SPATIAL AND TEMPORAL DISTRIBUTION OF OZONE OVER HOUSTON
DURING THE 2006 TEXAS AIR QUALITY STUDY

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE UNIVERSITY OF HAWAI‘I IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN METEOROLOGY

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ABSTRACT

This study documents the distribution of the ozone at the surface and aloft over the greater Houston area in the context of the synoptic atmospheric environment and the resulting boundary layer evolution. Data from surface stations, a portable ozone sensor, and NOAA research platforms used in this research were collected during the 2006 Texas Air Quality Study (TexAQS II). This study also provides an assessment of the utility of the NOAA smart balloon as a tool for gaining observations on the ozone concentrations above the surface and information on the boundary layer evolution. Results confirm the importance of local influences on tropospheric ozone concentration, including the impact of the urban heat island, vertical transport associated with a sea breeze front, and mixing within a summertime boundary layer. The analysis shows that enhanced surface ozone consistently accumulates downwind of the Ship Channel. If the background flow places the urban heat island downwind of the Ship Channel, higher temperatures associated with the urban heat island lead to additional enhancement of ozone concentration. The smart balloons helped document both the distribution of tropospheric ozone above the surface and boundary layer structure in the vicinity of Houston, providing critical information on the background meteorology. However, the analysis presented in this thesis represents only a part of the picture. For a complete understanding of the ozone evolution, the precursor chemistry must be simultaneously documented and the photochemical processes and chemical reactions must be modeled. These pieces the complex ozone puzzle are the subject of additional ongoing research.
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CHAPTER 1
INTRODUCTION

1.1 – Background

Ozone is one of the most common components associated with tropospheric air pollution. It is highly toxic to organic tissue due to its strong oxidizing power, and has been linked to numerous health problems and agricultural damages. By understanding the nature of ozone formation and distribution in the troposphere it is possible to improve air quality forecasts and issue informed health safety alerts. The Environmental Protection Agency (EPA) helps to monitor air quality and sets standards in the U.S. (Table 1).

Table 1. EPA Air Quality Index (AQI) for ozone in parts per billion (ppb) – Established in 1999 as part of the National Ambient Air Quality Standards (NAAQS).

<table>
<thead>
<tr>
<th>Index (ppb)</th>
<th>Value</th>
<th>One Hour Ozone</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 – 50</td>
<td>Good</td>
<td>None</td>
</tr>
<tr>
<td>51 – 100</td>
<td>Moderate</td>
<td>None</td>
</tr>
<tr>
<td>101 – 150</td>
<td>Unhealthy for Sensitive Groups</td>
<td>125 – 164</td>
</tr>
<tr>
<td>151 – 200</td>
<td>Unhealthy</td>
<td>165 – 204</td>
</tr>
<tr>
<td>201 – 300</td>
<td>Very Unhealthy</td>
<td>205 – 404</td>
</tr>
<tr>
<td>300 – 500</td>
<td>Hazardous</td>
<td>405 – 604</td>
</tr>
</tbody>
</table>

The most common method for formation of ozone in the troposphere is through photochemical transformation of anthropogenic pollutants. Atmospheric scientists refer to these as primary pollutants (EPA 2006a). These pollutants are mainly nitrous oxides (NOₙ, defined as NO + NO₂), peroxyacetyl nitrates (PAN) which act as reservoirs to
NO\textsubscript{x}, and volatile organic compounds (VOCs). VOCs consist of a large subset of industrially produced hydrocarbons that are linked with ozone production (EPA 2006b).

While VOCs are released from industrial refineries and petrochemical plants, NO\textsubscript{x}, mostly in the form of NO, is released largely from automobile combustion. These two source inputs act together with abundant naturally occurring background molecules (O\textsubscript{2}, OH) to aid in the formation of ozone (Fig. 1). For a more detailed description of this chemistry please refer to the Appendix. The production of ozone is dominated by O\textsubscript{2} combining with ground state oxygen and from photochemical breakdown of NO\textsubscript{2}. Ozone also breaks down photochemically into an oxygen molecule and an excited oxygen atom. The presence of NO acts as a sink for ozone and therefore large concentrations of NO\textsubscript{x} do not necessarily lead to high ozone concentrations. Emissions of VOCs help to gradually lead to the formation of PAN, but it is the temperature dependant breakdown of the PAN molecule that provides large amounts of additional NO\textsubscript{2}. Furthermore, the addition of VOCs helps to remove NO as a sink for ozone by providing an alternate chemical reaction into the formation of PAN. The combination of large emissions of NO\textsubscript{x} and VOCs will instigate the formation of higher concentrations of ozone.

Regardless of the concentration of the primary pollutants, ozone only forms as a photochemical byproduct. Ozone production requires sunlight to form as a secondary pollutant (EPA 2006a). Higher temperatures help to accelerate this process. There are several more factors that contribute to episodes of higher ozone formation. In order to produce the highest concentrations, however, the processes that promote ozone formation and accumulation become far more complicated. Such processes involve unique
combinations of chemical environments and meteorological triggers that are inherent to specific regions such as Houston, Texas.

1.2 – Chemical Environment Surrounding Houston

Eliassen et al. (1982) combined a chemical model with a Lagrangian model in order to predict the transport of ozone. In their study they identify that ozone concentrations are mostly influenced by emissions and deposition velocity. Previous studies on regional ozone found that midlatitude background ozone values contribute between 0 and 30 ppb in observed concentrations in the Northern Hemisphere, while an additional observed ozone range between 20 and 70 ppb arises from specific source regions (Kleinman et al. 2005). These observed values do not take into account the additional ozone produced on any given day, which complicates efforts to meet the ozone exceedance standard implemented by the EPA; requiring that the third highest 8-hour averaged ozone concentration does not exceed 85 ppb as an average over three years (Lei et al. 2004 and Table 1).

The first Texas Air Quality Study (TexAQS) occurred in the year 2000 over the region of Houston, Texas (Fig. 2). Houston contains the largest concentration of petrochemical industrial facilities in the United States (Ryerson et al. 2003); therefore it is no surprise that Houston has a significant problem with high ozone concentrations. The Ship Channel, located along the eastern edge of Houston, contains a large number of these petrochemical facilities. As such, there are tremendous quantities of NOx and VOCs emitted in this region of Houston (Table 2). The specific combination of these NOx and VOC emissions yields very rapid and efficient production of high
concentrations of ozone (> 125 ppb) from narrow and intense plumes emitted within the Ship Channel; which contributes to this process more than in any other region around Houston (Daum et al. 2002, Kleinman et al. 2002a, Kleinman et al. 2002b, Senff et al. 2002, Daum et al. 2003, Ryerson et al. 2003, Berkowitz et al. 2004, Lei et al. 2004, Kleinman et al. 2005, Cowling et al. 2006).

Murphy and Allen (2005) define a reportable emissions event as "any emissions event which, in any 24-h period, results in an unauthorized emission equal to or in excess of the reportable quantity." They found that most of these emissions events in the Houston region lasted less than 24 hours. Nam et al. (2006) isolated five emission events per day in Houston, in which two contained highly reactive volatile organic compounds (HRVOCs).

The hydrocarbons specifically contributing the most to the production of ozone are the low molecular weight hydrocarbons: alkenes, ethylene, propylene, and butenes (Daum et al. 2003, Ryerson et al. 2003, Murphy and Allen 2005). Kleinman et al. (2002b) found that average concentrations of ethenes, propenes, and butenes were 16, 8, and 2.5 ppb, respectively. These concentrations accounted for 60% of the reactivity from anthropogenic hydrocarbon sources, with individual samples of the hydrocarbons ranging from 4 to 91%. The remaining 40% of the anthropogenic hydrocarbon sources was split among alkanes and aromatic compounds, which can be present in very high concentrations. With oxidation by OH, each of these compounds can be converted into an additional ozone source within the troposphere. The indication of VOCs in Fig. 1 includes the numerous hydrocarbons listed in Table 2.
Table 2. The Average Mixing Ratios (pptV) adapted from Berkowitz et al (2004).

