



## **TexAQS II Radical Measurement Project (TRAMP)**

**TERC Project H78**

**Including Supplement projects:**

- 1) Nocturnal Mixing from Micropulse LIDAR measurements (TNMPL)**
- 2) PAN Measurements at the Aldine site [previously on Williams Tower (PAN-WT)]**
- 3) Vertical Mixing Experiment (VME)**

## **Final Report**

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**Houston Advanced Research Center (HARC)**

**By:**

**University of Houston  
Department of Geosciences  
Institute of Multi-Dimensional Air Quality Studies  
Houston, TX**

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Contact information:

Dr. Bernhard Rappenglück (PI)  
Department of Geosciences  
University of Houston  
4800 Calhoun Rd  
Houston, TX 77204-5007

Office 225A Old Science  
Phone 713-743-1834  
Fax 713-748-7906  
Email [brappenglueck@uh.edu](mailto:brappenglueck@uh.edu)

Dr. Barry Lefer (Co-PI)  
Department of Geosciences  
University of Houston  
4800 Calhoun Road  
Houston, TX 77204-5007

Office 223 Old Science  
Phone 713-743-3399  
Fax 713-748-7906  
Email [blefer@uh.edu](mailto:blefer@uh.edu)

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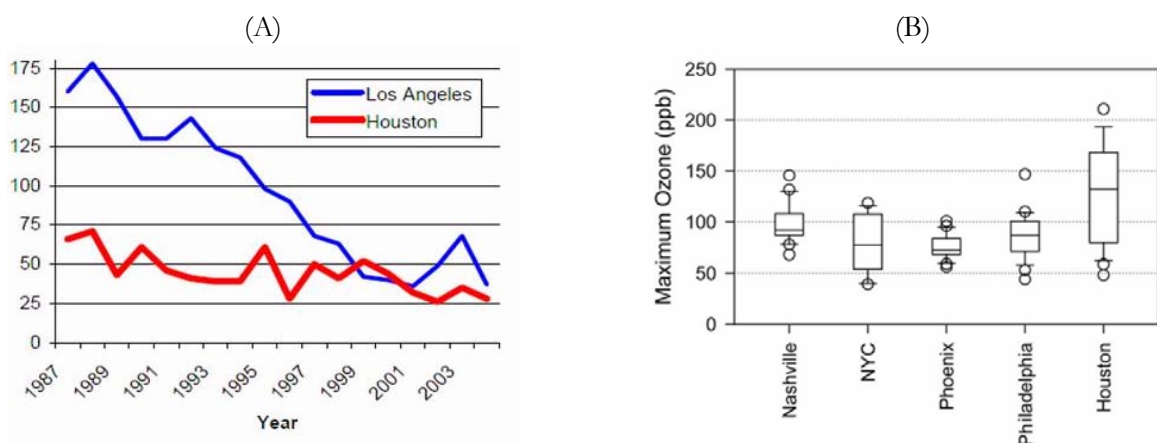


## 1. Introduction

### 1.1 Background

Urban zones represent areas in which significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. The Houston-Galveston Brazoria Area (HGB), located close to the Gulf of Mexico, is the fourth largest metropolitan area in the United States. Among major U.S. metropolitan areas, the HGB is the only one located in a subtropical region with extended hot and humid periods. Solar radiation is intense. Also, conditions with suppressed atmospheric mixing may occur. This specific climatology, along with strong emissions of primary species (carbon monoxide [CO], volatile organic compounds [VOCs] and nitrogen oxides [ $\text{NO}_x$ ;  $\text{NO}_x = \text{NO} + \text{NO}_2$ ]) favor strong photochemical processes. In reactions involving ozone ( $\text{O}_3$ ), hydroxyl ( $\text{OH}^\bullet$ ) and nitrate ( $\text{NO}_3^\bullet$ ) radicals, these primary emissions cause substantial formation of secondary species such as  $\text{O}_3$ , peroxyacetylic nitric anhydrides (PANs) and other trace gases [Atkinson, 2000; Jenkin and Clemmshaw, 2000]. In these reactions peroxy radicals ( $\text{RO}_2$ ) will be formed, which in turn will cause the conversion of NO to  $\text{NO}_2$  and subsequently the formation of  $\text{O}_3$ . With the degradation of VOCs, carbonyls will also be formed. These, in turn, may be photolyzed (e.g., formaldehyde) or oxidized by  $\text{OH}^\bullet$  and enhance PAN formation. Additionally, in the course of their oxidative degradation, the relatively volatile VOCs are transformed into higher boiling species that show a strong tendency to adhere to or to form particulate matter [Hoffmann *et al.*, 1997; Griffin *et al.*, 1999; Matsunaga *et al.*, 2003]. This secondary organic aerosol also activates atmospheric chemical feedback mechanisms, enhances cloud formation, and modifies the earth's radiation budget [Brasseur *et al.*, 1999].

The land-sea breeze system basically determines the distribution of trace gases in the HGB. In addition, the diurnal variation of the planetary boundary layer controls the accumulation of primary emitted species close to the surface and also decouples ozone enriched layers aloft during nighttime. Areas like HGB frequently suffer from severe loadings of a variety of air pollutants. High concentrations of primary toxic species and photooxidants in both the gas and particle phases can result in serious health effects, as well as ecological damage and economic losses. Photochemical smog episodes are common phenomena in the HGB. Comparisons with a number of other major US metropolitan areas indicate that while peak  $\text{O}_3$  levels have decreased significantly in Los Angeles and also appreciably in the HGB over the last few years, it seems that little improvement in the number of exceedances of peak ozone levels has been observed in the HGB (see Fig. 1). Although several U.S. cities have higher particulate levels than does Houston, the higher levels of a number of hazardous pollutants may exacerbate the health effects of area particles.



**Figure 1:** (A) Annual days exceeding federal one-hour ozone standard [HCPC, 2005]; (B) distribution for the peak ozone concentration observed on aircraft flights in five US cities [Kleinman *et al.*, 2002].

