages of the development of emission standards for point and mobile sources, VOCs were targeted as the key precursors of ozone formation. Future assessments of ozone levels indicated that the control of VOCs was ineffective. EPA based the decision of precursor control upon modeling the effect that the reduction of VOCs would have in the hourly production of peak ozone levels, a method known as Empirical Kinetic Model Approach (EKMA). This method yields isopleths of ozone production that depend on NO$_x$ and VOC emissions, as shown in Figure 1-1.

![Ozone Isopleth in ppbv (Sillman, 2003).](image)

According to this method, there are two regimes of ozone production, NO$_x$ sensitive and VOC sensitive. The effectiveness of controlling either NO$_x$ or VOCs depends on the ratio VOC/NO$_x$ in the ambient air. At the time of early regulations, it seemed apparent that VOC/NO$_x$ ratios of 10 or less would require control of hydrocarbon emissions, whereas control over NO$_x$ emissions would be effective provided the ratio VOC/NO$_x$ would be 20 or greater. Inventories of
volatile hydrocarbons indicated that in most polluted urban areas of the continental United States the ratio VOC/NO$_x$ was about 10. Such analysis guided EPA to mandate VOC emission reductions as a strategy to reduce the ambient ozone levels (NRC, 1991). This approach, however, failed to generate a substantial reduction in ambient ozone except for the highest ozone in urban centers. The problem with this strategy is the large uncertainty at predicting the transition point between regimes of ozone production. Additionally, the incompleteness of anthropogenic and biogenic VOC emission inventories may have taken a toll on predicting the right VOC/NO$_x$ ratio. Finally, the advection of ozone from polluted urban centers to suburban areas implies a time lag in which hydrocarbon oxidation along with NO$_x$ consumption can produce a shift in the regime of ozone production (Sillman, 1993). In response to the ozone transport dilemma, in 1998 EPA mandated a regional law called the NO$_x$ State Implementation Plan, to reduce the point emissions of nitrogen oxides, which has contributed to about a 13% reduction in the ambient ozone concentrations in the eastern United States (Gégo, 2007). Despite these reductions, ozone levels remain higher than the levels deemed safe for human health. Studies of radical propagation have suggested that a better control strategy is to reduce the rate of ozone production in areas where it is high (Tonnesen and Dennis, 2000).

At present, EPA uses three-dimensional chemical transport models as a tool to devise and evaluate air quality standards (U.S. EPA NERL, 1999). There are, however, a number of uncertainties associated with models that include chemical mechanisms, initial and boundary conditions, hydrocarbon inventories, ozone transport, boundary layer meteorology, and mathematical algorithms (NRC, 1991). Although chemical models have been improved significantly, EPA still faces the difficulty of setting standards that seem to come from a rather unreliable source. With the current pressure by environmental groups for setting a new “very strict standard” of 60 ppbv, new criticisms have been raised regarding the science behind the standards (Hansen, 2001).
The experience with the use of only models to estimate the rate of ozone production and associated levels of precursors indicate that it is necessary to count on other information to decide upon environmental regulations. With the purpose of creating a better basis for decision making, researchers have developed a number of observational indicator methods that could help determine the regime of ozone production in the ambient air. For example, the ratio peroxide ($H_2O_2$) to nitric acid ($HNO_3$) has been suggested as a way to determine whether the production of ozone is NO$_x$-sensitive or VOC-sensitive (Sillman, 1995; Kleinman, 1997, 2001). In addition, radical propagation studies introduce the fraction of hydroxyl radicals, OH, that react with hydrocarbons and the fraction of hydroperoxy radicals, HO$_2$, that react with NO as potential indicators of the regime of ozone production outside box models (Tonnesen and Dennis, 2000).

One of the issues concerning the use of constrained photochemical models is the difference between the modeled and calculated ozone production, P(O$_3$). The models underpredict the concentration of the HO$_2$ radical at high NO levels, which affects directly the modeled ozone production. In theory, the production of ozone increases with increasing NO up to a peak value (at a few ppbv of NO). After this point, P(O$_3$) decreases with increasing NO (Kleinman, 2002). The decrease in ozone production can be partially explained by the reaction of OH radicals with NO$_2$ to form nitric acid. Field observations, however, have shown a consistent increase of ozone production as a function of NO, which suggests a possible additional source of HO$_x$, OH and HO$_2$ (Martinez et al., 2003; Ren et al., 2003; Ren et al., 2004; Shirley et al., 2006; Kanaya et al., 2007). Measurements made using the Ground-based Tropospheric Hydrogen Oxides Sensor (GTHOS) have demonstrated HO$_2$ concentrations to be higher than the values predicted by a box model whose chemical mechanism is based on the Regional Atmospheric Chemical Mechanism (RACM) (Ren et al, 2003) or other mechanisms (Chen et al., 2009). As a result the calculated P(O$_3$) from observations turns out to be greater than the modeled ozone production.
Given the discrepancies and limitations that surround the estimation of the rate of ozone production, a direct measurement of the ozone production rate could become a powerful approach to design air quality standards as well as an efficient way to validate chemical models. In order to measure directly the rate of ozone production, the new technique needs to take into account all the chemistry relevant to ozone production.

1.2 The Chemistry of Ozone Production

The chemistry of ozone production has been summarized in a very comprehensible way by many authors (Finlayson-Pitts and Pitts, 1977, Logan et al., 1981; Seinfeld and Pandis, 2006). According to our current understanding of tropospheric chemistry, the only source of ozone, $O_3$, in the troposphere during daylight hours is the photolysis of $NO_2$, which peaks at 400 nm. Hence, in the presence of sunlight the total concentration of ambient ozone depends on the sum of $NO_2$ plus $O_3$. Chemically, the species $NO$, $NO_2$ and $O_3$ reach the photostationary state, PSS, which means that the net production of ozone is zero. This steady state is achieved without the participation of hydrocarbon species. This cycle is represented by reactions R1 to R3:

$$NO_2 + hv \rightarrow NO + O \quad \text{(R1)}$$

$$O + O_2 + M \rightarrow O_3 + M \quad \text{(R2)}$$

$$NO + O_3 \rightarrow NO_2 + O_2 \quad \text{(R3)}$$

At the same time, sunlight photolyzes ozone, producing oxygen gas, $O_2$, and an excited oxygen atom, $O(^1D)$, as expressed by R4. Collisions of $O(^1D)$ with oxygen or nitrogen (M)
quench it back to its ground atomic state, O. The large abundance of water vapor in the troposphere, however, opens a path for collisions of O(\(^1\)D) with H\(_2\)O, as shown by R6 towards the formation of hydroxyl radicals, OH

\[
\text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O}(^{1}\text{D}) \quad \text{(R4)}
\]

\[
\text{O}(^{1}\text{D}) + \text{M} \rightarrow \text{O} + \text{M} \quad \text{(R5)}
\]

\[
\text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \quad \text{(R6)}
\]

The hydroxyl radical, OH, along with ozone make up the oxidative nature of our atmosphere. The photolysis of ozone followed by reaction with water vapor is the main contributor to the formation of OH. Other sources include the photolysis of nitrous acid, HONO, and hydrogen peroxide, H\(_2\)O\(_2\).

The reaction of the OH radical with volatile organic compounds, VOCs, generates organic peroxy radicals, RO\(_2\), and hydroperoxy radicals, HO\(_2\). This reaction also generates secondary organic radicals, RO’ that propagate the oxidation chain increasing the formation of NO\(_2\) outside of the PSS and ultimately of ozone, as observed in reactions R7 and R8.

\[
\text{VOC} + \text{OH} \rightarrow \text{RO}_2 + \text{H}_2\text{O} \quad \text{(R7)}
\]

\[
\text{RO}_2 + \text{NO} \rightarrow \text{RO}’ + \text{NO}_2 + \text{HO}_2 \quad \text{(R8)}
\]

Peroxy radicals, RO\(_2\) and HO\(_2\), react with NO emissions and disturb the photostationary state of the species NO\(_x\) and O\(_3\) by producing additional NO\(_2\). The process continues as a catalytic cycle in which HO\(_2\) is transformed into OH while NO cycles into NO\(_2\), according with R9.

\[
\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \quad \text{(R9)}
\]
It is reasonable to say, therefore, that the concentration of ambient ozone has two components. The first is the photostationary state of the species NO, NO₂ and O₃. This source of ozone is not a source of pollution. The second component is the formation of ozone from the photolysis of non-steady state NO₂. As shown by reactions R7 and R8, NO₂ forms in addition to the photostationary state provided an atmospheric pool of HO₂, RO₂, and NO is available.

Ozone is produced continuously through the catalytic cycling of HOₓ and NOₓ, until a termination reaction stops the cycle. Depending on the concentration of NO, the ozone production can be NOₓ limited or NOₓ saturated. If NOₓ is in excess, the OH radicals react with NOₓ instead of continuing to oxidize VOCs. An example of HOₓ-NOₓ reactions is the formation of nitric acid, HNO₃, shown in R10. In contrast, when there are more hydrocarbon emissions than NOₓ, the ozone production is limited by NOₓ and the termination occurs due to radical-radical reactions. The formation of hydrogen peroxide, H₂O₂, is shown in (R11).

\begin{align*}
\text{OH} + \text{NO}_2 + \text{M} &\rightarrow \text{HNO}_3 + \text{M} \quad \text{(R10)} \\
\text{HO}_2 + \text{HO}_2 &\rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(R11)}
\end{align*}

The simplest example that illustrates the chain of reactions initiated by OH, is the oxidation of methane, CH₄. The first product of reaction R12 is the methyl radical, CH₃, which is rapidly oxidized to form the methyl peroxy radical, CH₃O₂, as shown in R13. Depending on the concentration of NO, peroxy radicals lead to the formation of new ozone or combine among themselves to stop the production of ozone. For example, when enough NO is present, the methyl peroxy radical can react with NO to form NO₂ and the methoxy radical CH₃O, as shown by R14. Under NO limited conditions, in contrast, the methyl peroxy radical can react with HO₂ to end momentarily the production of NO₂ and to form the radical reservoir species methyl peroxyde, CH₃OOH, as depicted by R16. Methyl peroxyde photolyzes in the sunlight, however, releasing a
new methoxy radical which resumes the production of NO₂, and hence of ozone. If the oxidation of methane follows the path of the production of NO₂, secondary formaldehyde, HCHO, forms as shown in R15. The photolysis of formaldehyde has two paths. One produces the neutral species H₂ and CO, as indicated by R19. The second produce radicals H and HCO that quickly combine with O₂ to individually contribute to the atmospheric radical pool by producing HO₂ (R20, R20.1 and R20.2).

\[
\begin{align*}
\text{CH}_4 + \text{OH} & \rightarrow \text{CH}_3 + \text{H}_2\text{O} & \text{(R12)} \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} & \text{(R13)} \\
\text{CH}_3\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 & \text{(R14)} \\
\text{CH}_3\text{O} + \text{O}_2 & \rightarrow \text{HCHO} + \text{HO}_2 & \text{(R15)} \\
\text{CH}_3\text{O}_2 + \text{HO}_2 & \rightarrow \text{CH}_3\text{OOH} + \text{O}_2 & \text{(R16)} \\
\text{CH}_3\text{OOH} + \text{hv} & \rightarrow \text{CH}_3\text{O} + \text{OH} & \text{(R17)} \\
\text{CH}_3\text{OOH} + \text{OH} & \rightarrow \text{CH}_3\text{O}_2 + \text{H}_2\text{O} & \text{(R18)} \\
\text{HCHO} + \text{hv} & \rightarrow \text{H}_2 + \text{CO} & \text{(R19)} \\
\text{HCHO} + \text{hv} & \rightarrow \text{H} + \text{HCO} & \text{(R20)} \\
\text{H} + \text{O}_2 & \rightarrow \text{HO}_2 & \text{(R20.1)} \\
\text{HCO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CO} & \text{(R20.2)}
\end{align*}
\]

For the path that yields the maximum production of ozone, the oxidation of methane produces 5 ozone molecules per molecule of methane fully oxidized (Seinfeld and Pandis, 2006).