<table>
<thead>
<tr>
<th>Species</th>
<th>(A) Ship Channel (21 Aug and 12 Sep)</th>
<th>(B) Nonship Channel</th>
<th>(C) Ratio, Ship Channel/Nonship Channel</th>
</tr>
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<tr>
<td>Ethene</td>
<td>3833</td>
<td>398</td>
<td>9.6</td>
</tr>
<tr>
<td>Propene</td>
<td>1006</td>
<td>140</td>
<td>7.2</td>
</tr>
<tr>
<td>Acetylene</td>
<td>2548</td>
<td>445</td>
<td>5.7</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>1672</td>
<td>295</td>
<td>5.7</td>
</tr>
<tr>
<td>Benzene</td>
<td>850</td>
<td>166</td>
<td>5.1</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2981</td>
<td>621</td>
<td>4.8</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>677</td>
<td>143</td>
<td>4.7</td>
</tr>
<tr>
<td>i-pentane</td>
<td>3316</td>
<td>706</td>
<td>4.7</td>
</tr>
<tr>
<td>Ethane</td>
<td>7943</td>
<td>2723</td>
<td>2.9</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>46</td>
<td>16</td>
<td>2.8</td>
</tr>
<tr>
<td>EthBenzene</td>
<td>131</td>
<td>51</td>
<td>2.6</td>
</tr>
<tr>
<td>Propane</td>
<td>5923</td>
<td>2313</td>
<td>2.6</td>
</tr>
<tr>
<td>i-butane</td>
<td>4938</td>
<td>2030</td>
<td>2.4</td>
</tr>
<tr>
<td>p- and m-Xylene</td>
<td>274</td>
<td>132</td>
<td>2.1</td>
</tr>
<tr>
<td>α-Xylene</td>
<td>103</td>
<td>54</td>
<td>1.9</td>
</tr>
<tr>
<td>2,2,4-TriMePentane</td>
<td>225</td>
<td>121</td>
<td>1.9</td>
</tr>
<tr>
<td>Toluene</td>
<td>826</td>
<td>458</td>
<td>1.8</td>
</tr>
<tr>
<td>t-2-Butene</td>
<td>24</td>
<td>17</td>
<td>1.4</td>
</tr>
<tr>
<td>2-MePropene/1-Butene</td>
<td>147</td>
<td>119</td>
<td>1.2</td>
</tr>
<tr>
<td>Isoprene</td>
<td>761</td>
<td>649</td>
<td>1.2</td>
</tr>
<tr>
<td>3-MePentane</td>
<td>393</td>
<td>386</td>
<td>1.0</td>
</tr>
<tr>
<td>c-2-Butene</td>
<td>17</td>
<td>17</td>
<td>1.0</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>175</td>
<td>239</td>
<td>0.7</td>
</tr>
<tr>
<td>2-MePentane</td>
<td>488</td>
<td>999</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Comparisons to other cities highlight the unique nature of Houston in terms of its chemical environment. The higher abundance of NO\textsubscript{x} emissions within Houston contributes to more efficient NO\textsubscript{x} photochemistry on the order of two to three times that of other major cities in the United States (i.e., Nashville, New York City, Phoenix, and Philadelphia) (Kleinman et al. 2002a, Lei et al. 2004). Among several different polluted cities in the United States with comparable urban NO\textsubscript{x} concentrations, the VOC concentrations in Houston were found to lead to ozone production rates that were 2 to 5 times higher than in these other polluted cities (Kleinman et al. 2002b). This implies the necessity for both NO\textsubscript{x} and VOC emissions to be present for high ozone formation.

Previous research on ozone over Houston revealed the complexities involved with ozone production. Conditions for the production of ozone over the Ship Channel were found to vary from strongly NO\textsubscript{x} limited to strongly VOC limited (Ryerson et al. 2003, Kleinman et al. 2005). Ozone production in the plumes was found to be more NO\textsubscript{x} limited than in typical urban plumes at equivalent times in their evolution (Daum et al. 2004). Ozone production efficiency (OPE\textsubscript{x} – the number of molecules of ozone produced per molecule of NO\textsubscript{x} converted into OH – (Kleinman et al. 2002a) was found to increase with plume age, and decreased with increasing NO\textsubscript{x} emissions (Springston et al. 2005). Higher OPE\textsubscript{x} values imply less NO\textsubscript{x} presence, which also implies less of a sink for ozone based upon the NO + O\textsubscript{3} reaction depicted in Fig. 1. Values of OPE\textsubscript{x} measured in Houston during the 2000 TexAQS ranged between ~ 6 to 12 molecules of ozone per molecule of NO\textsubscript{x} (Kleinman et al. 2002a, Daum et al. 2004), while simulated values of OPE\textsubscript{x} were typically between 3 to 8 (Lei et al. 2004). These findings support inferences of higher hydrocarbon utilization acting concurrently with NO\textsubscript{x} consumption.
Instantaneous ozone formation rates, based upon box-model calculations considering all sources and sinks for ozone, were found to be as high as 140 ppb h\textsuperscript{-1} over the Ship Channel with very high OPE\textsubscript{X} values of up to 28 (Daum et al. 2004). Kleinman et al. (2005) found that ten percent of samples from the Ship Channel region had ozone production rates between 30 and 155 ppb h\textsuperscript{-1}. A model simulation, on the other hand, found the net ozone production rates to be between 20 and 40 ppb hr\textsuperscript{-1} based upon summer time ground levels of NO\textsubscript{x} between 5 and 30 ppb (Lei et al. 2004). All of these findings support observations of high ozone production efficiency over the Ship Channel.

Preliminary findings from TexAQS II indicate that emissions of HRVOCs from industrial sources around Houston have decreased by a factor of two since 2000. There has also been a substantial decrease in NO\textsubscript{x} emissions from rural electric utility power plants around Houston. In the meantime, ethene emissions are still underestimated in model simulations by an order of magnitude based on the latest available emission inventories. There are also shortcomings in on-road mobile emissions inventories based on the MOBILE6 model, where current inventories appear to underestimate NO\textsubscript{x} to VOC emission ratios in urban areas of Houston (Cowling et al. 2006).

1.3 - Meteorological Contribution to Ozone Concentrations Over Houston

Investigation of tropospheric ozone has led researchers to isolate its various formation mechanisms and provide strategies to curtail its formation. Beyond these formation mechanisms, however, are several intricate meteorological processes that play a role in the distribution and accumulation of ozone in various locations in the troposphere. Sometimes these meteorological influences cause ozone and its source
pollutants to experience extended lifetimes in the boundary layer. Understanding such influences can help to provide insight into the vertical distribution and evolution of ozone.

Various meteorological mechanisms around Houston contribute to the distribution of ozone and its primary pollutants. Banta et al. (2005) provide an extensive review of the meteorological mechanisms for generating ozone concentrations as high as 200 ppb in the lower atmospheric boundary layer over Houston. Focusing upon the case study of 30 August 2000, Banta et al. isolate five leading factors for high ozone formation. (i) The timing of the sea breeze arrival, in which later afternoon arrivals were found to correlate more with high ozone episodes. (ii) A stagnation phenomenon develops in the presence of weak, northerly synoptic flow; specifically where the sea breeze front meets low level, weak offshore flow. Pollutants accumulate within this region of stagnated air. (iii) High temperatures help facilitate chemical reactions, including the thermal decomposition of PAN molecules. During the 30 August 2000 case study, Houston experienced a heat wave with temperatures above 100 °F (40 °C) for several days. (iv) Vertical transport along the sea breeze front brings pollutants to as high as 1.5 km into the boundary layer (Banta et al. 2002). Stronger winds in the middle to upper boundary layer increase the potential for large-scale transport of these pollutants. Boundary layer mixing on the next day will then recirculate this air to the surface. (v) Nocturnal transport of ozone and primary pollutants via low-level jets contributes to the ventilation of background pollution levels and with sufficient removal can potentially improve the next day’s air quality.
Synoptic scale phenomena influence ozone accumulation. Davis et al. (1998) found that the largest daily one hour maximum ozone concentrations are associated with either the frontside or backside of migrating anticyclones. The subsiding, stable air from a region of high pressure helps to cap ozone concentrations beneath an inversion layer. Ozone concentrations are therefore allowed to accumulate. Their study also found these occurring most often during the spring and summer months.

Berkowitz et al. (2004) found that extreme ozone concentrations readily occur higher in the boundary layer rather than at the surface. Their study also focused on ages of polluted plumes and identified that sampled plumes contained greater quantities of newer emissions, thus implying that long-range ozone transport is not as significant for Houston as local sources of ozone. The recirculation of local emissions has been found to contribute to the elevated background ozone levels in urban regions of Houston (Cowling et al. 2006).

Air stagnation associated with sea breeze arrivals contributes uniquely to the build-up of high ozone events (Banta et al. 2002, Senff et al. 2002, Darby et al. 2005). Darby et al. (2005) discovered that maximum ozone concentrations were greater than 120 ppb when occurring with sea breeze phenomena. These maximum concentrations occurred within six hours after a period of one hour stagnation in the winds as they transitioned from offshore to onshore. In this scenario, the ozone production typically occurred before the sea breeze front arrived so that the air flowing onshore was already enriched with high concentrations of ozone and primary pollutants (Daum et al. 2004). Not all of this air was emitted only in the earlier hours, though. As the air was recirculated over land it was transported back over the source areas by the sea breeze.
front, which provided additional ozone to the already heavily polluted air (Senff et al. 2002). Banta et al. (2002) calculated that vertical ventilation along the sea breeze front can sometimes bring ozone to as high as 2 km in altitude with concentrations of approximately 200 ppb throughout. (Banta et al. 2002).