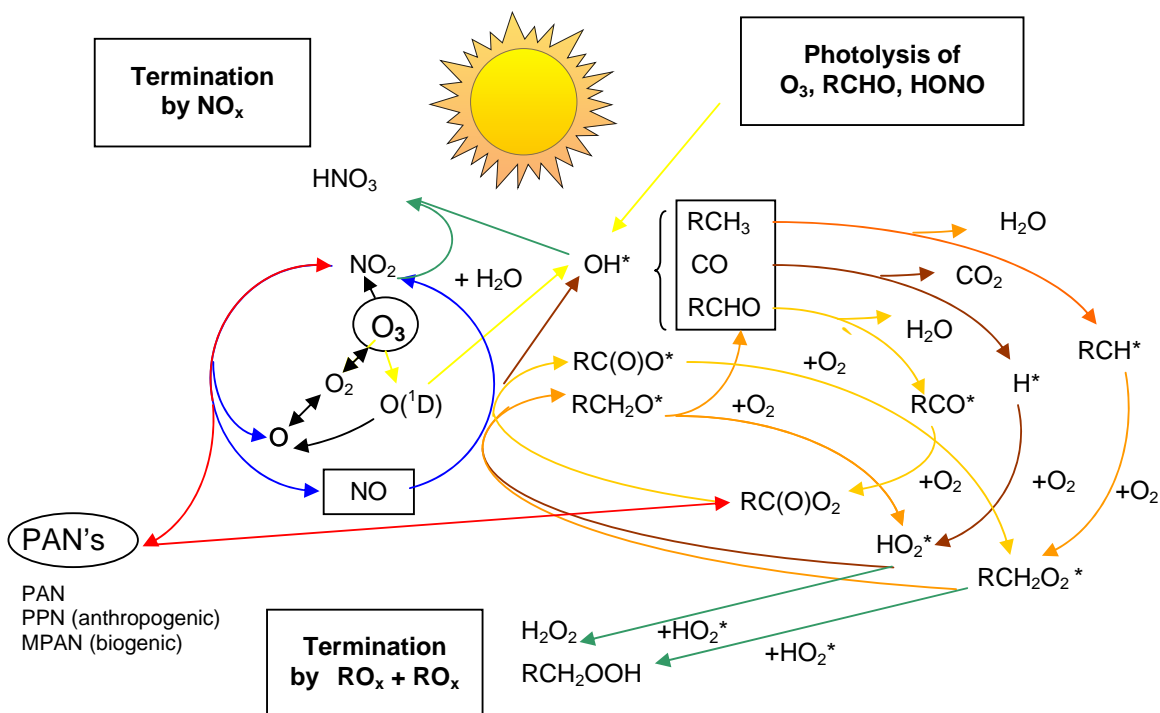
The Texas Air Quality Study 2000 campaign (TexAQS 2000) provided a wealth of data about the unique air chemistry and meteorological conditions that prevail in the Houston area. These studies revealed that the HGB often encounters critical loadings of a variety of species [Roberts *et al.*, 2001, 2003; Karl *et al.*, 2003; Ryerson *et al.*, 2003; Berkowitz *et al.*, 2004; Stutz *et al.*, 2004]. Investigations mainly focused on the rapid O<sub>3</sub> formation processes, which appear to be associated with releases of highly reactive VOCs from industrial facilities [Kleinman *et al.*, 2002 and 2004; Daum *et al.*, 2003; Ryerson *et al.*, 2003; Daum *et al.*, 2004; Berkowitz *et al.*, 2005; Springston *et al.*, 2005], and on the related HGB meteorological conditions that promote O<sub>3</sub> formation [Berkowitz *et al.*, 2004; Banta *et al.*, 2005]. These findings were supported by numerical modeling [Jiang and Fast, 2004]. A few recent publications address the formation of secondary species other than O<sub>3</sub>. For example, Wert *et al.* [2003] and Dasgupta *et al.* [2005] discuss measurements of oxygenated hydrocarbons, and Russell and Allen [2005] carried out the first modeling studies of the formation of SOA due to biogenic hydrocarbon precursors.

The objective of the TRAMP (TexAQS II Radical Measurement Project) is to support the TexAQS II field experiment with a selected ground-based supersite which will bring together a broad suite of instrumentation to collect a comprehensive data set which will allow to elucidate fast radical chemistry occurring under high pollution events typical for the HGB. The study will be accomplished by an analysis of radical sources and sinks (and production and loss rates) as identified by a steady-state time dependent photochemical box model.

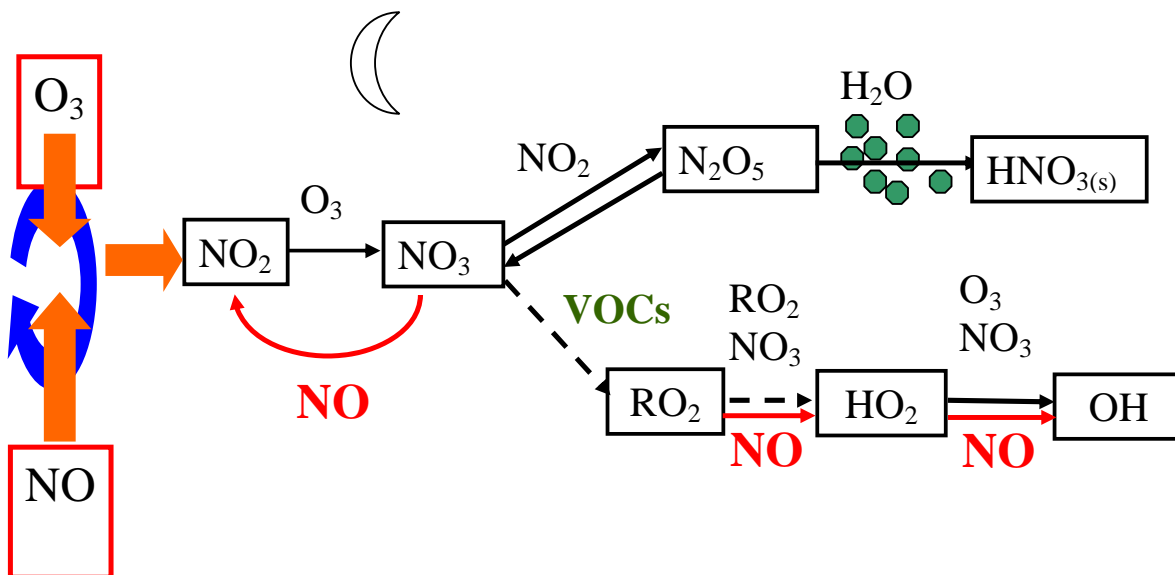
## 1.2 Project Goals

The project addresses the determination and quantification of sources and sinks for radicals in the urban atmosphere of Houston during the TexAQS II field campaign 2006. This is important for a better understanding of the formation processes of secondary species in the Houston area.

Fig. 2 describes in principle the fast reaction cycles involved in the formation of secondary species as well as the removal mechanisms from those cycles for nitrogen and carbon containing species. The hydroxyl radical (OH) is the most important oxidant in the atmosphere and controls the atmospheric lifetimes of most trace gases. OH is produced in photolysis processes of ozone (O<sub>3</sub>), formaldehyde (HCHO) and nitrous acid (HONO). OH initiates oxidation reactions with NO<sub>x</sub>, CO,



**Figure 2:** Daytime photochemical Processes



**Figure 3:** Nighttime radical chemistry.

anthropogenic and biogenic VOCs. These reactions form peroxy radicals ( $\text{RO}_2$ ) which in turn will cause the conversion of  $\text{NO}$  to  $\text{NO}_2$  and subsequently the formation of  $\text{O}_3$ . Within the degradation of VOC also carbonyls will be formed which either may be photolyzed (e.g. formaldehyde) or oxidized by  $\text{OH}$  and finally contribute to the formation of peroxyacetylic nitric anhydrides (PANs). Loss mechanisms for  $\text{OH}$  involve reactions between peroxy radicals leading to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) and organic peroxides, e.g. methylhydroperoxide (MHP) and hydroxymethylhydroperoxide (HMHP), and reactions with  $\text{NO}_2$  leading to nitric acid ( $\text{HNO}_3$ ) and PAN.

Figure 3 describes radical chemistry occurring during nighttime conditions. The main starting point in the absence of solar radiation is the formation of  $\text{NO}_3$  through the conversion of  $\text{NO}$  to  $\text{NO}_2$  and subsequently to  $\text{NO}_3$  in reactions involving  $\text{O}_3$ .  $\text{NO}_3$  may either react with  $\text{NO}_2$  or a suite of VOCs including aldehydes, alkanes, short lived alkenes, and fast reacting terpenes. This way either nitrogen compounds may be removed through formation of  $\text{HNO}_3$  on particles or  $\text{OH}$  radicals can be produced which in turn interact in fast reactions described in Figure 2.