The chemical production and loss of ozone as a function of NOₓ and VOCs can be represented by the kinetic rate equations for the corresponding reactions. Equation (1.1) summarizes the production of NO₂. The two terms in equation (1.1) indicate production of NO₂,
and therefore of ozone, from peroxy radicals reacting with NO. Equation (1.2) represents the possible paths for ozone loss. The first term corresponds to ozone loss due to the formation of nitric acid, the second term is the loss due to ozone photolysis, and the last term corresponds to organic nitrate production. The net production of ozone results from the imbalance between chemical production and chemical loss, as shown by equation (1.3).

\[
\begin{align*}
 p(O_3) &= k_{HO_2+NO}[HO_2][NO] + \Sigma k_{RO_2+NO}[RO_2],[NO] \\
 l(O_3) &= k_{OH+NO_2+M}[OH][NO_2][M] + k_{HO_2+O_3}[HO_2][O_3] + P\left(\text{RONO}_2\right) \\
 P(O_3) &= p(O_3) - l(O_3)
\end{align*}
\] (1.1) (1.2) (1.3)

The estimation of the rate of ozone production has been done traditionally by chemical modeling or by calculation when radical measurements are available. As discussed earlier, chemical models have limitations while discrepancies surround modeled and calculated values of ozone production. At the same time, from an environmental viewpoint, the important term to be known is the net rate of ozone production \( P(O_3) \) rather than the individual components that contribute to that rate. We propose MOPS, the Measurement of Ozone Production Sensor, an instrument in which the ozone formation chemistry that occurs in the atmosphere also occurs in the instrument and thus measures the net rate of ozone production in the ambient air.

**1.3 Ozone Production and Ozone Transport**

Ambient ozone is the result of local chemical production and transport processes. The concentration of ground-level ozone can be easily obtained from a direct measurement using a commercial ozone analyzer. Real time ozone concentrations as well as historical data are available from the AIRNOW website (US EPA et al., 2009). These ambient ozone measurements,
however, do not indicate whether ozone is locally produced or imported from other areas where it was chemically produced. In other words, the absolute measurement of ambient ozone cannot be used to quantify each of these two contributions.

The processes that influence the concentration of ozone in the ambient air are described in the ozone budget equation (1.4). From this equation, it is clear that ozone production depends on the ambient air chemistry, surface deposition, and local meteorology.

\[
\frac{\partial [O_3]}{\partial t} = p(O_3) - l(O_3) - \frac{v}{H} [O_3] + u_i \frac{\partial [O_3]}{\partial x_i} 
\]

\[ (1.4) \]

\[
P(O_3) \quad \text{SD} \quad \text{A}
\]

\( P(O_3) \) is net chemical production consisting of chemical ozone production, \( p(O_3) \), and chemical loss, \( l(O_3) \), SD is surface deposition consisting of the deposition velocity, \( v \), divided by the mixed layer height, \( H \), times the ozone concentration, and A is advection consisting of the velocity in three directions, \( u_i \), times the ozone gradient in those three directions.

Meteorological conditions play an important role in the local ozone budget. Transport processes such as horizontal advection and turbulence can modify substantially the accumulation of ozone over time at any given location in the atmosphere. For instance, a typical meteorological scenario that causes high ozone episodes in heavily polluted urban centers is light or no wind combined with strong solar radiation and high temperature. In such conditions, the term responsible for the accumulation of ozone in the ambient air is the net chemical rate of ozone production \( P(O_3) \). Additionally, in the same equation, the surface deposition and advection of ozone are proportional to the ambient ozone concentration \([O_3]\) that is produced predominately
by the local photochemistry. Hence, if the net ozone production $P(O_3)$ can be decreased by regulatory actions, the overall ozone level over time will decrease proportionally.

The contribution of the transport terms for the case of suburban areas located downwind of pollution centers is much greater than in the case described above. Likewise, areas located on the path of influential meteorological features such as low-level jets or high-pressure systems are directly affected by ozone advection (Taubman et al., 2008; Kemball-Cook et al., 2009). In these particular situations, high amounts of ambient ozone would come from transport of ozone rather than local ozone production.

All the terms in equation (1.4) need to be known to a high degree of accuracy in order for models to yield a good approximation of the rate of ozone production. Uncertainties in the chemical mechanisms, hydrocarbon inventories, ozone transport, and mathematical algorithms, however, represent potential sources of error in the estimation of modeled rates of ozone production (NRC, 1991). At present, however, it is difficult to determine in a quantitative way the importance of ozone transport versus ozone production for regions that are monitored by air quality networks.

A direct measurement of ozone production can address the different questions discussed above. First, direct measurements of ozone production could be added to existing air quality networks to provide important information for the design of air quality regulations. Second, they could be used to quantify the importance of ozone transport versus ozone production by comparing the direct measurement of ozone production to the observed ozone rate-of-change. Third, they would contribute to the understanding of the NOx and VOC sensitivity of ozone production. Fourth, they could help resolve the discrepancy between the ozone production calculated from measured and modeled HO$_2$. Finally, a direct measurement of ozone production would help improve chemical transport models.
This thesis describes the technical details and deployment studies of the Measurement of Ozone Production Sensor (MOPS). Chapter 2 describes the experimental methods and characterization of the instrument. Chapter 3 discusses measurements made with the MOPS at the Pennsylvania State University in 2008. Chapter 4 discusses ozone production rates measured during an intensive field campaign, SHARP 2009, in Houston Texas in April and May of 2009. Finally, Chapter 5 is devoted to conclusions.
Chapter 2

Experimental Methods

Measurements of the ozone production rate must meet the same criteria as the measurements of atmospheric species to ensure high quality data. The sensitivity and time response of the instrument are related directly to the abundance of the species to be measured and their atmospheric lifetimes. The instrument must be designed to minimize species losses and signal artefacts. Additionally, the electronics must be fast and minimize noise. Finally, the instrument must be accurate; hence, appropriate calibration methods or checking procedures need to be devised (Heard et al., 2006; Brock and Richardson, 2001). This chapter explains in detail the principle of operation, construction, data processing and characterization of the Measurement of Ozone Production Sensor (MOPS).

2.1 Principle of Operation of the Measurement of Ozone Production Sensor

The Measurement of Ozone Production Sensor, MOPS, obtains directly the rate of ozone production in the atmosphere by finding the difference between the ozone formed from radical chemistry minus the photostationary state component of ozone per unit time. MOPS has three components: two small environmental chambers made of Teflon film continuously exposed to solar radiation, a nitrogen dioxide-to-ozone conversion unit, and a modified ozone analyzer. A schematic of the instrument is shown in Figure 2-1.
The MOPS sample chamber has walls that transmit solar ultraviolet light. Hence, the air inside this chamber undergoes the same photochemistry that takes place in the ambient air. In contrast, the MOPS reference chamber has a film that blocks radiation of wavelengths less than 400 nm. As a result, the reference chamber limits the production of OH radicals generated by the photolysis of ozone followed by the reaction with water vapor. The photolysis of nitrous acid, HONO, is also eliminated. Similarly, the film on the reference chamber restricts the production of hydroperoxy radicals, HO₂, produced by the photolysis of formaldehyde, HCHO. With radical chemistry eliminated, ozone in this chamber comes only from the photostationary state, PSS, of the species NO, NO₂, and O₃. Since it is not possible to eliminate radical production without affecting NO₂ photolysis near 400 nm, the PSS in the reference chamber tends to shift O₃ toward NO₂. The total amount of ozone in the reference chamber, therefore, is conserved in the form of NO₂ plus O₃.

Some of the ozone produced in the sample chamber reacts with ambient NO and is partitioned into NO₂ according to the NOₓ PSS. At the same time, differences in the NO₂ photolysis in the two chambers could cause the partitioning of ozone and NO₂ in the two
chambers to be different. The difference between the total sum NO$_2$+O$_3$ in the sample chamber minus the same sum in the reference chamber, however, cancels out the PSS component of ozone production and yields only the component associated with the production of new ozone by radical chemistry.

The strategy, therefore, is to determine the differential of the sum O$_3$+NO$_2$ between the two chambers and divide it by the exposure time of the air inside them to determine the ozone production rate.

### 2.2 Technical Description

A description of the MOPS design begins with the sampling of the ambient air (Figure 2-1, on the left). Air is sampled by both chambers through a common short Teflon inlet. The flow is split equally between the two chambers. Two hollow cylindrical aluminum frames (17.78 cm diameter and 45.752 cm long) serve as support for Teflon film (PTFE, 0.05 mm thick) that is wrapped around the frames. The volume of the chambers is 11.3 L and the flow of ambient air through each chamber is 1.5 L/min. The inlets and outlets to the chambers are pieces of Teflon tubing that are 2.54 cm diameter and 6.35 cm long. The flow is induced by a pump located downstream of the chambers. The sample chamber is clear Teflon so the air inside is radiated by all the wavelengths of the solar radiation that occur in the atmosphere. The reference chamber, made the same as the sample chamber, is covered with an Ultem film (polyetherimide, 0.25 mm thick) that removes sunlight at wavelengths less that 400 nm.

Since the goal is to detect the difference in NO$_2$+O$_3$ between the sample and reference air, the flows that exit the chambers enter a NO$_2$-to-O$_3$ converter unit. This converter unit uses two photolytic conversion cells, one for the air from the sample chamber and one for the air from the
reference chamber. A light-emitting diode (395 nm wavelength, 5.4 watts of power) is attached to the end of each photolytic conversion cell as the source of radiation. The photolytic conversion cells are made of quartz with a reflective aluminum mirror coating on the outside. The dimensions of the cells are 30.5 cm in length and 5.1 cm in diameter. Light is also reflected by a round aluminum mirror placed at the end of each quartz cell opposite the light source. This dual cell conversion unit is attached to a differential ozone monitor. The converter unit uses the internal pump inside the ozone monitor to pull air so that the flow through each photolytic conversion cell is the same as the flow through each detection cell in the ozone monitor. This flow is 0.5 L/min. The residence time in each photolytic conversion cell is 103±14 seconds (95%, N=4) as determined by ozone pulse experiments described later.

The converter unit has two pairs of inlet and outlet ports. Each pair corresponds to each photolytic cell. The inlet connected to the sample chamber should correspond to the outlet connected to the sample channel in the modified ozone monitor. The second pair is connected in similar way to the reference chamber and reference channel in the ozone monitor, using Teflon PFE tubing with an outside diameter (OD) of 0.25 inches and inside diameter (ID) 0.0625 in. The converter and the ozone monitor are connected with short Teflon lines in a way that both instruments are practically locked together, one sitting on top of the other. The ozone monitor channels must be kept clean; therefore, two particle filters are placed in front of the inlets to the ozone monitor. The lines that connect the chambers to the converter are kept as short as possible to minimize loss and artifacts. MOPS have been deployed with lines less than 15 ft length.

To account for the possible differences between the two photolytic conversion cells in the conversion unit, the flows of sample and reference air switch between photolytic conversion cells every 5 minutes. To switch flows, the instrument has two pairs of solenoid valves. The first pair is located between the chambers and the conversion cells. The second pair of solenoid valves works synchronously with the first pair and is located between the conversion cells and the ozone
monitor. In this way, the sample channel in the ozone instrument always measures the ozone from the sample chamber. The final reading is obtained as an average of the ozone differential measured with each of the photolytic conversion cells switched to the sample chamber, giving an instrument time constant of twice 5 minutes, or 10 minutes.

After the conversion of NO$_2$ into O$_3$ has taken place, the MOPS uses a modified ozone monitor (Thermo Scientific, Model 49i) to obtain a differential measurement of the ozone between the two chambers. The main modification applied to the commercial dual channel ozone monitor is the removal of the ozone scrubber. These instruments use a dual channel detection system for reference and sample air. The reference air is ambient air that flows through an ozone scrubber so that its ozone content is zero (Thermo, 2005).

Commercial ozone analyzers rely on Beer’s law to relate the absorption of 254 nm light to the concentration of ozone in the sample air. Let the intensity of the light source radiating zero air be $I_o$. Looking at the air that exits both chambers and applying Beer’s law, the concentration of ozone that is measured by an ozone monitor without an ozone scrubber can be expressed using equations (2.1) and (2.2).