Zhang and Rao (1999) performed a model simulation of ozone in the troposphere. Their results indicated that photochemical ozone production gradually increases in the morning, reaches a maximum in the midday, and finally decreases in the late afternoon hours. Furthermore, next day ground-level ozone concentrations can be influenced by any concentrations of ozone and its precursors that are trapped above in the nocturnal residual layer within the middle to upper boundary layer. When surface temperatures during the next day increase, and the surface-based inversion starts to break up, the mixing layer grows rapidly into the overlying residual layer and entrains the trapped pollutants. Vertical mixing brings this air to the surface, where fumigation increases ground-level ozone concentrations. As the mixing layer grows further, it entrains less polluted air and contributes to dilution, while lingering and additional primary pollutants continue to instigate ozone production. High ozone concentrations have been observed sometimes above the boundary layer as a result of this complex mixing process (Cowling et al. 2006).

One of the leading contributors to the mesoscale circulation around Houston is its urban heat island. Nielsen-Gammon (2000) used the Penn State/NCAR Mesoscale Model, Version 5 (MM5), to show the impact of the Houston urban heat island on the sea-breeze circulation. In his analysis, Nielsen-Gammon described the “Houston Heat Pump,” which redirected the sea breeze toward the city and recirculated the polluted air.
The urban heat island lies ~ 30 km west of Galveston Bay and ~ 65 km northwest of the Gulf of Mexico, directly over the heart of Harris County. A weak wind forms in the direction of the urban heat island that Nielsen-Gammon described as a “city” breeze. The city breeze and the sea breeze combine to form one continuous band of southeasterlies from the northwestern portion of Galveston Bay to the eastern portion of Houston. This incoming flow tends to advect air from over the heavily polluted Ship Channel to Houston’s downtown area.

1.4 – Goals of this Research

One of the conclusions put forth by Banta et al. (2005) is that there is a lack of vertical data coverage. This deficiency underscores the importance for efforts to obtain in situ data in the middle to upper boundary layer. It is for this reason that the TexAQS II project provided an excellent opportunity for the National Oceanic and Atmospheric Administration Air Resources Laboratory Field Research Division (NOAA ARLFRD), the University of New Hampshire (UNH) and the University of Hawaii at Manoa (UHM) to deploy their smart balloon autonomous platforms.

A team comprised of researchers from NOAA ARLFRD (Randy Johnson and Shane Beard) and UHM (John Porter and Jonathan Tytell) met in Houston in August of 2006, during the height of TexAQS II, to arrange the release of six smart balloons over a three week period (Fig. 3). These balloons were equipped with instruments to measure several meteorological variables, as well as state-of-the-art miniature ozone sensors designed and built at UNH. The balloons were released from the La Porte airport located
just southeast of the metropolitan area of Houston, near the western coastline of Galveston Bay. This location is ideal for monitoring ozone due to its proximity to the Ship Channel (Banta et al. 2005).

The primary goal of this research effort was to document the distribution of the ozone at the surface and aloft over the greater Houston area in the context of the synoptic atmospheric environment and the resulting boundary layer evolution. A secondary goal of the research is to assess the utility of the NOAA smart balloon as a platform for collecting observations on the ozone concentration above the surface, while at the same time gathering information on the boundary layer evolution. The UHM team used a portable ozone sensor, also designed at UNH, to provide in situ sampling of the surface ozone beneath the balloons as long as they were over land. Urban ozone plumes were sampled and tracked with the smart balloons on days of expected high ozone accumulation.

These data sources were combined with observations from aircraft and from a network of surface stations to document the three-dimensional distribution and evolution of ozone within a changing atmospheric boundary layer. In addition, operational data from the National Weather Service were analyzed to document the mesoscale and synoptic scale meteorological processes operating over Houston on the days that smart balloons were deployed.
CHAPTER 2
INSTRUMENTATION AND METHODS

2.1 – The NOAA Smart Balloons

2.1.1 – Smart Balloon History

The smart balloons were designed and constructed at NOAA ARLFRD (Businger et al. 2006). The balloons are designed with buoyancy control to counteract external forcing such as precipitation loading and diurnal changes in short and long wave radiation. The balloons can also be instructed to fly and remain at any specific altitude in order to sample various layers throughout the boundary layer. Installation of affordable GPS and satellite cellular equipment allow the ability to easily track the balloons and communicate with them as they transmit low-altitude in situ data. In the absence of significant wind shear, the mean wind is negligibly small through the quasi-Lagrangian frame of reference provided by the drifting smart balloon (Businger et al. 1996). This makes the smart balloon a useful platform for observing the evolution and distribution of air pollution from both a chemistry and physics perspective.

Since the early 1990s, the smart balloons have evolved in design and functionality through experience with a sequence of field experiments (See Businger et al. 2006). These field experiments include ASTEX/MAGE near the Azores Islands in 1992, ACE-1 near Tasmania, Australia in 1995, ACE-2 between the Portugal coast and the Canary Islands in 1997, and ICARTT over the North Atlantic Ocean in 2004. The smart balloons released during the ICARTT campaign were the first to utilize miniature ozone sensors designed at UNH. One of the ICARTT balloons continued sampling ozone and standard
meteorological variables as it journeyed across the North Atlantic Ocean from Long Island to Morocco.

The data from the ICARTT experiment yielded many clues to the distribution of ozone as it passes over open ocean. Mao et al. (2006) demonstrated that ozone plumes that emanate from New England and New York City form into large stratified layers in the more stable marine boundary layer. These stratified layers persisted mainly in the middle to lower marine boundary layer, and were found to extend across the entire North Atlantic and affect the background ozone levels in the United Kingdom and Europe. This is in contrast to ozone plumes over land, which mix turbulently within the boundary layer. This convective mixing is especially larger over Houston during the summer time as a result of strong solar heating and thermals rising from the surface.

2.1.2 – Smart Balloon Design for TexAQS II

Prior to each field experiment changes are made to the design of the smart balloons to accommodate instrumentation and to incorporate design improvements. The improvements made for the TexAQS II program include an upgrade to the satellite communications package, improvement to the balloon shell design, and a new larger fiberglass enclosure that consolidates all the sensors and other equipment. High strength Spectra fabric was used for the balloon shell and installed with an aluminum interface plate to provide a complete physical seal around the fiberglass enclosure. Just like the balloon design for the ICARTT experiment, miniature ozone sensors from the University of New Hampshire were part of the instrument packaging (Fig. 4). A miniature pulse output type rain gage was installed to improve balloon precipitation measurement.
Rather than use a tipping bucket though, it uses a drip detector to send pulses to the onboard data gathering system each time a droplet falls from the gathering funnel. Table 3 lists the design specifications for the smart balloons during TexAQS II.
Table 3. Smart balloon onboard instrumentation used during TexAQS II. Adopted from Businger et al. (2006).

<p>| | |</p>
<table>
<thead>
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<tr>
<td>Battery life</td>
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</tr>
<tr>
<td>Communications</td>
<td>Iridium</td>
</tr>
<tr>
<td>Payload weight (kg)</td>
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<td>Instruments</td>
<td>GPS, Temperature, wetness, barometric pressure, balloon pressure, relative humidity, solar radiation, IR temperature, solar panel, helium pressure, ozone</td>
</tr>
</tbody>
</table>
2.1.3 – Balloon Data and Methods of Analysis

Each smart balloon records data once per minute. These data include outside temperature, relative humidity, rainfall accumulation, barometric pressure, averaged ozone, altitude, latitude, longitude, course and travel speed. Mixing ratio and virtual potential temperature ($\theta_v$) were calculated for each data record from the barometric pressure and relative humidity data for each balloon. These variables were used to conduct a boundary layer analysis for each balloon flight.

The ozone data are reported in ppb averaged over five minutes. Balloons 1, 2 and 5 contained the most reliable ozone data, while balloons 3, 4 and 6 experienced technical problems or could not be validated. There were a few spurious outliers among the data for balloon 2 that are currently under investigation. In the meantime, outliers beyond one standard deviation from the mean were removed. Overall the ozone data for balloon 2 is questionable in that the smaller-scale spikes do not accurately represent ozone fluctuations in the troposphere, however the overall trend of the data tells a different story. The analysis presented in Chapter 3 focuses on the portions of the balloon flights that occurred over or near land because pollution in these regions has a direct impact on Houston’s air quality (Fig. 5).

2.2 – NOAA Twin Otter Data

During TexAQS II, there were several different platforms in operation within the Houston region (Cowling et al. 2006). One of these platforms was the NOAA Twin Otter, which flew 21 missions during TexAQS II experiment. A downward-looking ozone/aerosol DIAL LIDAR system onboard the Twin Otter is used to profile lower
tropospheric structure. The horizontal resolution for the ozone measurements is \( \sim 600 \) m, while the vertical resolution is \( \sim 90 \) m. The range of precision for these measurements is 3 to 10 ppb. Ozone data from the Twin Otter’s 30 August flight are compared with balloon 1 data in chapter 3.