The TRAMP project is designed to determine photochemical processing which is representative for the urban boundary layer area of Houston and to study the following research issues:

- What are the main sources and sinks for radicals in the urban air of Houston?*
- What processes determine the radical budget in the urban air of Houston?*
- What are the impacts with regard to the formation of secondary species?*
- What are the anthropogenic vs biogenic contributions in photochemical processes?*

In order to address these research issues a ground-based measurement system was set up for the TexAQS II intensive in August and September 2006. This site was equipped with state-of-the-art techniques to collect a comprehensive data set covering meteorological parameters, gas-phase chemistry using in-situ and long path instrumentation, physical and chemical aerosol properties including analysis of inorganic and organic aerosol content, and highly resolved measurements of the atmospheric radiation field including a wide range of photolysis rates which are critical for photochemical processes. This field experiment will be accomplished by an analysis of radical sources and sinks (and production and loss rates) as identified by a steady-state time dependent photochemical box model.

### 1.3 Project Plan

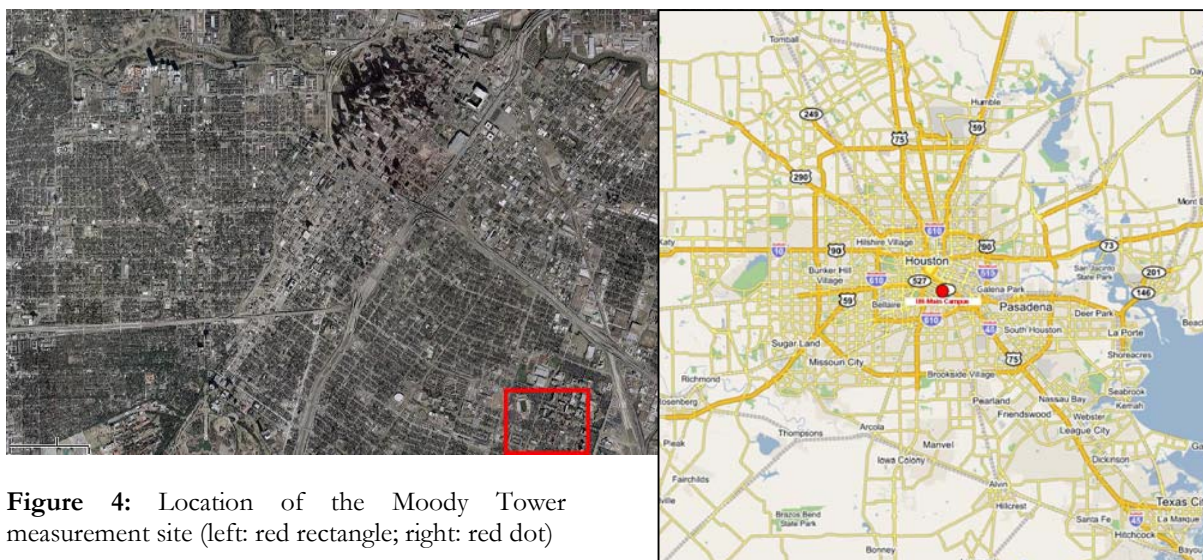
#### Infrastructure:

The University of Houston (UH) set up an air quality measurement facility at the University main campus on the roof of the 18-story tall North Moody Tower residence hall. The general information about this site is given in Table 1. This facility includes a 35 ft high sampling tower and is equipped with air chemistry measurements including O<sub>3</sub>, CO, NO, NO<sub>2</sub>, NO<sub>x</sub>, PAN, PPN, MPAN, online VOC, offline VOC capabilities, and meteorological instrumentation (T, RH, ws, wd, p, precipitation). It also includes measurements of photolysis frequencies for O<sub>3</sub>, NO<sub>2</sub>, HONO and HCHO and 16 other important photolysis reactions, aerosol optical depths (AOD) at UV/VIS/IR wavelengths, overhead O<sub>3</sub> column, and a cloud camera.

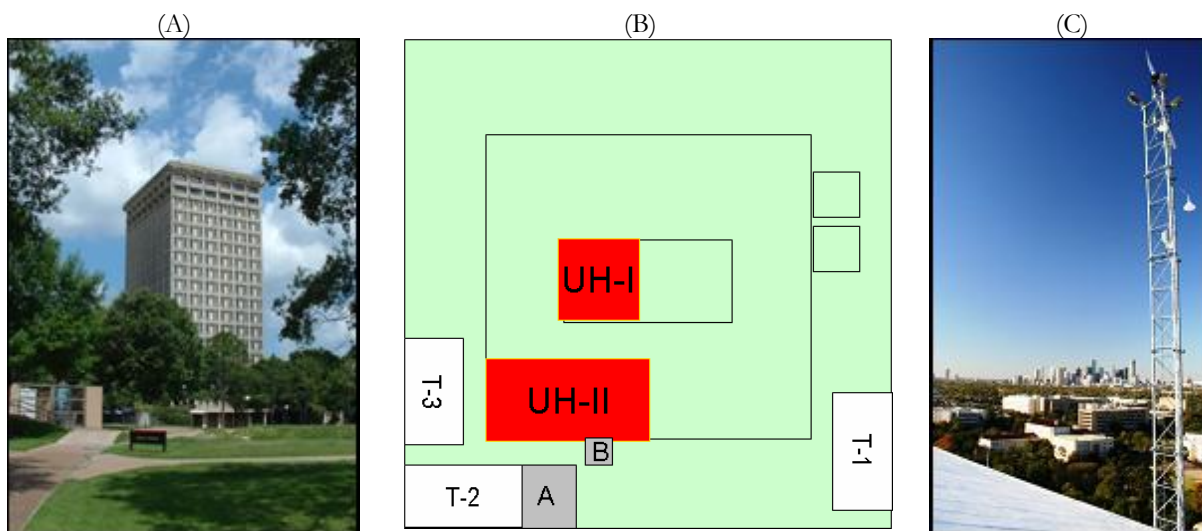
**Table 1: Moody Tower Site Description**

<b>Station Name:</b> Moody Tower	<b>Abbreviation:</b> MT
<b>coordinates:</b> 29° 43' 3.50" N, -95° 20' 28.50" W	
<b>Altitude:</b> 60 m a.g.l.	
<b>Responsible for site management:</b> B. Rappenglueck, B. Lefer, University of Houston	
<b>Notes:</b> Measurement site on campus of the University of Houston	

The UH campus is located in the Houston downtown area, however sufficiently away from any surface emission impacts and therefore an ideal location for the determination of photochemical processing which is representative for the urban boundary layer area of Houston and allows studies for source/sinks relationships. First measurements in 2005 revealed significant diurnal variations of trace gases. Maximum ozone values were comparable to surface sites. Also, mixing ratios of trace gases showed significant variations depending on the wind direction. Possible larger area and line emission sources are located at different distances to the Moody Tower measurements sites and thus allow to study different photochemical processing during day and nighttime.



**Figure 4:** Location of the Moody Tower measurement site (left: red rectangle; right: red dot)



**Figure 5:** The Moody Tower Measurement site: (A) The Moody Tower (60 m); (B) the layout for the TRAMP measurements on top of the Moody Tower: UH-I: UH radiation measurement platform; UH-II: UH atmospheric chemistry lab; T-1: trailer #1 hosting UCLA and UC instrumentation; T-2: trailer #2 hosting UNH, TAMU, and PSU instrumentation; T-3: trailer #3 hosting NOAA, PS, GaTech, and Rice U instrumentation; A: walk-up tower; B: UH meteorological tower equipped with air sampling inlets; (C) UH meteorological tower (denoted “B” in (C)) and view to Houston downtown.