Reference chamber: \[(n/v)_{pss} = -1/(l\Gamma) \ln (I_{reference}/I_o) \] (2.1)

Sample chamber: \[(n/v)_{new\ ozone} + (n/v)_{pss} = -1/(l\Gamma) \ln (I_{sample}/I_o) \] (2.2)

In these equations, the quantity $(n/v)$ is the ozone number density in the air, $l$ is the length of the absorption path, $\Gamma$ is the absorption cross section of the ozone molecule, $I_o$ is the intensity of the 254 nm light with zero air, $I_{reference}$ and $I_{sample}$ correspond to the intensity of the 254 nm light detected with air from the reference chamber and sample chamber. PSS refers to photostationary steady-state. By subtracting equation (2.1) from equation (2.2) we obtain equation (2.3):

\[(n/v)_{new\ ozone} = -1/(l\Gamma) \ln (I_{sample}/I_{reference}) \] (2.3)
Therefore, according with equation (2.3), by removing the ozone scrubber from the ozone monitor, the new ozone differential monitor allows detecting the “new ozone” by receiving a continuous supply of sample air from the sample chamber and reference air from the reference chamber.

As an additional improvement to the ozone monitor, the absorption cells inside the monitor were locked together by an aluminum block in order to stabilize temperature and thus ozone density. The quantity \( \text{\(n/v\)\textsubscript{new ozone}} \) in equation (2.3) corresponds to the ozone differential measured by the modified ozone monitor. This ozone differential, \( \Delta O_3 \), related to the mean exposure time of the air inside the chambers, \( \tau \), yields the rate of ozone production, as it can be observed in equation (2.4).

\[
P(O_3) = \frac{\Delta O_3}{\tau}
\]

(2.4)

Hence, in this equation \( P(O_3) \) is the net chemical ozone production and \( \Delta O_3 \) is the difference in \( O_3+NO_2 \) between the sample and reference chamber after the NO\(_2\) has been converted into O\(_3\).

The MOPS uses two National Instruments modules model NI-6009 and a LabVIEW application for data acquisition and solenoid control (National Instruments, n.d.). This application acquires additional information such as the temperature inside the MOPS chambers and the ambient NO\(_x\) mixing ratios. The temperature is monitored by 30 k\( \Omega \) thermistors. The NO\(_x\) concentrations are obtained from a NO-NO\(_2\)-NO\(_x\) analyzer Thermo Scientific, Model 42C (Thermo, 2004) that samples air near the MOPS inlet. The analog input channels of the NI-6009 are used to retrieve ground referenced voltage signals from the ozone monitor, the NO\(_x\) box and the thermistors, whereas two digital channels are used to control the solenoids on/off positions.
2.3 Raw Signal Processing and Data Averaging

In this section, the procedure that is needed to analyze the MOPS data is explained. Several averaging and filtering steps need to be performed before the ozone differential data are ready to be divided by the exposure time in the chambers. First, the raw data, whose rate of acquisition is 1Hz, need to go through an initial averaging step. Second, the data of the actual measurements need to be filtered and separated from invalid data. The final step is to obtain a 10 minute average of the ozone differential measurements. These steps are described in the following paragraphs.

The air flow from the sample and reference chambers are switched to flow through alternate photolytic cells every 5 minutes. Consequently, the raw signal of ozone differential is obtained in two channels (Figure 2-2).

![Figure 2-2. Channeled signal retrieved with the MOPS. Raw 1-second data from the data acquisition software (green) are averaged over the 10-second averaging time of the ozone monitor (black).](image-url)
The channeled signal shown (Figure 2-2) shows the switching between the two-cell configuration of the photolytic converter. The sharp downward branch in the channeled signal happens when the solenoids switch to redirect the air from one chamber to the other, and air from the photolytic cell that was connected to the reference chamber now flows into the sample absorption cell. At this time, flushing of the photolytic cells takes place and lasts 2 to 2.5 minutes, depending on the magnitude of the ozone differential. The flushing period is evident by observing the downward and upward branches between signal channels in Figures 2-2 and 2-3. When the flushing period ends, the measurements become steady on the upper portion of the channel. Every channel contains thirty 10-sec average points, which corresponds to 5 minutes for solenoid switching. The points when the signal becomes steady are retained for further averaging, and the flushing points are discarded. The number of points discarded on average is 12 to 15 10-sec average points, which corresponds to 2 to 2.5 minutes for flushing time. Figure 2-3 shows an example of the filtered top channel points in red.

![Figure 2-3. Filtered 10-sec data from channeled MOPS signal. The blue line depicts the 10 second data and includes measurements and flushing of the photolytic cells. Out of these data, only the red points are retained.](image-url)
The next step is to find the average of the retained points from the channeled signal, depicted by a red point in Figure 2-4. Once these points are found they need to be averaged by pairs because the MOPS solenoids switch to use the two photolytic cell for every ozone differential measurement. Hence, the red points in Figure 2-4, are averaged overlapping one point. For example, the first point is averaged with the second, the second with the third and henceforth, in order to find the 5-minute average. This averaging strategy takes into account potential differences in conversion efficiency in the photolytic cells. The circles on Figure 2-4 show the grouping used. Once the 5-minute average is done, a final 10-minute average is obtained.

![Figure 2-4. MOPS averaged retained signal and strategy to find 5-min average.](image)

The final ozone differential is obtained by processing the signal according to the method described above. The ozone production rate is obtained by dividing the ozone differential by the residence time. Figure 2.5 shows the major signal filtering and averaging steps towards obtaining the ozone differential for May 19, 2009 in the city of Houston. The ozone production in ppbv h$^{-1}$
has the same shape of the curve depicted on the bottom panel in Figure 2.5 but magnified by a factor of 10 for a residence time of 5.8 minutes.

Figure 2-5. Signal processing and averaging for data obtained on May 19, 2009 in Houston. The first panel shows raw 1-second data collected by the MOPS. The second panel is the 10-second average. On the third panel, the filtered measurements are colored green and the blue background...
represents upward and downward branches of points that occur due to flushing of the photolytic cells after solenoid switching. The final panel corresponds to the 10 minute average of the filtered 10-second data.

2.4 Instrument Characterization

The quantitative measurement of ozone production depends on the following factors: knowing the residence time in the chambers; having the atmospheric ozone production occurring in the sample chamber but not the reference chamber; measuring accurately the differences in the sum of $O_3$ and NO$_2$; and having all photochemistry that does not produce ozone but can affect the sum of $O_3$ and NO$_2$ be the same in the two chambers so that the differential measurement is not biased. Each of these factors was examined by extensive testing.

2.4.1 Mean Exposure Time

The ozone production measurement depends linearly on the exposure time. For a flow of 1.5 L/min through each 11.3 L chamber, the mean exposure time would be 7.5 minutes for a perfect plug flow. Ideally, the aim is to have plug flow so that the time spent in the chamber is the same for every air molecule.

The mean exposure time in the MOPS chambers was determined by adding a short pulse of ozone to the chambers and then monitoring the ozone at the exit. The pulse experiment not only helps determine the mean exposure time but also helps diagnose the type of flow inside the chambers. A normalized mean ozone distribution for a series of four pulses is shown in Figure 2-6. The mean time obtained through this method is $5.8 \pm 0.3$ minutes (95%, N=4).

In addition to the pulse experiment, reactions with known amounts of ozone and excess $\alpha$-pinene and ethene were performed independently. The decay of ozone was monitored over time
until it decreased to a steady value greater than zero. This steady-state ozone value represents the average concentration remaining from ozone that has experienced reaction times distributed according to the distribution function depicted in Figure 2-6. For example, while more ozone experienced 130 seconds of reaction than ozone did for any other time, some ozone experienced reaction for 1000 seconds or more.

The mean ozone mixing ratio is equal to the integral of the normalized mean pulse distribution multiplied by the exponential decay of ozone. The calculated mean ozone ratios agree to within 10% of the observed steady-state ozone that results from the reaction with α-pinene or ethene. The mean time was then calculated using the mean ozone mixing ratio, the initial ozone mixing ratio, and the rate coefficients. This calculated time agrees with the time required for the reactions that achieved steady state to within 5% and with the time from the pulse experiment to within 10%.

The results obtained from these experiments indicate that, for the current version of the MOPS chambers, the mean exposure time is less than the time calculated for perfect plug flow by 1.7 minutes. This feature is caused by a fast jet of air that enters the chamber through a wide inlet (2.54 cm) located at the center of the circular 17.78-cm diameter face of the chamber and exits through a similar outlet located on the other end. Further evidence for this jet is the peak ozone concentration in Figure 2-6 that appears at about 2 minutes. The pulse in Figure 2-6, also indicates that there is turbulence and probably uneven mixing that yield the tail of ozone distribution. The bulk of the ozone molecules, however, leave the chamber at a mean time of 5.8±0.3 minutes.
2.4.2 Radical abundances inside the chambers

One of the potential biases associated with the measurement of the rate of ozone production involves the abundances of the radicals OH, HO$_2$, and RO$_2$ inside the chambers. The radical abundances in the sample chamber should be the same as in the atmosphere, while the OH and HO$_2$ abundances in the reference chamber should be zero. Because ozone is produced by the reaction of HO$_2$ and RO$_2$ radicals with NO, as shown in reactions R8 and R9, an effective way to determine to what extent the proposed technique yields a quantitative measurement of ozone production is to compare the radical abundances inside the MOPS chambers with respect to the abundances in a controlled environment.

The strategy to determine radical loss was to create an artificial atmosphere in an environmental chamber and measure OH and HO$_2$ in it. The sample chamber was placed in this
artificial atmosphere and the radical concentrations were measured. The same procedure was followed with the reference chamber. A final measurement of OH and HO$_2$ radicals in the empty artificial atmosphere was obtained to confirm the initial measurement of radicals. This experiment was completed by flowing air with 60 ppbv of ozone and 40% of relative humidity into an environmental chamber consisting of a 100 L Teflon PTFE film bag with metal endplates and exposing it to external ozone-free mercury lamps to produce OH and HO$_2$ and black lights to set the NO$_x$ photostationary state. The OH and HO$_2$ radicals were measured with the Ground-based Tropospheric Hydrogen Oxides Sensor (GTHOS) (Faloona et al., 2004), which was attached to one of the ends of the large environmental chamber. The GTHOS sampling flow was 1 L/min, similar to the flow in MOPS. GTHOS sampled air directly from the artificial atmosphere and then from each MOPS chamber when they were placed inside the environmental chamber.

The results from one of the test runs are shown in Figures 2-7 and 2-8. The HO$_2$ radical abundance found in the MOPS sample chamber agreed with the abundance in the artificial atmosphere to within 5%. In the reference chamber (Ultem coated), the abundance of HO$_2$ radicals decreased to less than 10% of its initial value. RO$_2$ was not measured, but because RO$_2$ has reaction times similar to those for HO$_2$, it is likely that the behavior of RO$_2$ is similar to the observed behavior of HO$_2$. The abundance of OH in the clear chamber was half of the abundance in the artificial atmosphere.

The decrease in OH and no change in HO$_2$ indicate that the HO$_x$ production is the same as in the artificial atmosphere but the sample chamber may contain some additional OH loss. This difference in OH radicals, however, does not impact the rate of ozone production, as can be observed from equation (1.1). In the reference chamber, the OH abundance decreased to virtually zero, as expected. These results indicate that the ozone-producing photochemistry in the sample chamber is similar to that in the artificial atmosphere while the ozone producing photochemistry in the reference chamber is reduced to less than 10% of ambient.
Figure 2-7. HO₂ radical abundance test performed on September 30, 2009. The first rectangle shows HO₂ abundance in the artificial atmosphere with 60 ppbv of ozone and 40% relative humidity. The second rectangle shows the levels of HO₂ achieved inside the clear MOPS chamber. The data in between correspond to adjustment to initial conditions after the MOPS chamber was placed in the artificial atmosphere. Finally, the last rectangle indicates the HO₂ abundance when the reference (Ultem) chamber is placed inside the artificial atmosphere.