2.3 – TCEQ Surface Station Network

The Texas Commission on Environmental Quality (TCEQ) maintains a surface network of pollution and meteorological monitoring stations surrounding the Houston region. The TCEQ posts surface ozone data, which are available for approximately 40 stations during the TexAQS II experiment, on their website (http://www.tceq.state.tx.us/). They also post other meteorological variables, such as outdoor temperature, dew point, nitrogen dioxide, wind speed and relative humidity. Five minute averaged data were analyzed for each of the stations. A three dimensional mapping algorithm was used to generate contour maps for ozone and surface temperature from this surface network for the purpose of comparing with in situ car data.

The TCEQ surface station network undergoes regular quality control and collected data are screened at frequent intervals for validation purposes. Private organizations operate a few of the stations, and they are responsible for quality controlling their data, resulting in different validation timetables for these stations.

2.4 – In Situ Data from the UNH Portable Ozone Sensor

The UHM team collected a supplemental dataset that includes data from a GPS receiver and a portable ozone sensor from UNH, while tracking the smart balloons. The
UHM team sampled the air approximately 1.5 m above the surface using a five foot polyethylene tube installed at the front end of the portable ozone sensor, which was then fed out the rear window of the car. This tube was used for data collecting while tracking balloons 1 and 2, but was replaced with a Teflon tube for the remainder of the tracking missions. Polyethylene may have contributed to a titration of the ozone due to steady buildup of NOx along the inside walls of the tube. Calibration tests using each tube were conducted by comparing sampled data with a standard at the University of Houston (UH). These tests showed biases of sampled ozone between the polyethylene and the Teflon tubes, where the polyethylene sampled ~ 17 ppb on average below the Teflon tube and ~ 25 ppb below the standard. These biases were applied to the car data to not only account for the differences between the tubes, but to correct for a “washing out” phenomenon within the data that was related to decreasing ozone concentrations with higher car speeds and visa versa. This is further explained in chapter 4.

All data were logged into a laptop computer during the tracking missions. The ozone sensor required a warm-up time of at least 1.5 hours before data collection and balloon release. Data from the portable sensor and GPS receiver were combined to a common UTC time, and a five-minute running average was applied to match the balloon and TCEQ datasets.

2.5 – Ozonesonde Data

In addition to the previously mentioned ozone data sets, ozonesonde data are available for each of the three days that we have reliable balloon data. The ozonesondes were released from the UH campus under the direction of Dr. Gary Morris of Rice
University. Each ozonesonde reveals the extent of turbulent mixing in the boundary layer and also measures ozone concentrations in the free troposphere above. The lowest 2 km of each ozonesonde plot are of greatest concern since this region lies within the boundary layer.
CHAPTER 3
RESULTS

3.1 – Balloon 1: 30 August 2006

3.1.1 – 30 August Synoptic Scale Weather Summary

A weak cold front passed through the Houston region during 30 August. This cleansed the region of background ozone values and provided a northerly wind of 5 to 10 knots (Fig. 6). Winds behind the front were from the northwest by 0300 UTC (Fig. 6a). By 1200 UTC (0700 CDT) the front was well offshore (Fig. 6b). Soundings from radiosondes released at the University of Houston campus show a temperature inversion that fluctuated around the 900 to 800 mb range (~1000 to 2000 m altitude), but remained present throughout the day. These soundings also showed conditions in the lowest 150 mb to be relatively dry and stable after the frontal passage, with a dew point depression of approximately 15 °C at 1000 mb (Fig. 7). Temperatures at the surface reached a maximum of 34 to 35 °C, with the highest temperatures occurring in the mid to late afternoon over the metropolitan region of Houston. In terms of sky conditions, altostratus and altocumulus clouds were present for most of the day.

The maximum surface ozone concentrations occurred south of Houston, reaching into the 90s ppb by the mid afternoon over Brazoria County (Fig. 8). Overall, though, these ozone concentrations did not reach into unhealthy levels as designated in the AQI.

3.1.2 – Balloon 1 Flight Summary

Balloon 1 was released at 16:15 UTC on 30 August from the La Porte Airport into northerly and northeasterly winds following a frontal passage. The balloon followed a
track to the southwest, and then gradually turned to the southeast before reaching the coastline in Galveston after two hours. Its altitude fluctuated between 250 and 700 m during its trek towards the coast (Fig. 9). It remained over the Gulf of Mexico for about 4 days while drifting toward Florida. Eventually the balloon rose in the updraft of a thunderstorm near Tampa, Florida on 3 September, which damaged the balloon and ended its flight. This balloon was recovered several days after its release.

3.1.3 - Balloon 1 Comparison With NOAA Twin Otter Data

The balloon ozone data show a gradual upward trend from ~ 60 to 120 ppb during the first three hours of the flight, with periodic fluctuations (Fig. 9). The 30 August data from the Twin Otter (Fig. 10) shows an uneven ozone distribution that varies throughout the boundary layer. Processes of turbulence and convective mixing inherent to a summertime boundary layer over Houston are reflected in the ozone profiles from the Twin Otter (Fig. 11). These cross sections also indicate the depth of the mixed layer, where ozone concentrations of at least 100 ppb were found up to 1000 m above sea level. There is a deeper mixed layer (~ 1000 to 1200 m) over the portion of the plume corresponding with the highest concentrations of ozone. This feature appears to extend through the extent of the evolving plume. Smaller plumes of ozone with concentrations in excess of 150 ppb indicate regions of vertical ventilation for surface pollutants into the middle boundary layer, since these plumes extend directly to the surface. Although the balloon 1 flight began several hours before the Twin Otter transect, it is still possible to compare the general length scales for the fluctuations with those observed by the balloon.
and the conclusion is that the Twin Otter data document fluctuations in ozone that are consistent with the fluctuations seen in the balloon 1 ozone data (Fig. 9).

Data from the ozonesonde (Fig. 12) show elevated ozone concentrations to about 1200 m or just below cloud base, consistent with the aircraft and balloon data. Ozone concentrations of ~ 70 ppb are observed in the lowest 1.5 km. Above this altitude ozone falls off very gradually in the free troposphere and then increases sharply in the lower stratosphere above ~15 km.

One cross section from the Twin Otter flight coincided in general location and time with part of the car ozone data (Fig. 13). The Twin Otter data around 2200 UTC correlated the best with later half of the ozone sampled on the car route. Calculating the length of the cross section (Fig. 14) from the flight map required a conversion of ~ 96 km per degree latitude at 30 °N. For the time range of 21:38 to 22:06 UTC this distance was equal to ~ 121 km, or 4.32 km min⁻¹ over the 28 minute range (Fig. 15). This assumed a constant flight speed.

The Twin Otter cross section in this region was taken a few hours later from the balloon flight. The cross section shown in Fig. 15, suggests that the horizontal scale for ozone fluctuations is on the order of 1 km or less. In many cases the horizontal change is very sudden, particularly within the lower 200 m, suggesting a relationship between the sizes of the turbulent eddies and the depth of the boundary layer, where the scale of turbulence is limited by the boundary layer depth. There are also several plumes of ozone concentrations ≥ 150 emanating from the ground, indicating possible discrete near-surface sources of ozone.
Similar excursions from Fig. 15 are seen in the balloon 1 ozone data (Fig. 16). Both platforms show sudden spikes in ozone concentration as high as 400 m. It is important to note, however, the difference in sampling between the two platforms. While the balloon travels on an average of 10 m s\(^{-1}\), the Twin Otter flies at a much faster 4.32 km min\(^{-1}\). As a result, the balloon monitors much smaller sample sizes per unit time than the Twin Otter, and therefore observes much more ozone variability than the lidar. This is reflected in the number of spikes within the balloon data. Regardless the spatial scale for balloon 1 is similar to that of the Twin Otter. Balloon 1 also does not appear to sample the discrete near-surface ozone plumes of concentrations > 150 ppb since it samples above 300 m for most of its flight.

3.2 – Balloon 2: 1 September 2006

3.2.1 – 1 September Synoptic Weather Summary

A meandering high pressure ridge was the only synoptic influence over Houston on 1 September. Winds in the Houston region were between variable and 5 knots at 0300 UTC, but had switched to westerly by 1200 UTC (Fig. 17a, b). The westerly flow is explained by the formation of a land breeze just before midnight CDT on 31 August. Winds shifted from southerly to westerly while maintaining speeds of 10 knots (Fig. 18). This westerly flow shifted gradually to an easterly flow by the late morning on 1 September as a bay breeze from Galveston Bay developed (Fig. 19). There was a brief period of stagnation in the region roughly between 1500 and 1700 UTC. By the mid to late afternoon, a sea breeze developed and shifted the wind directions to southeasterlies (Fig. 17c). The winds remained southeasterly throughout the day. Surface temperatures
reached a maximum of about 34 °C in the northern areas of Houston, while temperatures to the south were generally 2 to 3 °C cooler. Skies were clear before 1600 UTC but thick cumulus clouds were developing during the day along both the bay breeze and sea breeze fronts.