#### Infrastructure enhancements made for TRAMP:

The accommodation of the additional instrumentation required some enhancements of the existing infrastructure, in terms of space and power needs. Figure 5 shows the layout for three additional temporary lab units on the balcony on the roof of the Moody Tower which were located close to the existing UH atmospheric chemistry lab. These labs were equipped with all necessary requirements, including work benches and air conditioning. Trailer T-1 had additional possibilities to locate instrumentation on the roof of their units. All labs were manufactured to carry all the instrumentation weight and will be hurricane proof.

Enhanced power requirements included all additional instrumentation as well as air conditioning devices needed for all 3 labs. Installation of these power needed wiring from the ground floor of the Moody Tower from central feeder units and installing several circuits serving 110V and 220V needs.

#### Measurements during TRAMP:

In order to address the project goals, a supersite was set up during the TexAQS II intensive in August and September 2006 which was equipped with state-of-the-art techniques to collect a comprehensive data set. The full suite of measurement activities and the corresponding responsible group is listed in Table 2. The exploitation and interpretation of the data sets obtained during the intensive, including modeling approaches, such as steady-state time dependant photochemical box model, will be coordinated in joint work groups. Data sets will also be made available to the entire TexAQS II scientific community.

**Table 2: List of Measurements at the Moody Tower Site**

Parameter	Measurement Instrument/Technique	Responsibility
Temperature	Campbell HMP45C	U Houston [Lefer & Rappenglueck]
Relative humidity	Campbell HMP45C	U Houston [Lefer & Rappenglueck]
Pressure	Campbell CS105	U Houston [Lefer & Rappenglueck]
Rain amount/rate	Campbell TE525	U Houston [Lefer & Rappenglueck]
Wind speed	Campbell 05103 R.M. Young	U Houston [Lefer & Rappenglueck]
Wind direction	Campbell 05103 R.M. Young	U Houston [Lefer & Rappenglueck]
O <sub>3</sub>	UV Photometry (TE 49C)	U Houston [Lefer & Rappenglueck]
CO	Gas Filter Correlation (TE 48C TL)	U Houston [Lefer & Rappenglueck]
NO, NO <sub>2</sub> , NO <sub>x</sub>	Chemiluminescence (TE 42C TL)/ BLD	U Houston [Lefer & Rappenglueck]
C <sub>2</sub> -C <sub>11</sub> NMHC	in-situ GC-FID (Perkin Elmer)	U Houston [B. Rappenglueck]
PAN, PPN, MPAN	in-situ GC-ECD (Metcon)	U Houston [B. Rappenglueck]
HCHO	Hantzsch reaction fluorescence	U Houston [B. Rappenglueck]
H <sub>2</sub> O <sub>2</sub>	liquid phase reaction fluorescence	U Houston [B. Rappenglueck]
Photolysis rates (O <sub>3</sub> , NO <sub>2</sub> , HONO, HCHO + 16 other photolysis rates)	Scanning actinic flux spectroradiometer (SAFS)	U Houston [B. Lefer]
UV/VIS AODs, Ozone Column	Brewer, CIMEL, UV-MFR, VIS-MFR	U Houston [B. Lefer]
Cloud camera	Total Sky Imager (Yes Inc)	U Houston [B. Lefer]
OH, HO <sub>2</sub> , RO <sub>2</sub>	GTHOS- Laser Induced Fluorescence	Penn State University [B. Brune]
OH reactivity	MAOR – discharge flow tube LIF	Penn State University [B. Brune]
Turbulent Heat Flux	3 D Sonic Anemometer	Penn State University [B. Brune]
NO, NO <sub>x</sub>	Chemiluminescence (TE 42C)	Penn State University [B. Brune]
O <sub>3</sub>	UV Photometry (TE 49C)	Penn State University [B. Brune]
Oxy-VOCs	PTR-MS	Texas A&M [R. Zhang]
HNO <sub>3</sub> , NO <sub>3</sub> , N <sub>2</sub> O <sub>5</sub>	ID-CIMS	Texas A&M [R. Zhang]
Aerosol Size Distribution	TDMA	Texas A&M [D. Collins]
Aerosol Size Distribution	SMPS, GRIMM, Streaker Impactor	Texas A & M [S. Brooks]
Aerosol backscatter remote sensing	Micropulse LIDAR	PNNL [C. Flynn]
SO <sub>2</sub>	Pulsed Fluorescence	NOAA – ARL [W. Luke]
NO <sub>y</sub>	O <sub>3</sub> Chemiluminescence	NOAA – ARL [W. Luke]
CO	Non-Dispersive Infrared	NOAA – ARL [W. Luke]
elemental, particle bound and reactive gaseous Hg	Cold Vapor Atomic Fluorescence (Tekran 2537a, 1130, 1135, and 1102)	NOAA – ARL [S. Brooks]
O <sub>3</sub> , SO <sub>2</sub> , NO <sub>2</sub> , NO <sub>3</sub> , HONO, HCHO	Long Path DOAS	U California Los Angeles [J. Stutz]
NO <sub>2</sub> , HCHO	Vertical profiles via Max DOAS	U California Los Angeles [J. Stutz]
NO <sub>2</sub> , HCHO	Vertical profiles via Max DOAS	Chalmers University [J. Mellquist]
CCN conc. at different supersaturations, exposure times and temperatures	Custom supersaturating column coupled to a phase-Doppler interferometer for drop sizing	University of California Santa Cruz [P. Chuang]
Aerosol optical extinction and scattering coeff., particle absorption coefficient, aerosol single-scattering albedo	tandem cavity ring-down transmissometer / nephelometer (CRD'N), TSI Model 3007 condensation particle counter	Portland State University [D. Atkinson]
Aerosol composition	AMS	U New Hampshire [R. Griffin]
Size-resolved mass concentration of organic carbon aerosol	Cascade Impactors	U New Hampshire [R. Griffin]
Fine and coarse aerosol composition	Versatile Air Pollutant Sampler (filter sampler)	U New Hampshire [R. Griffin]
Total number concentration of particles greater than 7 nm in diameter	Condensation particle counter (CPC)	U New Hampshire [R. Griffin]
Water soluble organic carbon gases and aerosols	Mist chamber collection and TOC analysis (Sievers 800 TOC Analyzer)	U New Hampshire [J. Dibb]
HNO <sub>3</sub> , HONO	Mist Chamber Ion Chromatograph	U New Hampshire [J. Dibb]
PM <sub>2.5</sub> Mass	TEOM	GaTech [R. Weber]
PM <sub>2.5</sub> Organic and elemental carbon	Sunset Labs	GaTech [R. Weber]
PM <sub>2.5</sub> aerosol composition	PILS	GaTech [R. Weber]
PM <sub>2.5</sub> Water soluble organic carbon	PILS	GaTech [R. Weber]
HCHO, C <sub>2</sub> H <sub>4</sub>	Laser Spectroscopy	Rice U [M. Fraser]
NO, O <sub>3</sub> , Aerosol Scat., total UV/VIS		Air Quality Design [M. Buhr]

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## 2. Individual Contributions of Participating Groups