Figure 2-8. OH radical abundance test performed on September 30, 2009. The levels of OH achieved in the artificial atmosphere and the MOPS sample and reference chambers are enclosed inside rectangular boxes. The data in between were taken while the chambers were placed inside the artificial atmosphere.
2.4.3 Measurement of photolysis frequencies

In addition to these radical measurements, radiometric measurements were made in both chambers. The photolysis frequencies of the species NO₂, O₃, and HONO were measured using a Scanning Actinic Flux Spectroradiometer (SAFS) by B. Lefer at the University of Houston (Shetter and Muller, 1999; Shetter et al., 2002). The measurements were performed on a sunny day, May 14 2009, at noon on the roof of Moody Towers in University of Houston.

The blockage of UV light by the Ultem film in the reference chamber was assessed by comparing the ambient radiometric measurements against the measurements obtained inside the reference chamber. A similar measurement and comparison were performed for the clear sample chamber. The results for the sample and reference chambers are shown in Figure 2-9 and Table 2-1. When the radiometer was introduced in the reference chamber coated with Ultem film, the photolysis frequencies for O₃, NO₂, and HONO dropped to less than 2% of the ambient values. In contrast, the photolysis frequencies measured inside the sample chamber remained within 3% of ambient values. These results confirm the radical measurements performed in the MOPS chambers and support the validity of the technique in terms of restricting radical formation in the reference chamber while conserving radical photochemistry in the sample chamber.

Table 2-1. Measurement of photolysis frequencies, J (s⁻¹), in the ambient air and the MOPS chambers. The shaded areas indicate measurements inside the reference chamber. Clear areas in the second and third columns correspond to measurements inside the sample chamber. The last column shows the transmission of chamber measurements with respect to the ambient.

<table>
<thead>
<tr>
<th></th>
<th>Ambient</th>
<th>Chamber</th>
<th>Transmission</th>
</tr>
</thead>
<tbody>
<tr>
<td>JNO2</td>
<td>7.70E-03</td>
<td>7.50E-03</td>
<td>0.974</td>
</tr>
<tr>
<td></td>
<td>7.00E-03</td>
<td>1.50E-04</td>
<td>0.021</td>
</tr>
<tr>
<td>JHONO</td>
<td>1.66E-03</td>
<td>1.62E-03</td>
<td>0.976</td>
</tr>
<tr>
<td></td>
<td>1.50E-03</td>
<td>1.00E-05</td>
<td>0.0067</td>
</tr>
<tr>
<td>JO3</td>
<td>2.88E-05</td>
<td>2.85E-05</td>
<td>0.991</td>
</tr>
<tr>
<td></td>
<td>2.60E-05</td>
<td>1.50E-07</td>
<td>0.0058</td>
</tr>
</tbody>
</table>
2.4.4 **Radical production simulation inside the MOPS chambers**

A simple computer model that includes the most important sources of daytime radical production in the ambient air was used to illustrate the effectiveness of the clear sample chamber and the partially shaded reference chamber at collecting the chemistry of ozone production. This simulation was done over 5.8 minutes (348 seconds) which correspond to the exposure time of the air inside the MOPS chambers.

The model consists of a set of rate equations run in MATLAB for the following reactions:
a) Photolysis of HONO, HCHO, H₂O₂, O₂ and NO₂;

b) Reactions of NO with HO₂ and RO₂

c) Ozone reactions: O₃+NO and O₃+OH

d) The reaction of hydrocarbons and OH was included by using a typical rate of reactivity of OH with hydrocarbons of 10 s⁻¹.

e) Termination reactions: HO₂+RO₂, OH+NO₂+M

The time step for the model was set to 0.1 seconds for a total integration time of 348 seconds, which corresponds to the exposure time of the air inside the MOPS chambers. The model calculation for the reference chamber does not contain any of the photolysis reactions, as it was observed during radiometric measurements of photolysis rates explained in section 2.4.3.

To initiate the model, typical concentrations of species and photolysis frequencies seen in Houston at 10 am during sunny days were used. These concentrations are: NO = 6 ppbv, NO₂ = 3 ppbv, O₃ = 45 ppbv, OH = 0.1 pptv, HO₂ = 10 pptv; HONO = 150 pptv; HCHO = 6 ppbv. The abundance of H₂O₂ was assumed to be 1 ppbv.

Figure 2-10 illustrates how the production of HO₂ and RO₂ grows continuously in the clear sample chamber whereas in the reference chamber the production of radicals plummet dramatically due to the lack of main radical sources, namely photolysis reactions. Figure 2-11 shows the effect of the MOPS configuration on the species NO, NO₂ and O₃. In the reference chamber NO is depleted faster than in the sample chamber. At the same time, NO₂ is produced in larger amounts if compared to the sample chamber as well. These effects occur due to the partitioning of ozone into NO₂ caused by the shading in the reference chamber.
Figure 2-10. Model calculation done in MATLAB for radical production in the sample (clear) and reference (Ultem) chambers. Partial shading in the Ultem chamber prevents radical production.

Figure 2-11. Model results for differences in NO, NO₂, O₃, and NO₂+O₃ in the MOPS sample and reference chambers. Ozone production is larger in the sample chamber due to radical chemistry. The photostationary state is reached in the reference chamber while radical chemistry in the sample chamber make the sum O₃+NO₂ grow continuously in time.
The sum NO$_2$+O$_3$, however, quickly becomes constant as the photostationary state of NO, NO$_2$ and O$_3$ is achieved. In contrast, in the sample chamber the sum NO$_2$+O$_3$ continues to grow in time as a result of high radical production. The ozone production for this particular case corresponds to the difference between NO$_2$+O$_3$ at the end of the run divided by the exposure time. This is about 4 ppbv in 348 seconds which yields 40 ppbv h$^{-1}$ of ozone production.

2.4.5 NO$_2$ conversion efficiency

The conversion efficiency of the photolytic converter unit was tested for different levels of NO$_2$ and is shown in Table 2-2. These results indicate that for most atmospheric abundances of NO$_2$ the efficiency of the conversion unit is 88% or higher. The conversion of NO$_2$ decreases as NO$_2$ increases because the rate of NO+O$_3$→NO$_2$+O$_2$ increases to stay in photostationary state with the greater NO$_2$ photolysis rate, thus shifting the NO$_x$ photostationary state away from O$_3$ and toward NO$_2$. At 88% conversion efficiency, the calculated photolysis rate from the exponential decay of NO$_2$ is 0.09 to 0.1 s$^{-1}$. In contrast, a typical atmospheric value for the NO$_2$ photolysis frequency is 0.008 s$^{-1}$ at midday on a sunny day.

Table 2-2. Percentage of NO$_2$ converted to ozone in the MOPS converter unit cells for different levels of NO$_2$.
To ensure that the NO₂ conversion cells are sufficient to allow accurate ozone production measurements, a simple computer model that includes the NOₓ photostationary state and the new production of ozone from the reaction HO₂ plus NO was run for typical atmospheric conditions. Inputs for the model were concentrations of O₃, NO, NO₂ and HO₂ that were measured in Houston during the Texas Radical and Aerosol Measurement Project (TRAMP) in 2006. The concentrations chosen are representative of a polluted day in the morning, at noon, at the peak of temperature, and in the evening. The rate coefficients for the model were taken from the data published by the Jet Propulsion Laboratory (JPL) (Sander et. al, 2006).

Table 2-3 presents the cases analyzed and results for the production of ozone with converter, without converter and the theoretical calculation of new ozone in ppbv hr⁻¹. The final columns are the difference between the MOPS measurement with the converter unit minus the theoretical calculation of new ozone and the ratio of the MOPS measurement with the converter unit to the theoretical calculation of new ozone.

The first case analyzed is the absence of production of new ozone, the concentration of HO₂ is zero and the photostationary state of ozone remains unperturbed. Consequently, the model theoretical calculation cancels out exactly the photostationary state and the ozone production is zero, as expected. The ozone that exits the reference chamber has partitioned mostly towards NO₂. Without the ozone converter unit, the modified ozone analyzer would be unable to see the ozone in the form of NO₂ from the reference chamber and the result is an unrealistic ozone differential of 43.4 ppbv hr⁻¹ of ozone production. Adding the NO₂ conversion in the converter unit minimizes the difference between the two chambers so the production of ozone is 0.0002 ppbv hr⁻¹.
Table 2-3. Model results ozone production (ppbv hr\(^{-1}\)) without converter unit (w/o C.U.), with converter unit (With C.U.), and theoretically calculated. The last columns are the difference between calculated production rates and modeled results with the converter unit and the ratio of the model results with the converter unit to the calculated ozone production rate. The residence time in the chambers is 5.8 min while the residence time in the converter cells is 103 seconds. The photolysis frequency inside converter is 0.09 s\(^{-1}\). The photolysis frequency in the atmosphere is 0.008 s\(^{-1}\) at noon. For the morning and evening cases, \(J_{NO2}\) was assumed to be half of the noon value.

<table>
<thead>
<tr>
<th>Case</th>
<th>O3</th>
<th>NO</th>
<th>NO2</th>
<th>HO2</th>
<th>w/o</th>
<th>with</th>
<th>Calculated</th>
<th>Difference</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero</td>
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<td>5</td>
<td>10</td>
<td>0</td>
<td>43.4</td>
<td>0.0002</td>
<td>0</td>
<td>-0.0002</td>
<td>--</td>
</tr>
<tr>
<td>Morning</td>
<td>15</td>
<td>5</td>
<td>20</td>
<td>6</td>
<td>92.1</td>
<td>23.8</td>
<td>26.9</td>
<td>3.1</td>
<td>0.88</td>
</tr>
<tr>
<td>Noon</td>
<td>98</td>
<td>2</td>
<td>10</td>
<td>60</td>
<td>71.4</td>
<td>54.8</td>
<td>54.8</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>T peak</td>
<td>120</td>
<td>1</td>
<td>10</td>
<td>110</td>
<td>81.7</td>
<td>69.3</td>
<td>70.3</td>
<td>1</td>
<td>0.99</td>
</tr>
<tr>
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<td>20</td>
<td>45</td>
<td>84.8</td>
<td>57.9</td>
<td>63.1</td>
<td>5.1</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Likewise, for the cases of ozone production due to the presence of HO\(_2\) radicals, model calculations show that without the conversion unit the ozone differential between chambers is overestimated when compared against the theoretical calculation. By adding the NO\(_2\) converter, the measurements become within 10% of theoretical values. The correction of the false signal is substantial as indicated by the morning case in Table 2-3. Without the conversion unit, the ozone monitor would measure 92 ppbv h\(^{-1}\). The theoretical rate, however, corresponds to 26.9 ppbv h\(^{-1}\). The MOPS result with the converter is within 10% of the calculated new ozone. A highly efficient conversion unit, therefore, helps avoid the loss of ozone in the form of NO\(_2\) and corrects a potential bias in the measurements.
2.4.6 Artefact due to high relative humidity and NO$_2$ loss

Ideally, the only difference between the sample and reference chambers is the photolysis in the sample chamber that enables ozone production. All other characteristics should be the same, including flows, relaxation towards NO$_x$ photostationary state, and wall effects, so that any changes they induce in either ozone or NO$_2$ cancel out in the differential ozone measurement. Thus, studies were devised to examine possible differences between the two chambers.

The wall loss of O$_3$ found in the MOPS chambers is less than 3%. For NO, the losses are less than 1%. The wall losses of these two species were not found to be a potential interference with the measurement. These losses were determined by preparing mixtures of ozone or NO in zero air and measuring the concentration before and after the chambers.

The wall loss of NO$_2$ in the MOPS chambers was found to be significant for high relative humidity cases and for differences in relative humidity in the two chambers. This loss was studied by preparing NO$_2$ mixtures with air and varying the relative humidity. During these experiments, as relative humidity increased, the concentration of measured NO$_2$ decreased in a nonlinear fashion. For relative humidity higher than 50%, more NO$_2$ was removed as the relative humidity became higher. Figure 2-10 shows the results obtained for these tests. Previous research demonstrates that the uptake of water on a Teflon surface is about three times as much at 70% relative humidity as it is at 50% (Svensson et al., 1981). This condition of the Teflon surface has been proven to have an impact on the rate at which NO$_2$ is removed at different relative humidities, resulting in nitric acid (HNO$_3$) formation and HONO off-gassing (Wainman et al., 2001). The experiments performed with the MOPS chambers confirm these findings.