Soundings on 1 September revealed the presence of an inversion at 700 mb that gradually rose to 600 mb (> 4 km altitude) by the end of the day. Above this inversion was a large region of very dry air with dew point depressions ranging between 40 and 50 °C (Fig. 20a, b). Surface conditions were moister than those on 30 August. The dew point depression at 1000 mb was less than 10 °C and remained so until at least 1600 UTC (Fig. 20c). By 0100 UTC on 2 September (2000 CDT) the air below the inversion was much more moist (Fig. 20d). Overall the soundings reveal stability throughout the boundary layer.

Surface ozone concentrations observed on 1 September were very high; > 150 ppb. Aside from the local emission and production sources from cars and industrial facilities, the brief period of stagnation, and the moderately high temperatures, there were also higher background levels of ozone. There were a few 8-hour ozone exceedance averages near the Ship Channel. The worst of these measured to be 129 ppb, which is much greater than the 85 ppb limit put forth by the NAAQS.

A large region of the city lay within ozone concentrations of at least 80 ppb for several hours. By 1700 UTC, a large plume with ozone concentrations above 100 ppb had formed in the stagnating air over Galveston Bay (Fig. 21b). This plume had moved well onshore with the sea breeze by 1800 UTC (Fig. 21c). The highest concentrations within the plume were above 160 ppb by 1900 and 2000 UTC, as the plume crossed back
over the Ship Channel and mixed with more recently emitted pollutants (Fig. 21d, e). Ozone concentrations > 100 ppb were widespread across Harris County and northern Galveston and Brazoria Counties by 2100 UTC (Fig. 21f). The 1800 UTC ozonesonde revealed ozone concentrations between 100 and 115 ppb within the lower 2 km of the boundary layer, with a sharp decrease to ~70 ppb within 1 km above this layer (Fig. 22). Above these lower 3 km the ozone concentrations fluctuate around an average of ~70 to 80 ppb.

3.2.2 – Balloon 2 Flight Summary

The balloon 2 flight on 1 September was a short but relatively interesting flight in terms of a vertical analysis (Fig. 23). The balloon was released at 15:48 UTC, and slowly moved east during the first leg of its journey. It had risen to about 600 m after release and drifted to the east in light winds. It then gradually turned to the south and then west as its slowly descended to about 300 m. The change in direction was associated with the arrival of a late morning bay breeze from Galveston Bay. The balloon continued moving west and northwest, with occasional periods of weaker background wind flow (0 to 5 knots). One period of light winds lasted nearly 15 minutes during which the balloon moved less than one eighth of a mile. The background flow then strengthened (5 to 10 knots) as a sea breeze front moved in and the balloon continued moving northwest.

Analysis of the surface wind patterns reveals a change in wind direction ahead of the bay breeze and sea breeze fronts. This pattern began at the coastline of Galveston Bay at 1600 UTC with a reversal to easterly winds (Fig. 24b). By 1800 UTC the wind reversals indicated penetration up to just south of the Ship Channel with a large plume of
highly concentrated ozone behind it (Fig. 24d). By 1900 UTC the surface wind reversals were just north of the Ship Channel (Fig. 24e).

At 19:35 UTC, the sea breeze front caught up with the balloon just as it crossed the Ship Channel. The balloon was lifted from ~ 325 m to ~ 1150 m due to vertical motion along the sea breeze front. This ascent took ~ 8 minutes, which translates to a rate of lift of ~ 1.7 m s\(^{-1}\). This rise in balloon height suggests that enhanced concentrations of ozone were brought higher into the boundary layer. The balloon was then brought back down in the sinking air behind the sea breeze front. Beginning at an altitude of ~ 1050 m, the balloon descended to an altitude of ~ 100 m by 2000 UTC. The descent took ~ 9 minutes, giving a rate of decent of ~ 1.8 m s\(^{-1}\).

The balloon 2 flight was terminated early by Randy Johnson as a precaution. There had been communication problems with the balloon as it was heading toward George Bush International Airport. Balloon 2 landed in a neighborhood 2 km southeast of the airport, where it was recovered (Fig. 25).

3.3 – Balloon 5: 13 September 2006

3.3.1 – 13 September Synoptic Weather Summary

The day of 13 September saw the arrival of another cold front through Houston. By 0300 UTC the cold front had not yet moved into Houston, but by 1200 UTC the front was moving through the city (Fig. 26a, b). By 2100 UTC the front had moved well offshore, pushed southward by northerly winds of 10 knots (Fig. 26c). As in the case of 30 August, the cleaner air advected behind the front, combined with precipitation, reduced background ozone values. Soundings from radiosonde balloons released on 13
September revealed that there was no well defined inversion in the lower troposphere present that day. Conditions in the lower troposphere were relatively moist from the surface to ~800 mb in the early morning hours (0700 UTC) before the front pushed through (Fig. 27a). By 1900 UTC, however, conditions above the surface were significantly drier, with a dew point depression of 22 °C at 1000 mb (Fig. 27b). Conditions were stable throughout the day. Surface temperatures were lower than normal, with the maximum temperatures between 33 and 34 °C over the heart of the city. Skies were mostly clear throughout the day with only a few cumuli developing.

The ozone concentrations on 13 September echoed those on 30 August in terms of reaching their maximum south of the city by the mid afternoon. Concentrations ranged between 70 and 80 ppb at their maximum for most of the regions south of the city, mainly over Brazoria County, with isolated observations into the 80s (Fig. 28).

3.3.2 – Balloon 5 Flight Summary

Balloon 5 was released at 13:00 UTC on 13 September into northerly flow under very clear sky conditions immediately following the passage of the cold front. The balloon remained between altitudes of 400 and 650 m for several hours as it moved south and off shore (Fig. 29). The balloon observed ozone concentrations increase from between 40 and 60 ppb at 1900 UTC to almost 100 ppb at 2000 UTC. This occurred during the early afternoon hours (1400 to 1500 CDT), which coincides with the timing for peak ozone production in the troposphere (Zhang and Rao 1999). The ozone values were as low as ~ 10 ppb at ~ 15:30 UTC when the balloon was flying over a rural and expectedly clean region in central Galveston County. The 13 September ozonesonde was
Released at 1700 UTC and revealed ozone concentrations between 50 and 70 over the lowest 5 km, consistent with the smart balloon observations. A peak concentration of 70 ppb is observed at ~2 km in the ozonesonde data, with falling values above this level, until the tropopause is reached and concentrations increase rapidly above ~15 km (Fig. 30).

At 19:45 UTC the balloon was raised quickly to 1600 m by the balloon operator and then gradually brought back down to 300 m over the next several hours. The timing of this altitude increase coincides with an increase in ozone concentrations of ~40 ppb over one hour, which may also be related to the generally conducive conditions of enhanced solar radiation and warmer afternoon temperatures during the afternoon of 13 September (Fig. 31). On 14 September, the balloon was instructed to perform a couple of soundings between 300 and 1500 m, but the balloon ended up striking the ocean surface during this process, and therefore the balloon was not recovered.

3.4 - Boundary Layer Characteristics

Balloon data were used to analyze the behavior of the air within the boundary layer over the vicinity of Houston. Balloon measured profiles of mixing ratio and $\theta_v$ can be used to assess the stability and degree of mixing, as well as the general location for the barrier between the surface and mixed layers (e.g., Fig. 1.9 in Stull 1988). The data show that balloon 1 flew near the top of the surface layer and into the lower portion of the mixed layer. The $\theta_v$ and mixing ratio profiles show relatively uniform values between 200 and 600 m, indicating significant vertical mixing in the lower boundary layer (Fig.
These data include balloon 1’s flight to just before arrival at the coast to remove additional moisture near the Gulf of Mexico.

The balloon 2 case was more complex than balloon 1, since it interacted with a sea breeze front, resulting in more scatter in the profiles (Fig. 33). Again, the data suggest that balloon 2 flew near the top of the surface layer and into the mixed layer. After being lifted up to 1200 m and descending back down, balloon 2 observed a general decrease in mixing ratio of approximately 2 g/kg (Fig. 34), as a result of the circulation at the sea breeze front bringing drier air from the upper boundary layer toward the surface; possibly from a residual layer. The mixing ratio trend line is less steep following the frontal passage, which implies drier air in the upper boundary layer. Note that Fig. 34a includes data from the ascent and descent along the sea breeze front. This figure represents both the process of motion along the sea breeze front as well as the collection of data (between 200 and 600 m) from the balloon flight segment before these motions.