### 2.1 University of Houston (PIs: B. Lefer, B. Rappenglueck)

#### Measurements of NO<sub>x</sub>, CO, O<sub>3</sub> and meteorological data during TRAMP

PIs: Barry Lefer, Bernhard Rappenglück

Collaborator: James Flynn

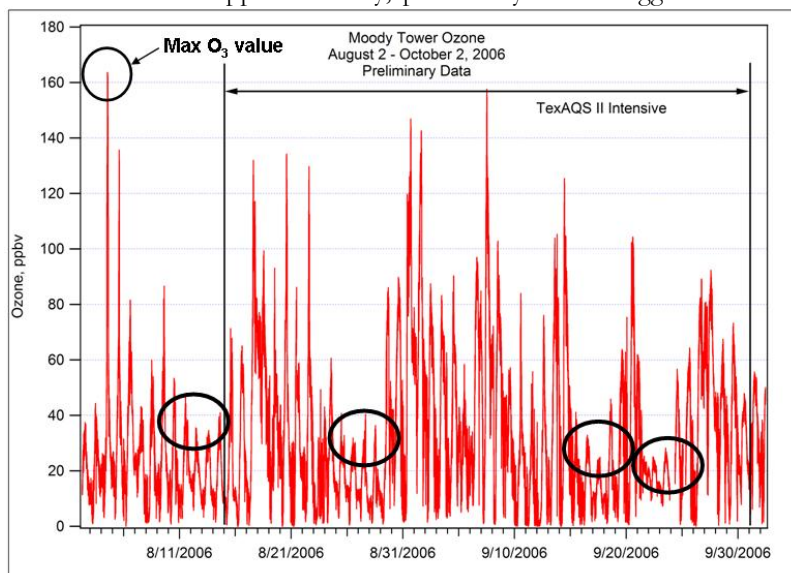
University of Houston

#### 1. Instrumentation

- Measured Parameters:
  - NO, NO<sub>2</sub>, NO<sub>x</sub>, CO, O<sub>3</sub>, and meteorological data
- Measurement Instrument/Technique:
  - NO, NO<sub>2</sub>, NO<sub>x</sub> Chemiluminescence (TE 42C TL) with a Blue Light Converter (DMT)
  - CO gas filter correlation (TE 48C TL)
  - O<sub>3</sub> UV photometry (TE 49C)
  - Meteorological data: temperature and relative humidity (Campbell HMP45C), pressure (Campbell CS105), rain amount/rate (Campbell TE525), wind speed and direction (Campbell 05103 R.M. Young)
- Deployment period:
  - 08/02 – 10/02/2006

#### 2. Preliminary results

Figure 1 shows the entire ozone time series as obtained at the Moody Tower during TRAMP. It can be seen that on quite a few days ozone levels exceeded 100 ppbv. The maximum ozone value occurred on 08/04 with more than 160 ppbv. Figure 1 also shows that on a couple of days maximum ozone levels were quite low between 20-40 ppbv. Actually, preliminary results suggest that low ozone values are associated with

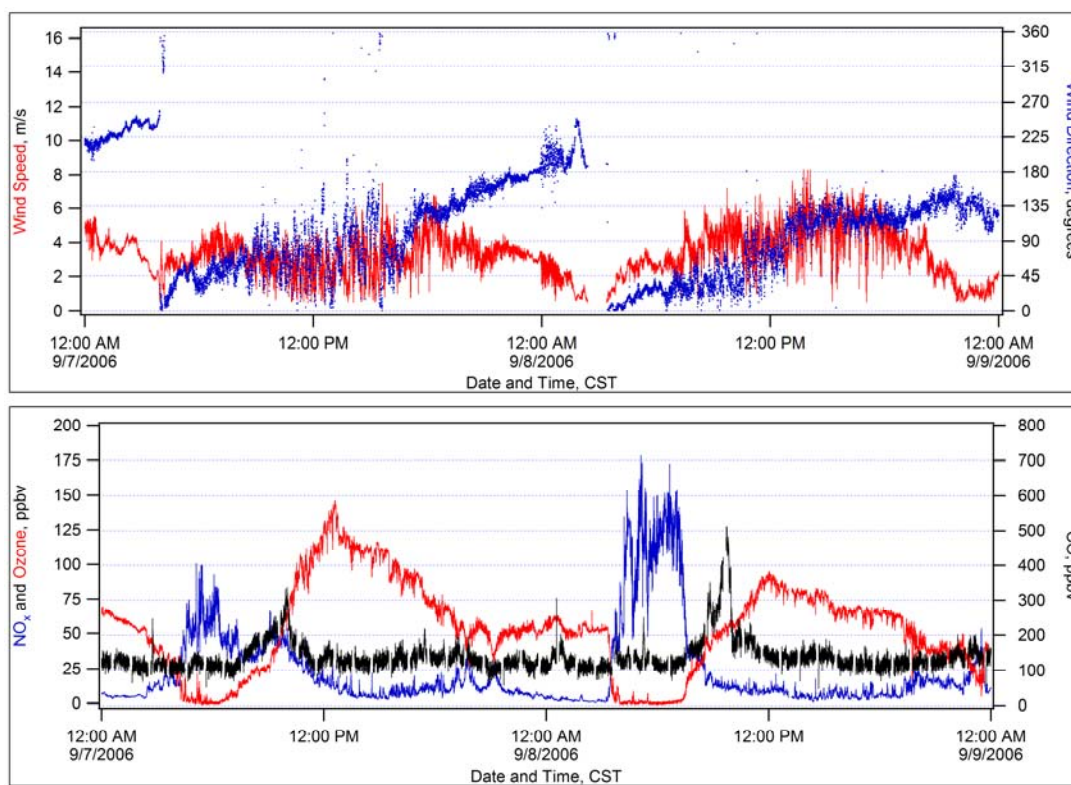


marine background air masses from southwesterly wind directions. Highest ozone values, including potential ozone O<sub>x</sub> [O<sub>x</sub> = O<sub>3</sub> + NO<sub>2</sub>], both under low wind and background conditions occur with easterly flow conditions. This large variability in ozone levels may also favour the conditions for high transient O<sub>3</sub> values.

**Figure 1:** Ozone time series during TRAMP in August and September 2006.

As an example Figure 2 displays time series of meteorological and air chemistry data obtained during an intensive observational period, when high ozone events were forecasted. On those days also rawinsonde launches were carried out on UH campus almost every 3 hrs. In addition tetheredsonde launches were performed during nighttime. As shown in Figure 2 wind patterns seem to follow a diurnal trend closely associated with the land-sea breeze system. In particular on the second day higher wind speeds are observed during the daytime. At that time wind direction is about SE. However, it seems that on the first day the land-sea breeze system is not fully developed. Wind speeds are slightly lower and wind flow is from E. This may be partly the reason why the maximum  $O_3$  value of both days actually occurred on the first day.

Looking into the precursors  $CO$  and  $NO_x$  some interesting features may be noted: comparing both days it seems that high mixing ratios of those precursors in the morning are not necessarily a prerequisite for high daytime  $O_3$  values. However, this may be partly due to the elevated location of this site (60 m a.g.l.). There are some indications based on the nighttime tetheredsonde launchings that on some days the site was above the boundary layer. Another observation is that though there are some coincident  $NO_x$  and  $CO$  peaks (e.g. on the morning of the first day) there are also periods with distinct elevated levels of  $NO_x$  and  $CO$  (e.g. morning hours of the second day) likely indicating different source patterns.