The removal of NO$_2$ in the chambers at high relative humidity directly affects the measurement of ozone production. Since MOPS is a differential measurement instrument, uneven relative humidity values in the MOPS chambers could potentially trigger false ozone production
signals. According to our laboratory studies, if the relative humidity in one of the chambers stays at about 30%, the removal of NO$_2$ is about 1 ppbv. In contrast, if the relative humidity in the second chamber is high, close to 80%, the NO$_2$ removal is about 7 ppbv. This uneven NO$_2$ removal causes a differential of about 6 ppb of NO$_2$, which represent a false ozone production signal as high as 60 ppbv hr$^{-1}$. This false background correlates with anomalous signals that were observed during evenings in Houston, Texas, in which the relative humidity of the air jumped suddenly to high values.

![Graph showing variation in NO$_2$ with increasing relative humidity inside MOPS chambers.](image)

Figure 2-12. Three experiments to study the variation in NO$_2$ with increasing relative humidity inside MOPS chambers.

An additional test was performed to ensure that the anomalies are actually associated with relative humidity. Air containing 60 ppbv of ozone, 60 ppbv of NO$_2$ and 94% relative humidity was prepared and sampled by the MOPS. The reference chamber was heated with an infrared lamp to decrease its relative humidity without altering the absolute humidity of the air.
flow. As the relative humidity in the sample chamber became higher, there was a negative value for the ozone differential due to NO$_2$ removal.

The relative humidity can be different in the MOPS chambers due to differences in temperature in the two chambers. This difference is caused by the UV blocking film (Ultem) that covers the reference chamber. At the temperature peak during a hot summer day, the temperature in the clear sample chamber was as much as 5 °C above the ambient temperature. The reference chamber was warmer than the sample chamber by another ~6 °C, thus up to 11 °C above the ambient temperature for the warmest cases. These temperature differences cause little difference for the ozone production rates, since the rate coefficients of the reactions of HO$_2$ and RO$_2$ with NO have little temperature dependence. However, these temperature differences do translate into differences in relative humidity between the two chambers.

During daytime, the higher-than-ambient temperatures inside the MOPS chambers caused the relative humidity to be much less than 50%. Experimental data indicate that for the most extreme daytime cases, which occur in the early morning, the interference due to NO$_2$ removal can introduce a loss of about 1 ppbv out of 7 ppbv observed, or a 14% error, for the ozone differential. After early morning, the relative humidity decreases as the solar radiation intensifies and the artifact error becomes insignificant. Later in the evening or at night, however, the artifact can sometimes affect the measurements. When the ambient temperature decreases in the evening, the relative humidity of the air increases. If the relative humidity is high but the same in both chambers, then any NO$_2$ removal on the Teflon film surfaces and HONO off-gassing will mostly cancel out in the differential O$_3$+NO$_2$ measurement. However, it is possible that relative humidity differences in the two chambers can cause the NO$_2$ removal and HONO off-gassing to be different in the two chambers. Thus, high relative humidity can introduce an artifact in the MOPS data.
With the current version of MOPS, therefore, we consider as valid only the data collected when the relative humidity inside the chambers is below 50%. Fortunately, the relative humidity is lower than 50% for much of the daytime conditions under which ozone production is greatest, so that the current version of MOPS can measure ozone production without artefacts during these polluted conditions.

2.4.7 Sensitivity, time constant and absolute uncertainty

The exposure time of the air inside the chambers is directly related to the sensitivity and detection limit of the instrument. Analysis of the MOPS signals indicates that the detection limit of the instrument corresponds to 0.06 ppbv for a 10-minute integration. This detection limit corresponds to 0.67 ppbv hr\(^{-1}\) for the 10-minute average data. A fast check of the level of sensitivity needed to measure urban ozone production can be done using the chemical production terms of equation (1.1) with atmospheric values for the species NO, HO\(_2\) and RO\(_2\). For example, for conservatively low levels of pollutants such as 10 pptv for the sum [HO\(_2\)+RO\(_2\)], 0.5 ppbv for [NO], and an effective rate coefficient of approximately 5x10\(^{-12}\) (cm\(^3\)molecules\(^{-1}\)s\(^{-1}\)), the rate of ozone production is approximately 2.1 ppbv h\(^{-1}\). For highly polluted conditions, the ozone production rate can be in the range of 50 ppbv h\(^{-1}\). So, although the current MOPS is not sensitive enough to detect ozone production rates in the remote atmosphere, the MOPS detection limit of 0.67 ppbv hr\(^{-1}\) for the 10-minute average is sufficient to measure even low ozone production rates in urban and suburban air.

The main sources of uncertainty in the measurement of ozone production are the accuracy of the ozone differential measurement and the uncertainty in the determination of mean exposure time. The accuracy of the MOPS ozone differential measurement was determined experimentally. Two ozone mixtures were prepared and their concentrations were measured using
an ozone monitor (Thermo Scientific 49i). The difference in mixing ratios between the two mixtures was determined with the same ozone monitor without the ozone scrubber. As a next step, the same two ozone mixtures were connected to the MOPS instrument in its operating mode. Figure 2-11 shows the ozone difference seen by MOPS as a function of the difference seen by the ozone monitor.

The slope of the line is 0.90 and the mean of the ratio of the MOPS differential relative to the ozone monitor differential is 1.22±0.31 (95%, N=7). Thus, the uncertainty in the differential ozone measurement is approximately ±25% (95%, N=7). The uncertainty in the mean exposure time was obtained from the estimate of error in the pulse experiments and reaction experiments and is ±5%. The uncertainty introduced by differences in relative humidity is ±14% for the early morning data. Other factors, such as the temperature difference between the sample and reference chambers and ambient, contribute additional estimated uncertainty of ±10%. Thus, the absolute uncertainty (95% confidence level) of the current MOPS measurement is ±30% for daytime operating conditions and ±35% for data that could be affected by relative humidity such as in the early morning.

The uncertainty, $e$, was calculated applying the rule of the squares for the propagation of error, equation 2.1. The main terms involved in this calculation are the ozone differential and the exposure time (equation 1.8). The deviation of the ozone differential and the exposure time with respect to the mean values are represented by $\delta(\Delta O_3)$ and $\delta\tau$. The mean values correspond to the denominator of every fraction, $\Delta O_3$ and $\tau$.

$$e = \sqrt{\frac{\delta(\Delta O_3)}{\Delta O_3} + \frac{\delta\tau}{\tau}}$$  \hspace{1cm} 2.1
Figure 2-13. Ozone differences seen by MOPS as a function of differences seen by a Thermo Scientific 49i ozone monitor. The intercept is not statistically significant since the calculated error is 30%.
Chapter 3

Results I: PSU 2008

The first version of the MOPS (Cazorla and Brune, 2009) was tested successfully on the University Park campus of the Pennsylvania State University in the late summer of 2008. This chapter summarizes test results of ozone production in the ambient air. In addition, this chapter includes results for the sensitivity of ozone production when the NO\textsubscript{x} sources in the air increase.

3.1 Ozone Production is State College, PA

The MOPS was deployed on the roof of Walker Building, on the campus of Penn State, 30 meters above one of the main streets in State College, located in a rural area in Central Pennsylvania. Measurements of ozone production rates were obtained in the month of September 2008. In this area the background atmosphere is in general clean and becomes disturbed by spikes of pollution coming from the main road, in particular during the morning rush hour. A second spike of traffic emissions occurs at around noon. The afternoon remains generally clean with low levels of pollutants.

Figure 3-1 shows measurements collected during September 1 to 4, 2008. The left column corresponds to time series of P(O\textsubscript{3}) and NO between 8 am and 4 pm. The right column contains the corresponding correlation of P(O\textsubscript{3}) with ambient NO for every day. The shape and magnitude of some of the observed NO spikes make evident that the MOPS was sampling fresh emission plumes coming from vehicles in transit.

On two days, September 1 and 4, the ozone production rates peak at the same time as the NO. September 1 was a Monday, but it was also the Labor Day holiday, while September 4 was a
Thursday. These two days are characterized by similar NO emission peaks, one in the morning and one at around noon. On the other two days, September 2 and 3, the NO mixing ratios are greatest during morning rush hour, as would be expected for a weekday. The highest NO concentration, 80 ppbv, was recorded on September 2 between 7 and 8 am. A second NO peak took place little after 9 am and reached 60 ppbv. In this case the ozone production was rather low when the NO was the highest, above 30 ppbv, which occurred before 8 am. On September 3 the morning NO was also high, between 20-30 ppbv before 10 am, but no data were recorded before 8 am when NO and P(O₃) were anticorrelated for September 2.

![Graphs showing NO and P(O₃) concentrations on different dates.](image_url)

Figure 3-1. Test measurements of P(O₃) obtained with the MOPS at Penn State in September 2008.
From the results of September 2, \( P(O_3) \) as a function of ambient NO, first peaks at 7 ppbv h\(^{-1} \) when NO is 20-30 ppbv and then decreases. For the other three days, \( P(O_3) \) grows linearly with NO. However, the experimental plots \( P(O_3) \) vs. NO shown in Figure 3-1, cannot be directly compared to theoretical plots obtained in previous studies for different \( P(HO_x) \) levels (Thornton et. al., 2002). In order to compare to theoretical plots, the data must be sorted for different levels of radical production, \( P(HO_x) \), but for these MOPS measurements, not enough ancillary measurements, particularly of radicals, were taken to quantify the radical production. However, these plots of measured \( P(O_3) \) as a function of measured NO show early evidence of the existence of a correlation between \( P(O_3) \) and NO for atmospheric conditions. Thus, these results indicate that the MOPS could potentially clarify the discrepancies in the calculated ozone production rates from measured and modeled HO\(_2\).

Ren et. al. (2005) measured OH and HO\(_2\) radicals and trace gas species in Rock Springs, a rural area located in Central Pennsylvania in 2002. In that study, the calculated ozone production rate reached a mean diurnal calculated peak of 5 ppbv h\(^{-1} \). Furthermore, values for individual days reached as high as 15 ppbv h\(^{-1} \) in that study. The 2008 MOPS deployment yielded production rates comparable to those previous calculations.

These first tests demonstrate the feasibility of the MOPS technique. The instrument responded physically to the presence of solar radiation and ozone precursors and yielded rates of ozone production in ranges that are within expected values for a rural environment.
3.2 Sensitivity of P(O₃) to increased NOₓ sources

In addition to testing the MOPS for its ability to measure ambient ozone production, the MOPS was tested for its potential to investigate further the correlation between P(O₃) and NO by adding precursors to the ambient air. Figures 3-2 and 3-3 show additions of NOₓ to the ambient air in order to look at the response of P(O₃) when the sources of NO and NO₂ increase. The additions were done in the afternoon when the levels of NO were low, near the NOₓ instrument’s detection limits.

On September 18, small flows of NO mixtures in nitrogen (<10 sccm) were added directly to the MOPS to produce mixing ratios at the inlet of 12.5, 25, 37.5, 50, 62.5, 93.8, and 125 ppbv of NO with the main flow entering the chambers. The top panel of Figure 3-2 shows time series of P(O₃) and added NO. On the bottom panel of the same figure, the response of P(O₃) to NO additions is depicted in different colors. P(O₃) continues to grow as NO is added up to about 60 ppbv of NO; after this point, P(O₃) starts to decrease. The NO levels inside the MOPS chambers are expected to have shifted below the mixture values due to the photostationary state of NOₓ. The P(O₃) increased up to 12 ppbv h⁻¹ during this test.

NO additions were performed in two batches, between 12:30 to 3 pm and 3:30 to 4:30 pm, in order to make sure that the effect of increasing NO on P(O₃) was consistent. Although there is some scattering of the points, the trend of the curve indicates that P(O₃) increases first, reaches a peak and then decreases.
Figure 3-2. Additions of NO to the ambient air performed on September 18, 2008.