There was also a 2 °C increase in $\theta_v$ (Fig. 35) in the air behind the sea breeze front. Air from the middle boundary layer descended dry adiabatically from higher than 1200 m and $\theta_v$ remained unchanged. Based upon Fig. 1.9 in Stull (1988), there is usually an inversion cap above a mixed layer indicating an entrainment zone between the boundary layer and the free atmosphere. $\theta_v$ is found to increase within this inversion. This implies that the air descending behind the sea breeze front must have descended from an entrainment zone in order to properly represent an increase in $\theta_v$. It should also be noted that Fig. 35a represents the data in terms of the process of motion along the sea breeze front as well as the collection of data before these motions.
The mixing ratio profile for balloon 5 over land looked much like that of balloons 1 and 2 (Fig. 36a). The $\theta_v$ profile, however, showed a slightly different structure (Fig. 36b). These data indicate that the top of the mixed layer was located at $\sim 400$ m just after the release of the balloon at 1300 UTC. Figure 36 reveals the stability of the air which is consistent with a post-frontal environment. The data varies $\pm 1$ g/kg in Fig. 36a, and $\pm 1$ $^\circ$C in Fig. 36b. Furthermore, the time and scale of $\theta_v$ changes are consistent with the diurnal deepening of the mixed layer, with $\theta_v$ steadily increasing during the course of the day (e.g., Fig. 1.7 and 1.12 in Stull 1988).

Pre-flight comparisons between the portable ozone sensor and the balloons revealed that the portable sensor consistently sampled an average of $\sim 10$ ppb below balloon 1 and $\sim 26$ ppb above balloon 2. Insufficient data were collected prior to the balloon 5 flight for a similar analysis. A comparison of ozone data from the balloons 1 and 2 and the surface data collected by car during tracking shows the mean ozone concentration increases with elevation in the boundary layer, and it also shows consistent trends in the ozone concentrations at the two levels (Fig. 37). Taking into account the pre-flight comparisons, the balloon 1 data trend is very close to the portable sensor trend (within 10 ppb apart) if 10 ppb is either added to the portable sensor data or subtracted from the balloon 1 data (Fig. 37a). Conversely, similar analysis for balloon 2 indicates an additional separation between the two datasets by $\sim 26$ ppb. The reduction of ozone concentration near the ground reflects the fact that the surface acts as a sink for ozone. This is also reflected in a significant downward spike of ozone within the car data at $\sim 19:35$ UTC, coinciding with travel through the Washburn Tunnel beneath the Ship Channel. The lower bounds of the ozone values measured by balloons 1 and 2 fall near
that of the concurrent car observations, suggesting the impact of significant vertical mixing taking place in the lower boundary layer. The 13 September case did not reveal much correlation, which may be explained by low magnitudes of turbulence and mixing during the morning hours (Fig. 37c).

A comparison of the in situ car data and the nearest grid-point values of the TCEQ surface analyses shows reasonable agreement (Fig. 38). The slight high bias may reflect drift in the calibration of the portable ozone sensors. Some of the localized periods of larger discrepancy may be partly explained by errors in the objective analysis over outlying parts of the surface network where observations are more widely spaced.

3.5- Spectral Analysis of Balloon Data

The boundary layer analysis confirms that turbulent mixing is occurring over Houston on the three days, particularly for 30 August and 1 September. The mechanism for this mixing involves the formation of thermals along the surface that circulate the air via eddies within the boundary layer. Eddies occur on all space and time scales in the boundary layer, and as the boundary layer grows so do the sizes of the thermals. The balloon behavior essentially provides information on the size of the thermals. While the complete details of the balloon behavior are beyond the scope of this thesis, a spectral analysis was applied to the balloon data in order to confirm that a Lagrangian frame of reference does not apply under a highly mixed environment. Confirmation of this within the vertical speed, vertical acceleration, and ozone data would validate, at least to some extent, the fluctuation in ozone associated with the vertical motion of air past the balloons.
Figure 39 is a collection of power spectra plots revealing the results of the spectral analysis. Balloon 1 vertical speeds and accelerations reveal common frequency bands with each other and with ozone in several locations (Fig. 39a, b). The highest energy common to all three products lay at 13.9 minutes, with supporting peaks at 8.06, 15.15 and the region between 23.8 to 26.3 minutes. For balloon 2 these common frequency bands lay at 31.3 and 23.3 minutes, with another peak at 55.6 minutes for vertical speeds and ozone and 58.9 minutes for vertical accelerations and ozone (Fig. 39c, d). Each matching frequency band denotes a cyclical phenomenon in the corresponding data at the specified time intervals. Analysis of the balloon 1 and 2 frequency bands indicates a common energy pattern among the three parameters between 23.3 and 23.8 minutes. The balloon 5 data, however, reveal no matching frequency bands among the three parameters (Fig. 39e, f).

Balloon 1 and 2 were released on days in which vertical mixing and turbulence were present, particularly for 1 September. Balloon 5, on the other hand, flew over land primarily during the morning hours of 13 September when vertical mixing is expected to be at a minimum. The spectral analysis data for balloons 1 and 2 suggest that ozone circulates with the air past the balloons as they are moved vertically by thermals. Balloon 5 yields no such suggestion since vertical mixing is low.
CHAPTER 4
DISCUSSION AND CONCLUSIONS

4.1 – Discussion

The smart balloons performed very well in terms of their ability to collect data that document conditions in the atmospheric boundary layer important to understanding the evolution of the ozone distribution. Observations of mixing ratio and virtual potential temperature reveal significant vertical mixing in the lower boundary layer that increases by the early afternoon. Ozone and primary pollutants disperse thoroughly within this mixed layer. Both the balloon and the NOAA Twin Otter platforms show evidence of vertical ventilation of ozone throughout the boundary layer, with lidar cross sections revealing concentrations of 100 ppb extending to at least 1200 m. As Zhang and Rao (1999) discuss, such transport allows ozone and primary pollutants to become trapped in stable and residual layers overnight; thus providing an influence on air quality the next day. These observations also have significance for long-range ozone transport. Spectral analysis confirms common frequencies among the vertical motion and ozone data, suggesting movement of ozone with vertical ventilation.

The smart balloons document the presence and influence of thermals in terms of their ability to mix pollutants within the boundary layer. Thermals come to rest, with a burst of mixing, when they reach their levels of (dilute) neutral buoyancy, while the interior of a thermal is inhomogeneous and contains fluid that is undiluted (Sánchez et al. 1989). This supports the argument that "spikes" in ozone occur when the thermal in which a balloon is embedded "bursts" at the end of its trajectory. This could possibly account for much of the balloon ozone variability at discrete times. Furthermore,
comparison between the car and balloon data should take into consideration that plumes of ozone are isolated both horizontally and vertically. There is a decrease in vertical velocity the closer in proximity a parcel is to the ground, and anything sampled near the ground would essentially be sampled within a thermal that has had little chance to become organized.

Each dataset within this analysis depicts the evolution of ozone as the three days progress. Trends in the balloon data correlate with those observed in the car data (Fig. 37), and the car data are shown to correlate with the TCEQ surface network data with similar evolution trends at the surface (Fig. 38). In sum, the data presented here document a consistent temporal and spatial evolution of ozone.

A “washing-out” phenomenon was observed primarily in the car datasets collected with the polyethylene tube. The consistent patterns for this phenomenon revealed that ozone concentrations would decrease with increasing car speed and visa versa. A reasonable explanation for this involves the aerodynamic lift of cleaner air at the road surface over the top of the car as it moves at higher speeds. This air is then sampled by the tube instead of the typical air at 1.5 m.

The events described here verify many of the key elements identified by Banta et al. (2005) for extreme ozone formation events, including a stagnation episode, pollutant transport along a nocturnal jet, a late morning bay breeze arrival, and vertical transport along a sea breeze front. However, consistent with the observation of ozone levels remaining ≤ 150 ppb, not all five elements occurred on the same day during TexAQS II. Banta’s event occurred in the midst of a heat wave. Temperatures had been over 40 °C
for more than a week. The three days in this analysis, however, were much cooler by comparison (~35 °C maxima), therefore, chemical reactions were slower.

On both 30 August and 13 September the prevailing synoptic flow was northerly at ~10 knots, and on both days the maximum ozone concentrations occurred south of the city. In this scenario there are two factors contributing to these observations of ozone: First, there was a contribution of ozone that had already been produced over the metropolitan region of Houston which was then carried south in the background, northerly flow. Second, primary pollutants were also pushed to the south of Houston, where ample sunlight photochemically produced ozone from NO₂. In addition to this were NO₂ molecules originating from PAN after oxidation of VOCs. This supports previous findings of higher ozone production efficiency in the Houston region (Kleinman et al, 2002, Lei et al. 2004).