**Figure 2:** Time series of meteorological data (upper panel) and  $O_3$ ,  $CO$ , and  $NO_x$  on IOP days 09/7-8.

### 3. Work in Progress

Apart from more detailed evaluation of the  $NO_x$ ,  $CO$ , and  $O_3$  data set, including statistical interpretation, this data set will also be used in a collaborative effort with colleagues from Penn State and UCLA for photochemical box modelling to elucidate radical chemistry process. Also, this data will support studies of the nocturnal chemistry of  $NO_x$  and related species.

### 4. PIs Contact Address

Barry Lefer, [blefer@uh.edu](mailto:blefer@uh.edu), phone: 713-743-3250, fax: 713-748-7906

Bernhard Rappenglück, [brappenglueck@uh.edu](mailto:brappenglueck@uh.edu), phone: 713-743-1834, fax: 713-748-7906

## 2.2 University of Houston (PI: B. Rappenglueck)

### Measurements of VOCs, PANs, Formaldehyde, and Hydrogen Peroxide at the Moody Tower Site in Houston During TexAQS II

PI: Bernhard Rappenglück

Collaborators: Michael Leuchner, Bridget McEvoy-Day, Richard Fuller

University of Houston

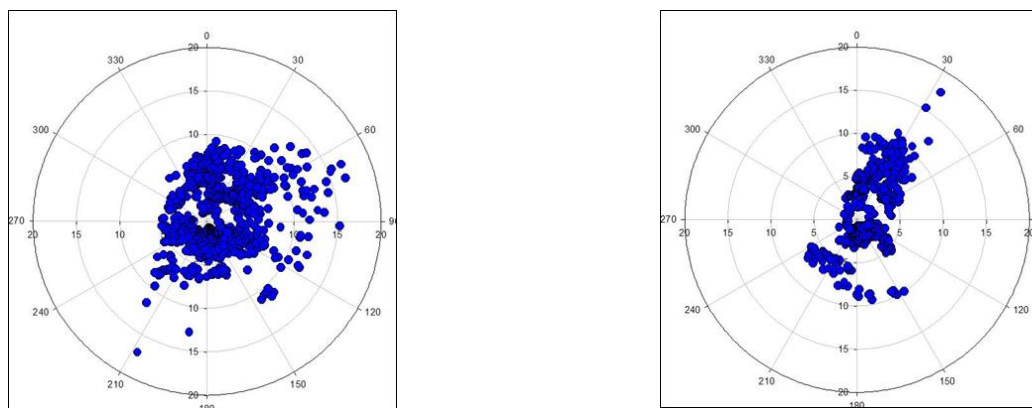
#### 1. Instrumentation

- Measured Parameters:
  - volatile organic compounds (VOCs), peroxyacetylic nitric anhydrides (PANs), formaldehyde (HCHO), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)
- Measurement Instrument/Technique/Period:
  - Speciated VOCs: on-line VOC GC-FID (Perkin Elmer Clarus 500 & Turbomatrix 650 ATD); 08/07 – 10/15/06
  - Speciated PANs: Metcon GC-ECD; 07/03 – 10/15/06
  - HCHO: AL4021 Aero-Laser, Hantzsch reaction fluorescence; 08/18 – 10/15/06
  - H<sub>2</sub>O<sub>2</sub>: AL2021 Aero-Laser, liquid phase reaction fluorescence; 09/14 – 10/15/06

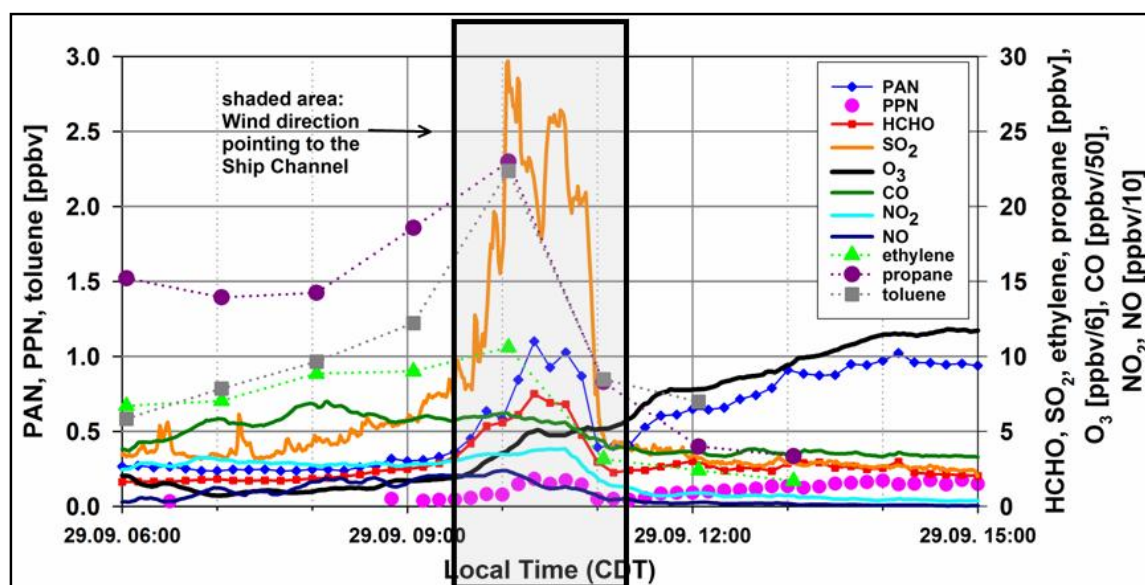
#### 2. Preliminary results

During the TexAQS II campaign in summer 2006 continuous measurements of speciated VOCs and PANs, HCHO, and H<sub>2</sub>O<sub>2</sub> were performed at the Moody Tower supersite on the University of Houston main campus. H<sub>2</sub>O<sub>2</sub> data has been finalized. Evaluation of the entire VOC and PAN data set is in its final stage. An intercomparison of the Hantzsch based HCHO instrumentation of UH and Baylor has been successfully carried out. We are still awaiting final crosschecks of the formaldehyde calibration gas cylinder at NCAR.

Some additional analysis based on the preliminary data are shown in Figure 1 and 2. As indicated in the Interim Report there are some indications for elevated nighttime levels of HCHO. Figure 1 displays HCHO wind roses for day- and nighttime for the selected time period September 15-30, 2006. These plots indicate that most secondary HCHO during daytime is associated with E-winds, presumably from Ship Channel direction. During nighttime however, there seems that elevated levels of HCHO are related to NE-winds. The nature of the origin of nighttime HCHO and whether it can be considered secondary or primary still needs to be further investigated. One potential source might also be coffee roasting facilities in these areas.



**Figure 1:** HCHO wind roses for daytime [6 am -8 pm] (left) and nighttime [8 pm – 6 am] (right) during the period September 15-30, 2006.