The sensitivity test performed with NO was repeated including NO₂ as part of the added mixture on September 19. NO and NO₂ were mixed in the same proportions with zero air in a separate Teflon bag and exposed to the solar radiation to ensure that the NOₓ photostationary state was achieved. The calculated mixtures correspond to 17, 37, 76 and 114 ppbv of NO and NO₂. The actual amounts of NO and NO₂ inside the MOPS chambers, however, would have shifted toward those in the NOₓ photostationary state for the ambient conditions of NO₂ photolysis and ozone. Small flows (<10 sccm) of these mixtures were added to the MOPS inlet. The response of P(O₃) to the added mixtures is depicted as time series on the top panel of Figure 3-3 and as correlation with added NO on the bottom panel.
Figure 3-3. Additions of pre-mixed NO and NO\textsubscript{2} in equal proportions and photostationary state to the ambient air, performed on September 19, 2008.

As it can be observed on the top panel of Figure 3-3, P(O\textsubscript{3}) steps up for the first three additions of mixture NO-NO\textsubscript{2} and seem to start decreasing during the last and highest addition. Once again, there is some scattering of the points on the bottom panel of Figure 3-3, however P(O\textsubscript{3}) grows continuously up to 76 ppbv of added NO and NO\textsubscript{2}. At this point, P(O\textsubscript{3}) seems to have stopped increasing. The blue points indicate P(O\textsubscript{3}) levels with ambient NO in the morning, prior to added mixtures, and the green points also correspond to P(O\textsubscript{3}) at ambient NO levels once the afternoon additions concluded. These two sets of ambient P(O\textsubscript{3}) points at low levels of NO indicate how the P(O\textsubscript{3}) returns to low levels once the perturbations have stopped.
The tests performed on September 18 and 19 required high levels of added NO to produce a pattern of the P(O_3) vs. NO plot that increases first, reaches a peak, and then decreases for the highest NO_x amount. As mentioned earlier, the effective levels of NO that correlate with P(O_3) should shift towards lower NO values than the added concentrations due to the photostationary state achieved inside the MOPS chambers with sunlight. Comparing these NO_x additions to the test results obtained on September 2, it is interesting to observe that on this day the required levels of NO to produce the curving pattern on the plot P(O_3) vs. ambient NO was about 30 ppbv.

The addition tests, therefore, agree with the findings done on September 2 in as much high levels of NO in the air were required to reach a peak in the curve P(O_3) vs. NO. These results suggest that during this period in State College, the chemistry of ozone formation was limited by NO_x and the regime of ozone production shifted to about 15 ppbv h^{-1} at high NO levels.
Chapter 4

Results II: Houston 2009

Ozone production rates, \( P(O_3) \), were measured directly with the MOPS during the Study of Houston Radical Precursors (SHARP 2009). This chapter presents the results of the direct measurements compared against calculated ozone production rates. Correlations of measured and calculated ozone production with ambient NO are analyzed. Finally, results of the response of \( P(O_3) \) when NO\(_x\) was added to the ambient air are presented.

4.1 Description of the SHARP Campaign

The Penn State Measurement of Ozone Production Sensor, MOPS (Cazorla and Brune, 2009), was deployed during the Study of Houston Atmospheric Radical Precursors between April 15 and May 31, 2009. The sampling site was the roof of Moody Tower located in University of Houston, 70 meters above the ground level and 5 km away from downtown Houston. The MOPS was deployed on top of the roof of science trailer #3. A map of the site and a sketch of the location of the instrument are shown in Figure 4-1.

MOPS obtained real time \( P(O_3) \) and NO measurements simultaneously for 20 days of the 42-day study. A fairly complete suite of atmospheric chemical species and meteorological parameters were measured. In particular, OH and HO\(_2\) radicals were measured by the Ground-based Tropospheric Hydrogen Oxides Sensor, GTHOS (Faloona et. al., 2004) about five meters away. Preliminary measurements were made of NO and NO\(_2\) by NOAA (Luke, W. and Kelly, P.), and ambient ozone and meteorological data by the University of
Figure 4-1. Location in Houston of the SHARP site and science trailer arrangement.
Houston (Lefer et. al) on a tower about six meters from the MOPS. A second measurement of NO was made with a Penn State Thermo 42C NO$_x$ monitor connected to the MOPS data acquisition. The comparison of the MOPS NO measurements with those from NOAA shows good agreement, with a slope of 0.98 and an intercept of 0.15 ppbv (Figure 4-2). This agreement indicates that all the instruments were sampling basically the same air masses despite the slight separation in the measurement inlets for the different species. Thus, all of the chemical species needed to calculate the ozone production rate were measured during SHARP with the exception of the organic peroxy radicals (RO$_2$).

Figure 4-2. Correlation between NO from MOPS and NOAA.
4.2 Calculation of Ozone Production Rates

The calculation of instantaneous ozone production requires knowledge of the abundance of HO$_2$, RO$_2$, ambient NO and the rate coefficients in equation 1.1 for the chemical production and the abundance of OH, NO$_2$, HO$_2$ and O$_3$ for the losses in equation 1.2. The abundance of RO$_2$ radicals for the SHARP campaign was estimated by multiplying the median diurnally varying ratio RO$_2$/HO$_2$ that was modeled for Houston during the Texas Air Quality Study (TRAMP 2006) by the observed HO$_2$ from SHARP. Given the substantial VOC emissions from petrochemical facilities in the Houston area, the median diurnal ratio RO$_2$/HO$_2$ is expected to remain at similar levels over time. Figure 4-3 shows the ratio HO$_2$/RO$_2$ for Houston in 2006.

![Figure 4-3. Median diurnal variation for the ratio RO$_2$/HO$_2$ seen in Houston during TRAMP 2006.](image)
The entire set of data, namely observations of NO, HO$_2$ and estimated RO$_2$, as well as their mean diurnal patterns for SHARP 2009, is shown in Figure 4-4 top and bottom panels, respectively. For the rate coefficient of the reaction NO+RO$_2$, the rate coefficient for the methoxy radical CH$_3$OO and NO was used. (JPL, 2006).

Figure 4-4. Observed NO and HO$_2$ and estimated RO$_2$ for SHARP. The top panel represents the 1-minute data set. The bottom panel shows the mean diurnal pattern for HO$_2$, RO$_2$ and NO.
Ozone production was calculated using the daily data shown on the top panel of Figure 4-4. Losses due to the production of nitric acid (first term of equation 1.2) via reaction of OH and NO₂ were calculated using OH observations from GTHOS and 1-minute NO₂ data from NOAA. These losses were found to be small and the net ozone production was found to remain within 10% of the chemical ozone production from equation 1.1. The reaction of HO₂ with O₃ (second term of equation 1.2) has a smaller impact, less than 1% of the total chemical production. Figure 4-5 shows the correlation between the net ozone production (production minus losses) versus the chemical production of ozone. The net ozone production, calculated with equation 1.3, was used in this work for the comparison between measured and calculated ozone production.

![Figure 4-5. Correlation between net ozone production (production minus losses) and ozone production from the reaction between peroxy radicals and NO.](image)
4.3 Comparison between measured and calculated $P(O_3)$

Time series for the 10-minute measured and calculated $P(O_3)$, as well as ambient ozone are shown in Figure 4-6. The meteorological observations corresponding to the $P(O_3)$ measurement days are depicted in Figure 4-7.

A first look at the plot of the measured and calculated $P(O_3)$, for all overlapping days, shows a general agreement between them. Figure 4-8 shows the mean diurnal pattern obtained using all the points. The MOPS 2-sigma absolute uncertainty is 30% (95% confidence level) and the calculated $P(O_3)$ has an absolute uncertainty of 35% (95% confidence level) given mainly by uncertainty in radical measurements. Figure 4-8 includes error bars for 1-sigma absolute uncertainty on both sets of data. Overlapping of the error bars confirms an agreement for the majority of the data. These error bars include the absolute uncertainties on both the measurements and calculations of ozone production.

The measured and calculated $P(O_3)$ are plotted against ambient NO in Figure 4-9. This figure indicates an agreement among the points of measured and calculated $P(O_3)$ located in the quadrant below 1 ppbv of NO and 40 ppbv h$^{-1}$ of $P(O_3)$. At higher NO levels, there is a scattering of the points and a closer look is needed in order to identify differences. The plots shown in Figure 4-9 contain all the effects happening in a day and represent ozone production for all levels of HO$_x$ production. In order to analyze finer details, the measured and calculated $P(O_3)$, during daylight hours only, were separated in two subsets according with the magnitude of the peak rate of ozone production. A day-by-day analysis allows identifying scattered points in Figure 4-9.
Figure 4-6. Time series of $P(O_3)$ and ambient ozone between Apr 29 and May 30, 2009 in Houston.
Figure 4-7. Meteorological data for Houston between Apr 29 and May 30, 2009 (Lefer et. al).
Figure 4-8. Mean diurnal pattern for calculated and measured ozone production. Points for overlapping days (green and yellow) are 10-min avg. Mean diurnal variation points are 30-min avg.

Figure 4-9. 10-min measured (MOPS) and calculated ozone production rates as a function of ambient NO
4.4 High Ozone Production Days

The first subset of data corresponds to days in which P(O_3) reached about 40 ppbv h^{-1} or higher. These days correspond to May 4, 19, 20, 21, 22, 28, 29 and 30. Of these days, May 4, 20 and 29 were reported officially as pollution events by the Texas Commission on Environmental Quality (TCEQ, 2010). Figures 4-10 and 4-11 depict the measured and calculated P(O_3) and NO in the left column, and the correlation P(O_3) vs. NO for every one of these days, in the right column. Figure 4-12 corresponds to ozone 8-hour peak maps for May 4, 20 and 29 (AIRNow, 2010).

Figure 4-10. Measured (blue circles) and calculated (magenta stars) ozone production and their correlation with NO (green dots) for May 4, 19, 20 and 21, Houston in 2009.
Figure 4-11. Measured (blue circles) and calculated (magenta stars) ozone production and their correlation with NO (green dots) for May 22, 28, 29 and 30, Houston in 2009.

Figure 4-12. Maps of ozone 8-hour peaks observed in Houston (AIRNow, 2010).
The meteorological conditions for May 4, 19, 20 and 21 were similar, as is shown in Figure 4-7. The afternoon temperatures peaked at about 30ºC and the sky conditions were clear. The wind speed was low in the morning, between 1 m/s and 4 m/s blowing from the N, NE directions and the relative humidity ranged between 30 – 50% at noon. Additionally these days were characterized by low relative humidity during the early mornings and nights. Such low relative humidity minimizes the artifact that affects MOPS with high relative humidity, which might cause prolonged HONO off-gassing and uneven loss of NO₂. Hence, for these days, the data quality is similar and the conditions allow high confidence for measurements during daylight hours.

The correlations of measured PO₃ vs. NO in the semi-log plots depicted in Figure 4-10 have the shape of smooth curves that increase with NO, peak at about 2, 5 and 7 ppbv of NO on May 4, 19 and 20 respectively, and then decrease. The peaks are broader on May 21 and 22 between 2 to 5 ppbv of NO.

The curve of calculated P(O₃) vs. NO follows the tendency of the measured P(O₃) with NO on May 4. There are some higher calculated values, mainly in the afternoon. On May 22, there is also an agreement, although there are gaps of calculated P(O₃) data between 7 and 9 am and 10 to 12 am due to tests applied on the GTHOS instrument. The calculated P(O₃) for May 19, 20 and 21 agrees with the measured ozone production mainly for NO levels below 2 ppbv and P(O₃) less than 40 ppbv/h. For higher NO levels, the shape of the calculated P(O₃) is not entirely clear. Some of these points are higher than the measured ozone production, and the shape is not a smooth curve like the MOPS measurements. During these days, there is also loss of data for about 1 to 1.5 hours in the morning due to tests applied to the GTHOS. Hence, the number of calculated ozone production points available during in the morning affects the comparison between the two sets of data.
The meteorological conditions on May 22 were different from the previous three days. There was some cloudiness and a chance of storms in the morning. The measured production of ozone during May 22 decreased in comparison to May 21, reaching 37 ppbv h\(^{-1}\) at 9 am. This production of ozone did not lead to high ambient ozone (Figure 4-6). Furthermore, the relative humidity in the early morning reached 80% and ranged between 50 and 60% at noon and in the afternoon, as can be observed in Figure 4-7.