The maximum temperatures for all three days were over the urban core (Figs. 2 and 40), and to the north of the maximum ozone, while the coldest temperatures were to the southeast over Galveston Bay and the Gulf of Mexico. It is expected that higher temperatures speed up the formation of additional ozone based upon the conversion of PAN molecules into NO₂ (Banta et al. 2005). However, advection by the stronger synoptic flow appears to dilute and disperse the contribution of PAN from over the city. The colder temperatures overlying Brazoria and Galveston counties would not be expected to yield as efficient production of NO₂ as the warmer temperatures over the urban core.

Meteorological conditions on 1 September 2006 were closest to the conditions described in Banta et al (2005). A nocturnal jet was present in radar profile data on the
night before the 1 September ozone episode (Figs. 18 and 19). In addition, stagnant conditions allowed enhanced accumulation of pollutants, which supports similar findings by Banta et al. (2002), Senff et al. (2002), and Darby et al. (2005). During the afternoon, a sea-breeze front moved onshore and advected enhanced ozone concentrations northwestward over the city. The northerly flows on 30 August and 13 September were too strong to allow such stagnation and sea breeze events to occur.

The smart balloons helped document both the distribution of tropospheric ozone above the surface and boundary layer structure in the vicinity of Houston, providing critical information on the background meteorology. However, it should be stressed that these data provide only a part of the picture. For a complete understanding of the ozone evolution, the precursor chemistry must be simultaneously measured and the photochemical processes and chemical reactions must be modeled. These topics are beyond the scope of this thesis and are the subject of active investigation by other researchers involved in TexAQS II, including the team from UNH.

4.2 – Conclusions

This thesis presents an analysis of the synoptic-scale influences and boundary layer processes associated with the accumulation and distribution of tropospheric ozone over Houston, Texas. Smart balloons represent a special tool to better understand the evolution of the ozone above the surface. In addition, observations taken at the surface and from aircraft supplement these balloon data.

The analysis focuses on three days during TexAQS II, 30 August, 1 September and 13 September 2006. Two synoptic weather regimes occurred: northerly flow
following a frontal passage, and light background flow instigating stagnant conditions followed by bay breeze and sea breeze events bringing southeasterly flow to the Houston metropolitan region. Primary conclusions of the research include the following.

- Analysis of surface temperature data reveals a large urban heat island near the center of Harris County. Temperatures in the heat island were ~ 1 °C warmer than surrounding surface temperatures.

- In each case enhanced surface ozone accumulates downwind of the Ship Channel, indicating the importance of advection by the background flow. If the background flow places the urban heat island downwind of the Ship Channel, higher temperatures there lead to additional enhancement of ozone concentrations.

- Cross sections from the NOAA Twin Otter lidar confirm the degree of turbulence and extent of the mixed layer in the boundary layer over Houston. Comparisons between ozone values observed by car, Twin Otter lidar, and smart balloon suggest local variability of ozone concentrations on the scale of thermals (~1 km).

- The balloon data provide evidence that the boundary layer over Houston contains a complex mixed layer that grows rapidly during the day. For the 30 August and 1 September cases this mixed layer was characterized by a greater amount of mixing as deduced by the steep slope of mean mixing ratio profile (Figs. 32, 34a).

- Spectral analysis of the balloon data reveals common frequency bands among the vertical speed, vertical acceleration and ozone data for balloons 1 and 2 (Fig. 39). This suggests vertical movement of ozone past the balloons as they interact with thermals and eddy circulation from the surface.
Data from balloon 2 show a vertical transport up to 1200 m along the sea breeze front. This underscores the significance of ozone transport into the middle and upper boundary layer by sea breeze processes.

Behind the sea breeze front mixing ratios were found to decrease by ~2 g/kg, and \( \theta_v \) values increased by ~2 °C (Figs. 33, 34). These observations show evidence of subsidence of drier air from the upper boundary layer associated with the vertical circulation of the sea breeze front.

Balloons 1 and 2 both show an unstable boundary layer. In the balloon 1 case the ozone trend measured at the surface correlates well with that at the balloon level. Overlap in the observed values reflects vertical mixing and the destruction of ozone at the ground.

Balloon 5 shows a stable boundary layer. In this case the ozone trend measured at the surface correlates less well with that at the balloon level.
Fig. 1. Schematic overview of the basic tropospheric cycle for ozone photochemistry. Thicker arrows indicate faster reaction speeds and visa versa. Yellow denotes photochemical reactions, blue are standard chemical reactions, and red is a reaction that depends on higher temperatures. Boxed chemicals are anthropogenic source inputs.
Fig. 2. Satellite image of Houston, Texas, with the four main counties of interest. Image © 2007 Google Imagery, © 2007 TerraMetrics, NASA, Map data © 2007 NAVTEQ™.
Fig. 3. Release of balloon 1 from La Porte Airport in La Porte, Texas, on 30 August 2006. On the left is Dr. Porter from UHM. In the center is Jonathan Tytell, a graduate student from the Department of Meteorology at UHM. On the right is Randy Johnson from NOAA ARLFRD.
Fig. 4. Mechanical schematic of the single tube single photodiode system (top). The system is composed of 3 subsystems: Optical, Gas Flow and Electrical subsystem. Finalized miniature ozone sensor used during TexAQS II (bottom). Designed at UNH.
Fig. 5. Flight trajectories for all six NOAA smart balloons from 8/30 to 9/14 with release dates indicated. The Balloon 1 track continues beyond 28° N.
Fig. 6. Surface analysis for Texas on 30 August, 2006 at (a) 0300 UTC, and (b) 1200 UTC.
Fig. 6. (c) As in Fig. 6a, but for 2100 UTC.
Fig. 7. Radiosondes launched from UH on 30 August 2006 at (a) 0700 UTC, and (b) 1315 UTC.
Fig. 7. (c) As in Fig. 7a. but for 1900 UTC.
Fig. 8. Ozone contour map and car location (star) with in situ sampled ozone concentrations on 30 August 2006 at (a) 1620 UTC, (b) 1830 UTC, (c) 2130 UTC, and (d) 2300 UTC. Car tracking route (black line) also plotted for (a), (b), and (c).
Fig. 9. Balloon 1 ozone (black line) and altitude (dashed green line) vs. time between 1610 UTC and 2107 UTC on 30 August.
Fig. 10. Flight path for NOAA Twin Otter on 30 August, 2006. Ozone reported as layer averages between 500 and 1000 m ASL.
Fig. 11. Ozone lidar cross sections from the 30 August, 2006 flight of the NOAA Twin Otter. Boxed section is shown in Fig. 15.
Fig. 12. Ozone sonde launched from UH at 1800 UTC on 30 August. Red line is ozone mixing ratio in ppbv, green line is ozone mixing ratio in ppmv, blue line is relative humidity in percent.
Fig. 13. NOAA Twin Otter flight leg (black line), balloon 1 track (red line), and car route portion (grey line) on 30 August.

Fig. 14. Zoomed in portion of the 30 August NOAA Twin Otter flight leg shown in Fig. 11. Boxed section depicted in Fig. 15.