**Figure 2:** Selected time series of trace gases on September 29, 2006.

Figure 2 exhibits a special event in the early morning hours on 09/29/06 which showed enhanced HCHO together with significantly enhanced SO<sub>2</sub>, PAN, and PPN. O<sub>3</sub> does not seem to produce a similar peak. As far as primary species are concerned NO and selected VOC show highest values around 10 am. Afterwards there is a significant decrease of NO and VOCs while SO<sub>2</sub> stays at high levels and HCHO, PAN, and PPN develop a well defined peak. NO<sub>2</sub> seems to remain at constant levels throughout this time. It decreases at the same time, when SO<sub>2</sub>, HCHO, PAN, and PPN decrease. During this event wind direction pointed to the Ship Channel. As Dasupta et al. (2005) pointed out that the occurrence of elevated NO<sub>2</sub>, SO<sub>2</sub> and HCHO seems to be closely related to flares from refineries. Figure 2 shows an early morning event which is presumably also superimposed by the break-up of the morning inversion. If this is the case there might be an indication of downward mixing of SO<sub>2</sub>, HCHO, PAN, and PPN during this event. This also implies layers aloft which contain these species. Possible explanation might be high rising hot plumes of flares penetrating the nighttime/morning time inversion layer. However, still at this point further analysis will be necessary to assess the primary and secondary fraction of formaldehyde.

### 3. Work in Progress

Extensive evaluation of the data obtained during TRAMP is in its final stage. The data will be examined in terms of source reconciliations for VOCs, the photochemical processes involving HCHO, PANs and H<sub>2</sub>O<sub>2</sub>, and the assessment of primary vs. secondary fraction of HCHO.

### 4. References

Dasgupta P.K., Li J., Zhang G., Luke W.T., McClenny W.A., Stutz J., Fried A. (2005) Summertime ambient formaldehyde in five U.S. metropolitan areas: Nashville, Atlanta, Houston, Philadelphia, and Tampa, *Environ. Sci. Technol.*, **39**, 4767-4783

### 5. PI Contact Address

Bernhard Rappenglück, [brappenglueck@uh.edu](mailto:brappenglueck@uh.edu), phone: 713-743-1834, fax: 713-748-7906

## 2.3 University of Houston (PI: B. Lefer)

### Measurements of the impact of clouds and aerosols on solar radiation during TRAMP

PI: Barry Lefer, (University of Houston)

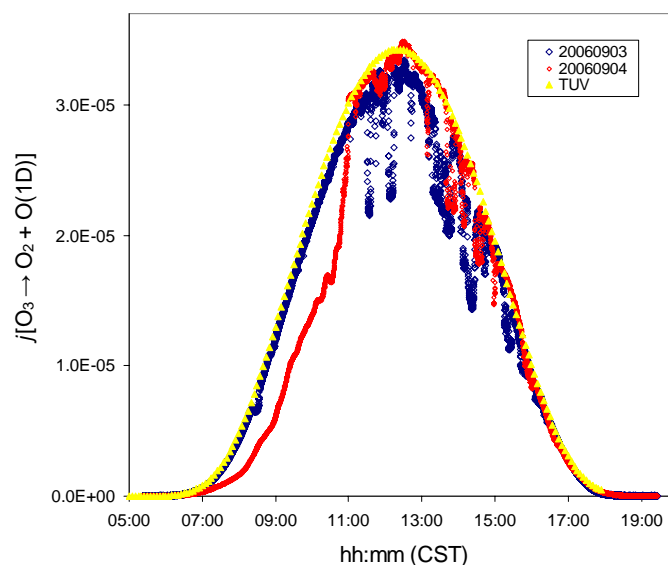
Collaborators: James Flynn (University of Houston), James Slusser (Colorado State University), Brent Holben (NASA GSFC), Patrick Disterhoff (NOAA ESRL)

#### 1. Instrumentation

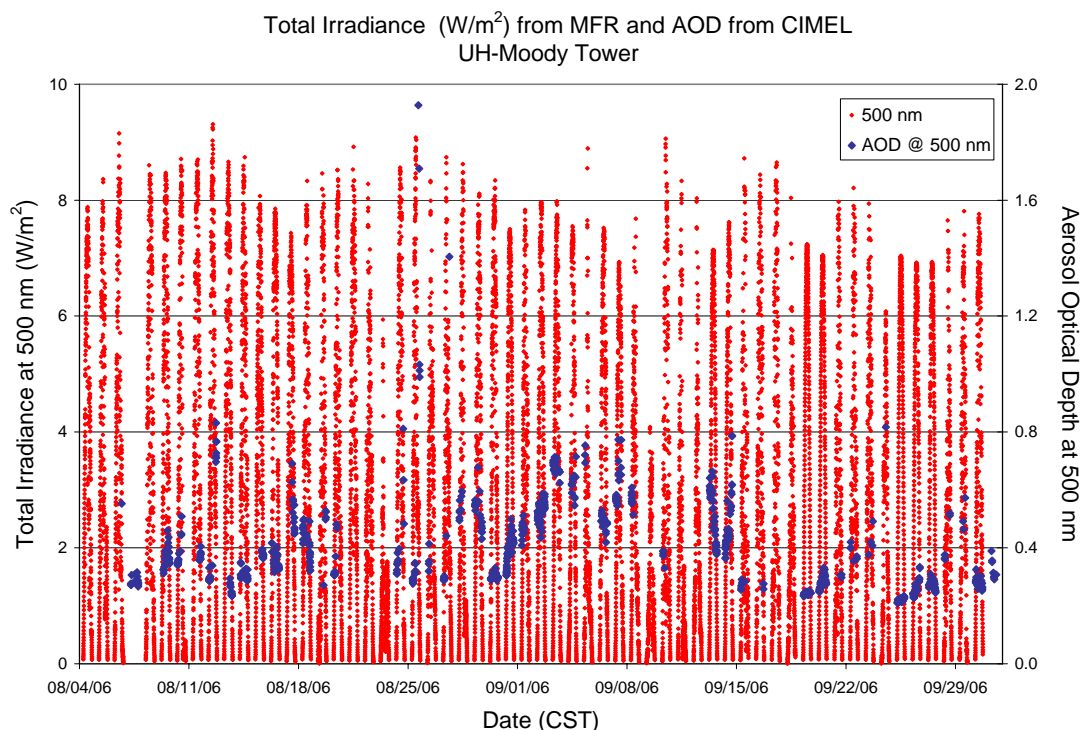
- Measured Parameters:
  - Actinic Flux (photolysis frequencies), Spectral direct/diffuse/total irradiance at selected UV & VIS & IR wavelengths.
- Measurement Instrument/Technique:
  - Scanning and Diode Array Actinic Flux Spectroradiometer (NCAR SAFS and Metcon DAAFS) used to calculate 23 different photolysis frequencies with 10 s time resolution. SAFS scans from 290 – 420 nm with 1 nm FWHM while DAFS spectrograph obtains actinic flux data from 280-700 nm with 2.7 nm FWHM with 1 pixel corresponding to approximately 0.8 nm.
  - UV and VIS Multi-Filter shadowband Radiometer (UV- and VIS-MFR) from YES used to measure total and diffuse irradiance at **300, 305, 311, 317, 325, 332, 368**, 415, 500, 610, 665, 862, and 940 nm. This dataset will be used to calculate aerosol + cloud optical depths and total ozone columns. The instrument suite also includes a broadband UV-B and PAR radiometers and is part of the USDA UV-B Monitoring Network administered by Colorado State University.
  - NASA AERONET CIMEL Sunphotometer (CE 318) site to calculate aerosol optical depths at 440, 500, 670, 870, 936, 1020 nm as well as total O<sub>3</sub>, NO<sub>2</sub>, and H<sub>2</sub>O columns. All sky scans can be used to infer other aerosol optical properties such as total column single scattering albedo.
  - Brewer Mark IV (S/N 154) Sunphotometer calibrated to obtain total ozone columns. This instrument will be part of a new NOAA EPA mini-network of Brewers in the continental United States.
  - Sky Cam (Metcon) with one hemispheric sky photo automatically taken every minute to build visual database of sky conditions (overcast, partly cloudy, sun occlusion, clear, etc).
- Deployment period:
  - 08/10 – 10/02/2006