On May 28, 29 and 30, the relative humidity in the early morning reached 80% (Figure 4-7). MOPS recorded anomalous high signals between midnight and 3 am on these days, associated with the high relative humidity artifact. On May 28, the ambient ozone at Moody Tower peaked at 70 ppbv in the afternoon and the measured ozone production was approximately 45 ppbv h\(^{-1}\) at 11 am. On May 29, the ambient ozone spikes up to 110 ppbv at noon and then comes down to 90 ppbv in the afternoon. The measured ozone production on this day peaked at 110 ppbv h\(^{-1}\) between 10:30 and 11:30 am, and then fluctuated between 20 to 50 ppbv h\(^{-1}\) in the afternoon. This spike seems to be out of range if it is compared with the rest of the P(O\(_3\)), which describes smooth curves within a very well defined 40-80 ppbv/h range for the rest of these days. It is possible that some circumstance induced this spike; however, nothing anomalous was recorded on the MOPS journal, and hence the spike is shown as is. Additionally, during these two days the measured P(O\(_3\)) is shifted toward lower values of NO, if compared with the rest of the days.

The calculated P(O\(_3\)) on May 28 and 29 is 20 ppb hr\(^{-1}\) and less than 40 ppbv h\(^{-1}\), respectively. These values are considerably lower than the measured P(O\(_3\)). During May 28 and 29 the levels of HO\(_2\) are comparable to the other high ozone production days; nevertheless, when NO is high in the morning, HO\(_2\) was still low, and when it reaches high levels, NO decreased from 4 ppbv at 9 am down to less than 1 ppbv after 11 am, henceforth affecting the calculation of P(O\(_3\)).
On May 30, both the measured and calculated P(O₃) agree on a peak of ozone production of about 50 ppbv h⁻¹ at 7 am. After this time, the ozone production decreased. On this day, the campaign of measurements ended and so afternoon data is not available. The ambient ozone reached 140 ppbv at noon.

The mean diurnal patterns for measured and calculated P(O₃) during high ozone production days indicate that the mean calculated ozone production is in bulk agreement with the measured P(O₃) when the individual differences are averaged, as can be inferred by overlapping error bars in Figure 4-13.

Figure 4-14 shows the correlation of measured and calculated P(O₃) with ambient NO for high ozone production days and daylight hours in Houston. The color scale corresponds to hours of the day as an indicator of radical production rates, P(HOₓ). As previous studies show, P(HOₓ) is low in the early morning, grows rapidly during mid morning hours, reaches a maximum before or at noon and decreases again later in the afternoon (Shirley et al., 2006; Ren, 2005; Martinez 2003). P(HOₓ) during the high ozone production days reached peaks that ranged between 0.5 to 1 pptv s⁻¹ in May 2009 as obtained from a quick check using the photolysis of ozone and formaldehyde.
Figure 4-13. High ozone production data and mean diurnal variations for measured and calculated $P(O_3)$

Figure 4-14. Correlation of $P(O_3)$ with NO during high ozone production days
Using NO levels from Fig 4-10 and 4-11 and the time of the day to infer qualitatively levels of P(HO\textsubscript{x}), Figure 4.14 can be interpreted as follows, despite some scattering of the points:

- During rush hour (6-8 am), P(HO\textsubscript{x}) just begins to grow and NO is (>10 ppbv). The measured and calculated P(O\textsubscript{3}) are mostly clustered below 20 ppbv h\textsuperscript{-1} for NO>10 ppbv (orange points).

- Between 9-11 am, P(HO\textsubscript{x}) is expected to grow rapidly. NO starts to decrease from 10 to 2 ppbv. The measured P(O\textsubscript{3}) reveals the curving patterns (green points) depicted in Figures 4-10 and 4-11 at these NO levels. Some points for the calculated P(O\textsubscript{3}) present a growing tendency with NO while there is a branch that turns down and corresponds to the points seen on May 4.

- At around noon, P(HO\textsubscript{x}) is expected to reach the highest point. Measured P(O\textsubscript{3}) lies between 20-40 ppbv/h (cyan points). Calculated P(O\textsubscript{3}) describes a longer cluster, yet covers the same range.

- In the afternoon hours, P(HO\textsubscript{x}) is expected to decrease and the NO level stays below 1 ppbv. Dark blue points for measured P(O\textsubscript{3}) lie between 0-25 ppbv h\textsuperscript{-1} while calculated P(O\textsubscript{3}) ranges between 5-30 ppbv h\textsuperscript{-1}. The measured P(O\textsubscript{3}) is disturbed by the points seen on May 28 and 29 that shifted towards the left.

- In the evening, both P(HO\textsubscript{x}) and NO are low, leading to low values of measured and calculated P(O\textsubscript{3}) (magenta and red). Similarly, on the measured P(O\textsubscript{3}) vs. NO plot, the points scattered below 1 ppbv of NO correspond to data from May 28 and 29 as it is shown on Figure 4-11.

- Finally, the MOPS measured negative rates of ozone production, between 0 and -10 ppbv h\textsuperscript{-1}, in the early mornings and in the evenings. These negative values appear at
times when the formation of nitric acid has been observed in previous studies (Martinez et al., 2003). The clear chamber of the MOPS instrument collects all the radical reactions including OH+NO₂, while the reference chamber contains only the photostationary state. This reaction is capable of yielding a negative balance or loss of ozone recorded by the MOPS. Some of those points, however, might be affected by a larger uncertainty in the measurements (35%) due to increased relative humidity.

4.5 Low Ozone Production Days

The second subset of data corresponds to days in which the recorded P(O₃) had values below 25 ppbv h⁻¹ and low ambient ozone. Days with low ozone production were May 1, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 16. These days were characterized by high winds, considerably cloudiness and morning or afternoon showers. During these days, some data was lost due to bad weather conditions.

Figure 4-15, shows overlapping points for measured and calculated P(O₃) as well as the corresponding mean diurnal patterns. The morning agreement is fairly good between both sets of data as it can be inferred from overlapping of the 1-sigma error bars calculated using the absolute uncertainty in the measurements and calculation of P(O₃). After 2 pm, the error bars barely touch and the mean diurnal curve for the calculated P(O₃) begins to diverge from the measured P(O₃). This difference, however, is not significant since it is less than 5 ppbv h⁻¹ and ends in the evening.
Figure 4-15. Ozone production rates and mean diurnal patterns for low ozone production days.

Figure 4-16. Correlation of P(O_3) with NO during low ozone production days.

Figure 4-16 depicts the correlation of P(O_3) vs. NO and the colors indicate the hour in the day as an indicator of the radical production level. The trend of morning, mid-morning and
afternoon points is similar for both sets of data but the afternoon values (blue) are slightly higher for the calculated P(O₃). During these days, the production of radicals, P(HOₓ) was less than 0.3 pptv s⁻¹, due to increased cloudiness, according with a check calculation done using formaldehyde and ozone photolysis. Additionally, the NO levels stayed below 2-3 ppbv. As a result, the measured P(O₃) did not achieve the full span of curving values as it happened during the high ozone production days and the chemistry of ozone production remained mainly limited by NOₓ. The negative MOPS measurements are explained in similar way as the negative values seen over the high ozone production days.

4.6 Implications for Radical Chemistry

Comparing the measured P(O₃) vs. NO plots for the high and low ozone production days the difference in ozone production and the NO value when P(O₃) peaks is dependent on P(HOₓ), as has been shown in previous studies (Ren et al., 2003). In this Houston study, the turning point occurs when the NO levels range between 1 ppbv and 10 ppbv. In order to look more closely to this feature, May 19, 20 and 21, which share the same meteorological conditions and high data quality, can be analyzed. Figure 4-17 shows color map plots of measured and calculated P(O₃) vs. NO for these three days. On the left plot, there are three distinctive curves of measured P(O₃) versus ambient NO. The lower curve corresponds to May 21, the middle curve to May 19 and the highest one, to May 20. The peak of each line shifts slightly to the right starting with the lower, middle and high curves. In addition, the curving patterns depicted by the green dots for all curves, happen at around 10 am every day. The curves of measured P(O₃) vs. NO obtained during these three days might look as if they have been smoothed over several points; however, no additional smoothing technique has been applied. The data shown are the same 10-minute average data
shown in Figure 4-6. During these three days, we have an experimental example of how the NO level at which the $P(O_3)$ peaks increases slightly for higher levels of $P(HO_x)$. Similar features have been shown in previous model studies of OH with NO (Brune et al., 1999). It is important to emphasize, however, that a direct comparison with model results is not possible since models fix the radical production levels while the experimental results contain all the $P(HO_x)$ levels happening naturally in a day. The calculated $P(O_3)$, to the right of Figure 4-17, does not describe a distinctive curving pattern but keeps growing with NO except for a cluster of points in the morning hours (orange dots) that behave similarly to the measured values.

The MOPS measurements describe a more constrained and nonlinear ozone production mechanism than the one that is obtained by applying equation 1.1. Our current understanding of ozone forming chemistry, reflected in the equation used to calculate $P(O_3)$, hence, seems to match the observations mainly for levels of NO greater than 10 ppbv, before 8 am, and for low NO levels in the afternoon.

![Figure 4-17. Measured and calculated $P(O_3)$ vs. NO for May 19, 20 and 21 in Houston](image-url)
The high ozone production episode that took place on May 19 to 21 in Houston depicted in Figure 4-17, reveals differences found between calculated and measured $P(O_3)$ that resemble discrepancies between modeled and calculated $P(O_3)$ attributed to low modeled HO$_2$ values (Martinez et al., 2003; Ren et al., 2003; Ren et al., 2004; Shirley et al., 2006; Kanaya et al., 2007). In some of those studies, the calculated $P(O_3)$ increases monotonically with NO while model studies show that $P(O_3)$ describes curves that reach a maximum and then decrease with NO.

The calculated ozone production comes from the product of the concentration of peroxy radicals (HO$_2$+RO$_2$), NO and the rate coefficient for the reaction of NO with RO$_2$ and HO$_2$, as an effective rate coefficient, according to equation (1.1). The uncertainties in the calculation are 30-35\% for radicals and 6\% for NO. If the measurements of radicals and NO with a verified level of uncertainty are available, the question is why equation 1.1 did not yield the same pattern for calculated $P(O_3)$ in previous studies? Likewise, in the particular case of the $P(O_3)$ observations done with the MOPS, on May 19, 20 and 21, why the calculation of ozone production rates yields similar points for the ends of the curve $P(O_3)$ vs. NO but skips the curving pattern at mid levels of NO producing some few high points that keep growing with NO?

An important observation is that differences do not appear randomly at any point in the measurements but rather seem to be correlated with specific levels of NO. Furthermore, during the low $P(O_3)$ days, measured and calculated ozone production behave similarly with NO. This agreement occurs even when the detection of radicals is pushed towards lower limits.

Hofzumahaus et al. (2009) proposed a mechanism for the production of OH that maintains the ratio HO$_2$/OH and does not involve the reaction of HO$_2$ with NO and, therefore, does not result in the production of ozone at low NO levels. Measurements of ozone production in Houston raise the question of whether a similar mechanism, that constrains the production of ozone but does not stop the production of radicals, could be happening at moderate NO concentrations and to what extent this mechanism could modify the calculation of ozone
production. It would be interesting to explore if a potential error is being induced by using the product \( k[\text{NO}][\text{HO}_2+\text{RO}_2] \) to calculate \( P(\text{O}_3) \), when this product is being modified by a factor, as in \( f[k[\text{NO}][\text{HO}_2+\text{RO}_2}] \). Looking at the magnitude of the measured and calculated \( P(\text{O}_3) \) in the morning in Houston, the calculated \( P(\text{O}_3) \) in some particular cases is twice the measured \( P(\text{O}_3) \), as if this non-ozone forming mechanism involved an important fraction of radicals under certain conditions.