Fig. 15. Closer analysis of 30 August NOAA Twin Otter segment around 2200 UTC with data presented in 1 km intervals. Blue marks indicate range of balloon 1 flight.
Fig. 16. Five-minute averaged ozone data (black line) and altitude (green line) vs. distance and time for Balloon 1 on 30 August. Superimposed grid uses same color spectrum as NOAA Twin Otter. The color scale is the same as in Fig. 15.
Fig. 17. Surface analysis for Texas on 1 September 2006 from (a) 0300 UTC, and (b) 1200 UTC.
Fig. 17. (c) As in Fig. 17a, but for 2100 UTC.
Fig. 18. La Porte Airport time series of data from 31 August.
Fig. 20. Radiosondes launched from UH on 1 September 2006 at (a) 0500 UTC, and (b) 1000 UTC.
Fig. 20. As in Fig. 20a, but for (c) 1600 UTC on 1 September 2006 and (d) 0100 UTC on 2 September 2006.
Fig. 21. As in Fig. 8, but for (a) 1600 UTC, (b) 1700 UTC, (c) 1800 UTC, (d) 1900 UTC, (e) 2000 UTC, and (f) 2100 UTC on 1 September 2006.
Fig. 22. Ozonesonde launched from UH at 1800 UTC on 1 September. Red line is ozone mixing ratio in ppbv, green line is ozone mixing ratio in ppmv, blue line is relative humidity in percent.
Fig. 23. Balloon 2 ozone (black line) and altitude (dashed green line) vs. time between 1545 UTC and 2140 UTC on 1 September.
Fig. 24. Standard surface wind directions with wind barbs for (a) 1500 UTC and (b) 1600 UTC on 1 September 2006. Surface ozone concentrations and balloon 2 position (white circle) and 5 minute average altitude are also shown.
Fig. 24. As in Fig. 24a, but for (c) 1700 UTC and (d) 1800 UTC. Ozone contours based upon 5-minute averages: Grey 100-124, Light Orange 125-144, Dark Orange > 144 ppb.
Fig. 24. As in Fig. 24a, but for (e) 1900 UTC and (f) 1930 UTC. Ozone contours based upon 5-minute averages: Grey 100-124, Light Orange 125-144, Dark Orange > 144 ppb.
Fig. 24. As in Fig. 24a, but for (g) 1945 UTC and (h) 2000 UTC. Ozone contours based upon 5-minute averages: Grey 100-124, Light Orange 125-144, Dark Orange > 144, Red > 164 ppb.
Fig. 24. (i) As in Fig. 24a, but for 2100 UTC. Ozone contours based upon 5-minute averages: Grey 100-124, Light Orange 125-144, Dark Orange > 144, Red > 164 ppb.
Fig. 25. Recovery of balloon 2 at 2145 UTC on 1 September 2006.
Fig. 26. Surface analysis for Texas on 13 September 2006 from (a) 0300 UTC and (b) 1200 UTC.
Fig. 26. (c) As in Fig. 26a, but for 2100 UTC.
Fig. 27. Radiosondes launched from UH on 13 September 2006 at (a) 0700 UTC and (b) 1900 UTC.
Fig. 28. As in Fig. 8, but for (a) 1400 UTC, (b) 1600 UTC, (c) 1800 UTC, and (d) 1945 UTC on 13 September 2006. 1945 UTC does not have in situ sampling of ozone.
Fig. 29. Balloon 5 ozone (black line) and altitude (dashed green line) vs. time between 1300 UTC and 1935 UTC on 13 September.
Fig. 30. Ozone sondes launched from UH at 1700 UTC on 13 September. Red line is ozone mixing ratio in ppbv, green line is ozone mixing ratio in ppmv, blue line is relative humidity in percent.
Fig. 31. Solar radiation (red line) and ozone trend (black line) vs. time for balloon 5 on 13 September 2006.
Fig. 32. Black dashed lines are cubic polynomial best-fit lines. (a) Balloon 1 altitude vs. mixing ratio. (b) Balloon 1 altitude vs. virtual potential temperature, $\theta_v$. 
Fig. 33. As in Fig. 32a, but for balloon 2.
Fig. 34. As in Fig. 32a. (a) Balloon 2 altitude vs. mixing ratio before interaction with sea breeze front. (b) Balloon 2 altitude vs. mixing ratio after interaction with sea breeze front.
Fig. 35. As in Fig. 34, but for $\theta_v$. 
Fig. 36. As in Fig. 32, but for balloon 5.
Fig. 37. Balloon 1 (a) and balloon 2 (b) ozone in the form of 5 minute moving averages (red) compared with in situ ozone sampled via the car (blue) vs. time. Black dashed lines are quadratic polynomial approximations indicating ozone production.
Fig. 37. (c) As in Fig. 37a, but for balloon 5 ozone and corresponding car ozone.
Fig. 38. Car ozone 5 minute averages (black dots) plotted in the midst of color contour ranges from TCEQ data (green bars) for (a) 30 August and (b) 1 September 2006.
Fig. 38. As in Fig. 38a, but for (c) early daylight hours and (d) late morning to early afternoon hours on 13 September 2006.
Fig. 39. Spectral analysis of balloon 1. (a) Spectral density of vertical speeds (black) and ozone (red) vs. frequency. (b) Spectral density of vertical acceleration (black) and ozone (red) vs. frequency. Common frequency bands are labeled in terms of their corresponding timescales in minutes.
Fig. 39. As in Fig. 39a, b but for balloon 2.
Fig. 39. As in Fig. 39a, b but for balloon 5.
Fig. 40. Maximum surface temperature contours for (a) 2300 UTC on 30 August, (b) 2120 UTC on 1 September, and (c) 2140 UTC on 13 September 2006. Black circle denotes general location of urban heat island.
Background understanding of ozone chemistry and distribution is required before exploring the meteorological environment around Houston. \( \text{NO}_x \) chemistry is actually defined by the combination of the molecules \( \text{NO} \) and \( \text{NO}_2 \). Reactions governing \( \text{NO}_x \) in relation to ozone (\( \text{O}_3 \)) directly determine the production of ozone in the troposphere:

\[
\text{NO}_2 + \text{hv} \rightarrow \text{NO} + \text{O}^3\text{P} \quad (1)
\]

\[
\text{O}^3\text{P} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \quad (2)
\]

Where \( \text{O}^3\text{P} \) is a ground state oxygen atom, and \( \text{M} \) is an air molecule. Reaction (1) is a rapid photochemical process via solar ultraviolet radiation, while reaction (2) is the only significant reaction that forms ozone in the troposphere (EPA 2006b, Seinfeld and Pandis 2006).

Titration of ozone occurs as follows:

\[
\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \quad (3)
\]

This reaction occurs in locations where there are large concentrations of \( \text{NO} \), such as near freeways, and is a primary sink for ozone in the troposphere. This reaction is also part of the nighttime removal of ozone. Another important nitrogen based reaction involves the formation of the nitrate radical:

\[
\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2 \quad (4)
\]

Which photolizes rapidly to produce:

\[
\text{NO}_3^- + \text{hv} \rightarrow \text{NO} + \text{O}_2 \quad (10\%) \quad (5)
\]

\[
\text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2 + \text{O}^3\text{P} \quad (90\%) \quad (6)
\]

Nitrate concentrations are very low during the day, but increase at night.
Nighttime NO\textsubscript{x} chemistry is critical to understand because the presence of lingering NO\textsubscript{x} from the previous day will aid in the formation of additional ozone concentrations the following day. The titration reaction (3) is a very fast reaction that can completely or almost completely destroy ozone concentrations at night. Meanwhile, the formation of the nitrate radical (4) is tempered at the surface through a very fast reaction with NO:

\[ \text{NO}_3 + \text{NO} \rightarrow 2 \text{NO}_2 \]  

NO\textsubscript{x} can be removed at night through conversion to N\textsubscript{2}O\textsubscript{5}:

\[ \text{NO}_2 + \text{NO}_3 + \text{M} \leftrightarrow \text{N}_2\text{O}_5 + \text{M} \]  

This equilibrium reaction is temperature dependant. N\textsubscript{2}O\textsubscript{5} can be easily deposited to the surface directly or through combination with water vapor (Stuntz et al. 2004, Seinfeld and Pandis 2006):

\[ \text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 \]  
\[ \text{N}_2\text{O}_5 + 2 \text{H}_2\text{O} \rightarrow 2 \text{HNO}_3 + \text{H}_2\text{O} \]

Contribution from VOCs to ozone chemistry first involves the production of OH radicals. OH is considered to be the primary means of cleansing the troposphere as it photochemically oxidizes most anthropogenic and biogenic VOCs. The primary source for OH radicals occurs through photolysis of ozone by solar ultraviolet radiation at short wavelengths (less than 340 nm):

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}_2 + \text{O}(^1\text{D}) \]  
\[ \text{O}(^1\text{D}) + \text{H}_2\text{O} \rightarrow 2(\cdot\text{OH}) \]
O(\textsuperscript{1}D) is an activated form of oxygen that can revert to the ground state O(\textsuperscript{3}P) after collision with an O\textsubscript{2} or N\textsubscript{2} molecule, otherwise it combines with water through reaction (12) to produce additional OH radicals.

One of the many oxidation products from VOCs are organic peroxy radicals (RO\textsubscript{2}), where R is an organic molecule chain. These radicals combine with NO\textsubscript{x} to form peroxynitrates:

\begin{align*}
\text{RO}_2^- + \text{NO} & \rightarrow \text{RONO}_2 \quad (13) \\
\text{RO}_2^- + \text{NO}_2 & \rightarrow \text{RO}_2\text{NO}_2 \quad (14)
\end{align*}

Peroxynitrates commonly have very short lifetimes and are thermally unstable. In other words, they break down to their original reactants with the presence of additional heat. Under normal circumstances this implies that peroxynitrates are not very good reservoirs for NO\textsubscript{x}. Some exceptions to this, however, are the peroxycetyl nitrites (PANs), which are formed through oxidation and photolysis of carbonyl compounds. The lifetime for a PAN molecule depends on the environmental temperature. Warmer temperatures cause PAN molecules to break down and release NO\textsubscript{x} on a timescale of about one hour. The primary PAN molecule is peroxyacetyl nitrate [CH\textsubscript{3}C(O)OONO\textsubscript{2}], which is produced in significant quantities through the oxidation of most VOCs. The decomposition of PAN has been identified as a major source of NO\textsubscript{x} in remote regions of the troposphere (EPA 2006b).
REFERENCES