Additional modeling work is required to propose answers that resolve differences observed. Radical measurements, MOPS \( P(\text{O}_3) \) measurements and chemical modeling with tunable variables for the SHARP campaign and further campaigns would help identify the effective dependence of ozone production with radical production and NO.

4.7 NO\textsubscript{x} Additions in Houston

Figure 4-18. NO\textsubscript{x} additions to the ambient air in Houston on May 26, 2009
Mixtures of NO and NO$_2$ in equal amounts were prepared with zero air and exposed to the solar radiation in a Teflon film bag in order to achieve the photostationary state (PSS) of NO, NO$_2$ and O$_3$. The test was performed in Houston on May 26, 2009. Every addition was done over a period of one hour, starting at 11:18 pm and ending at 4:18 pm. The ambient levels of NO during this time remained below 0.5 ppbv. The results are shown in Figure 4-18. The first group of data, depicted by green stars, corresponds to the response of ozone production to the addition of 1.7 ppbv of NO and NO$_2$. This group of points is scattered between 10 and 80 ppbv h$^{-1}$, which makes it difficult to define the actual P(O$_3$) value. The next three additions, 5, 8.3 and 11.6 ppbv of NO and NO$_2$, yielded better packing of P(O$_3$) points at about 80 ppbv h$^{-1}$. The final addition of 16.6 ppbv of the same mixture, produced again some scattering of P(O$_3$) points between 45 and 85 ppbv h$^{-1}$. The NO levels in Figure 4-17 should shift towards lower values due to the PSS. With this shift in mind, the three additions performed between 12:18 and 3:18 pm, indicate that the levels of NO necessary to achieve the NO$_x$ saturated regime of ozone production is likely to be between 1 and 15, which is consistent with the MOPS ambient observations during the high ozone production days.
4.8 Final Remarks

Figure 4-19 shows a scatter plot of calculated versus measured P(O₃) for all days during daylight hours. In this plot the data obtained on May 28 and 29, detailed earlier, have been excluded from the linear regression due to reasons explained in earlier sections. Individual differences and details that make the calculated ozone production higher or lower than the measured ozone production need to be explained more thoroughly via further field studies and chemical modeling. Despite individual differences, however, the majority of the calculated data agrees with the bulk of the measured data even when this study corresponds to the first field deployment of the MOPS. This bulk agreement is an indication that studies that include the MOPS in addition to radical measurements and chemical modeling can contribute substantially to understand the chemistry of ozone production and the fine mechanistic details that potentially produce differences between the calculated ozone production and the modeled or measured ozone production.

Figure 4-20 shows a potential pilot deployment of the MOPS to carry on ozone chemistry and transport investigations at a regional scale in the Houston area. This figure illustrates the location of the precursor and ozone plumes in the afternoon and evening of May 20, 2009. It is clear how point pollution sources affect the air quality regionally. An extended use of the MOPS marked by four blue dots in this figure, on the path of the NE wind that characterizes pollution events in Houston can contribute substantially to learn about the regional air chemistry and to quantify ozone production and ozone advection within the context of the regional ozone budget.
Figure 4-19. Scattered plot of calculated $P(O_3)$ versus measured $P(O_3)$ during daylight hours in Houston between Apr 29 and May 30, 2009.

Figure 4-20. Evolution of the ozone plume in Houston on May 20, 2009. (a) Precursor plume position at 5 pm CST. Line colors correspond to individual NOx and VOCs point sources (b), (c) and (d) Ozone plume at 5 pm, 6 pm and midnight. Grey: 76-95 ppbv, light orange: 96-105 ppbv, dark orange: 106-115 ppbv, (TCEQ, 2010). (d) Blue dots mark the potential pilot deployment of four MOPS located on the path of typical plumes at current air quality monitoring stations.
Chapter 5

Conclusions

The first deployable version of the Measurement of Ozone Production Sensor (MOPS) has been fully developed and is currently operational. The feasibility of the technique has been proved by laboratory experiments and field deployment in rural and urban environments.

The principle of operation of the MOPS is to separate physically the ozone-producing photochemistry from the non-producing photostationary state (PSS) of NO, NO$_2$ and O$_3$. Hence, the MOPS detects the ozone formed via radical chemistry only. Laboratory tests demonstrate that the abundance of peroxy radicals in the MOPS sample chamber is similar to the atmosphere while these radicals are virtually not present in the reference chamber. These conditions ensure that the differential of ozone between the MOPS chambers yields the measurement of the ozone produced by reactions between peroxy radicals and NO. The detection limit of the current MOPS is 0.67 ppbv h$^{-1}$ for the 10-minute average data. The absolute uncertainty of the instrument is 30% at the 95% confidence level for measurements not affected by relative humidity. For early morning data, the uncertainty increases to 35% at the same confidence level, due to an artefact that occurs when the relative humidity inside the chambers grows beyond 50%.

The next step is to reduce further the wall effects on the MOPS chambers and improve the flow pattern towards laminar plug flow so that losses and high relative humidity conditions do not cause a negative impact on the measurements. It is important to remark, however, that the current 50% relative humidity constraint is for the inside of the MOPS chambers and not for the ambient air.

The first experimental plots $P(O_3)$ vs. NO were collected in September, 2008 on the campus of Penn State University. The MOPS was deployed in an urban environment during
Study of Houston Atmospheric Radical Precursor, SHARP 2009. The MOPS yielded ozone production rates within expected values for rural and urban environments.

The ability of the MOPS to retrieve ambient P(O\textsubscript{3}) vs. NO correlations brings about the possibility of rethinking the scientific basis for air quality regulations. In situ measurements of P(O\textsubscript{3}) vs. NO contain the real effect that precursors have at forcing the chemistry of ozone production. Using these experimental plots it is possible to determine in situ under which pollution conditions the ozone production chemistry is controlled by NO\textsubscript{x} and under which conditions the production of ozone moves to NO\textsubscript{x} saturation. Prior to this proposed experimental method, a common practice to decide upon air quality regulations has been to run models assuming fixed pollution conditions, namely NO\textsubscript{x}/VOC\textsubscript{s} ratios, a method of questionable accuracy. An extensive use of the MOPS to retrieve real time information under real pollution conditions is a practical and inexpensive answer to the challenges associated with ozone air quality standards.

In Houston, diurnal patterns of ambient ozone production as well as experimental plots P(O\textsubscript{3}) vs. NO were collected over 20 days of campaign. The MOPS set of data contains three verified episodes of high ozone in Houston. These pollution events occurred when the MOPS recorded peaks of P(O\textsubscript{3}) above 40 ppbv h\textsuperscript{-1}. Such large production rates combined with stagnant meteorological conditions developed into ozone episodes. The measured ozone production was analyzed as a function of ambient NO. Distinctive and smooth curves of ozone production that grow with NO, reach a peak and then decrease were found. P(O\textsubscript{3}) was not sorted quantitatively for different levels of P(HO\textsubscript{x}), however, the time of the day was used as an indicator of such levels. Remarkable examples of curving P(O\textsubscript{3}) vs. NO plots were found during the ozone episode that started on May 19, developed on May 20 and dissipated on May 21. These three days have been interpreted as the first experimental example of how the peak of the curve P(O\textsubscript{3}) vs. NO respond to different pollution conditions by shifting slightly to the right. Direct comparisons with
theoretical calculations are not possible because the MOPS collects all the radical production
levels that occur naturally in a day. An important point that this work intends to demonstrate is
that the study of ozone production and its correlation with precursors should go beyond
comparisons with theoretical calculations and should be done under real conditions with all the
varying effects that occur in the ambient air. In this way, the practical purpose of contributing to
the improvement of air quality can be achieved.

The data collected in Houston by the MOPS was compared against calculated ozone
production rates using peroxy radical and NO measurements. A bulk agreement was found
between the two independent sets of data as given by overlapping of the 1-sigma uncertainty error
bars on the mean diurnal patterns. Specific differences were found when the ozone production
was high, climbing above 40 ppbv h⁻¹. During these days, there is a general agreement that occurs
for NO levels lower than 2 ppbv and greater than 10 ppbv. For moderate levels of NO, between 2
to 10 ppbv, the calculated P(O₃) skips the curving pattern found by the MOPS for P(O₃) vs. NO.

A question to answer in future work is whether our current understanding of ozone forming
chemistry reproduces observations. Within this context, a hypothesis that needs to be verified is
to what extent and under which NO and P(HOₓ) conditions the equation applied to calculate
ozone production, using peroxy radicals and ambient NO, reflects the actual ozone forming
chemistry in the ambient air. To this end, further work is required to compare the data obtained
by the MOPS in Houston with model results. This step will allow a deeper scrutiny of the
chemistry and the mechanistic details that contributes to reproduce the patterns seen by the
MOPS in Houston.

NOₓ sensitivity tests were performed in a rural and urban environment, at Penn State in
September 2008, and in Houston in May 2009, respectively. The level of added NOₓ needed to
produce the turning point in the regime of ozone production was an order of magnitude larger at
Penn State and the P(O₃) was substantially lower if compared with Houston. The ozone
production chemistry in a city loaded with anthropogenic VOCs such as Houston requires about 10 ppbv of added NO\textsubscript{x} in order to force the production of ozone to levels as high as 80 ppbv h\textsuperscript{-1}. On the Penn State campus, characterized by a clean background atmosphere, it was necessary to add NO\textsubscript{x} of about 100 ppbv in order to produce 15 ppbv h\textsuperscript{-1} of P(O\textsubscript{3}). The sensitivity tests performed on both locations are in agreement with ambient measurements taken in each site under real conditions. These tests reveal differences in the ozone forming capacity of the urban and rural environments and bring up the need of quantifying local ozone production versus ozone transport. Likewise, these results emphasize the importance of reducing the production of ozone in areas where it is high as an strategy to improve air quality in those areas and prevent the transport of pollutants away from the source.

The extended use of the MOPS placed on the path of known meteorological features that affect the air quality of locations downwind of pollution clusters can help quantify not only the production of ozone in those pollution centers but also the effect of ozone advection at a regional scale.

For the practical purpose of contributing to the improvement of air quality regulations, the results presented in this work demonstrate the benefit of adding the MOPS to air quality monitoring networks. The MOPS is an inexpensive instrument that monitors in real time the production of ozone in the ambient air. With the information that the MOPS provides it is possible to elucidate the NO and P(HO\textsubscript{x}) conditions under which high ozone production rates lead to ozone episodes in the ambient air. In other words, it would be possible to make regulatory decisions based on experimental observations of P(O\textsubscript{3}) as opposed to using exclusively model results. Furthermore, models can benefit from a network deployment of MOPS as means of validation and improvement.
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VITA
Maria Cazorla

Education

PhD  **Meteorology**, The Pennsylvania State University, 2010
  (GPA 3.9/4.0)

MSc  **Environmental Pollution Control**, The Pennsylvania State University, 2005
  (GPA 4.0/4.0)

BSc  **Chemical Engineering**, National Polytechnic School (EPN), Quito, Ecuador, 2001
  Cum Laude

Honors

NASA Postdoctoral Fellowship, 2010
Fulbright Scholarship, 2003 – 2005
University Graduate Fellowship, Penn State, 2005 - 2006
Anne C. Wilson Graduate Research Award, Penn State, 2005
Graduate Exhibition Award Recipient, Penn State, 2005
Engineering Research Symposium “Mindbend” Award Recipient, Penn State, 2005
Chi Epsilon Pi Meteorology Honor Society, Inducted 2006
Graduate Exhibition Award Recipient, Penn State, 2007

Publications


Manuscript in preparation:
Cazorla, M. and Brune, W. H., Direct Measurement of Ozone Production Rates in Houston in
May 2009.

Conference Proceedings:
Cazorla, M. and Grutzeck, M., Indoor Air Pollution Control: Formaldehyde Adsorption by
Synthesized Zeolite Rich Materials, Environmental Issues and Waste Management Technologies
in the Ceramic and Nuclear Industries XI: Proceedings of the 107th Annual Meeting of The
American Ceramic Society, Volume 176, 3-13, 2005.

Academic Events

Co-chair, 12th Annual Environmental Chemistry Student Symposium, Penn State, March
27th and 28th, 2009.