#### 2. Preliminary results

The  $j[\text{O}_3 \rightarrow \text{O}(1\text{D}) + \text{O}_2]$  at the Moody Towers for two consecutive days (September 3<sup>rd</sup> and 4<sup>th</sup>, 2006) during TRAMP is shown in Figure 1. September 3<sup>rd</sup> it was fairly clear in the morning, while the 4<sup>th</sup> started off completely overcast and cleared up in the late morning. The cloud-free TUV radiative transfer model calculation for the 3<sup>rd</sup> is shown for comparison. Significant changes in photolysis frequencies due to clouds and aerosols were observed during the TRAMP campaign. The total irradiance at 500 nm measured by the MFR is shown for the entire TRAMP measurement period in Figure 2, along with the Level 1.5 (with preliminary cloud screening) AOD at 500 nm from the CIMEL for the same time period.



There were a few cloud-free days in mid- and late Sept., where the impact of aerosols on photolysis frequencies can be studied in more detail. It is worth noting that during the TRAMP measurement period a few “special” aerosol events (e.g., Saharan dust and biomass burning) were encountered.



### 3. Work in Progress

The measurements of ozone column (Brewer), optical depth (CIMEL /MFR), boundary layer height (PNNL aerosol LIDAR), single scattering albedo (Portland St) will be used to constrain TUV and then allow for more detailed photolysis frequency measurement/model comparisons. The ground-based aod and ozone column measurements will be compared to data from satellite overpasses, airborne LIDAR flights, and ozone sonde launches at the UH Main Campus.

Additional testing and calibrations are planned to further characterize the UH DAAFS system with respect to the NCAR SAFS. The data from the DAAFS will be used to fill gaps that may exist in the SAFS data and to support long-term measurements at UH.

Extensive evaluation of the impact of clouds and aerosols on ozone production during the TRAMP campaign will begin after the first preliminary data merge is complete. At that point we will start using the NASA LARC photochemical box model to calculate ozone production rates for three different j-value datasets: the measured j-values, the cloud-free, and aerosol-free model.

### 4. PI Contact Address

Barry Lefer, [blefer@uh.edu](mailto:blefer@uh.edu), phone: 713-743-3250, fax: 713-748-7906

## 2.4 Penn State University (PI: B. Brune)

### Atmospheric OH, HO<sub>2</sub> and OH reactivity Measurements during TRAMP

PI: William H. Brune

Collaborators: Xinrong Ren, Jingqiu Mao, Zhong Chen, Chris Beatty, Maria Cazorla-Andrade

Department of Meteorology, Pennsylvania State University

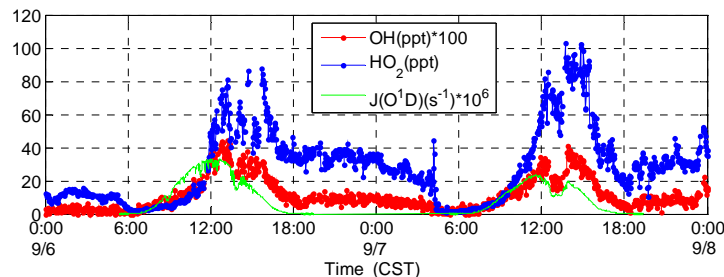
#### 1. Instrumentation

- Measured Parameters:
  - OH and HO<sub>2</sub> mixing ratios; OH reactivity; O<sub>3</sub>; NO; NO<sub>x</sub>; 3-D wind speed and wind direction
- Measurement Instrument/Technique:
  - GTHOS/LIF; MAOHR/discharge flow tube-LIF; commercial O<sub>3</sub> and NO<sub>x</sub> analyzers; 3-D sonic anemometer
- Deployment period:
  - August 11 – September 29, 2006

#### 2. Preliminary results

High quality measurements were made over the entire study period. Analysis of these measurements will test the understanding of oxidation chemistry and the dependence of that chemistry on the gaseous emissions in the Houston environment. The selection of the measurement site proved to excellent; the highly variable pollution levels that were encountered during the study allow us to examine the atmospheric oxidation chemistry over wide ranges of NO<sub>x</sub> and HO<sub>x</sub> sources that control the chemistry. In this preliminary report, we focus on just two days as an example of the types of analyses that will be possible with the larger, more variable data set.

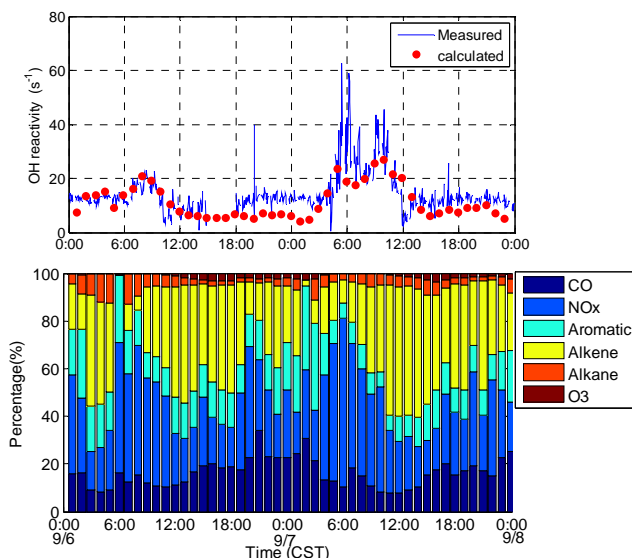
Observed mixing ratios of OH and HO<sub>2</sub> on 6 and 7 September 2006 at Moody tower show expected diurnal variations with respect to intensity of solar radiation (Fig. 1) because OH and HO<sub>2</sub> are primarily produced from photolysis reactions during the daytime. Significant nighttime HO<sub>2</sub> and OH levels were frequently observed, especially when nighttime ozone levels were high. For example, on the night of 6 and 7 September, ozone concentrations were as high as 60-80 ppbv. During the same period, 20-40 pptv of HO<sub>2</sub> and 0.05-0.1 pptv of OH were observed. High HO<sub>2</sub> mixing ratios on 7 September resulted in high ozone concentrations up to 150-160 ppbv. Ozone production rate from HO<sub>2</sub>+NO reaction was 30-40 ppbv/hour in the morning of 7 September.



**Figure 1:** Observed OH and HO<sub>2</sub> mixing ratios on 6 and 7 September, 2006 at Moody Tower during TRAMP. Also plotted is the ozone photolysis frequencies, J(O<sup>1</sup>D), indicating the variation of solar radiation.

Observed OH reactivity on 6 and 7 September shows that in the morning of 7 September, higher OH reactivity was observed than that on 6 September (Fig. 2). Higher OH reactivity on 7 September resulted in higher ozone level on 7 September than on 6 September. Calculated OH reactivity based on the observed

inorganic gases and VOCs shows a similar variation as the observed OH reactivity, although the calculated OH reactivity tends to be lower than the observed OH reactivity (Fig. 3). Preliminary analysis also shows that alkenes, NO<sub>x</sub>, CO are the main contributors to the OH reactivity (Fig. 2).



**Figure 2:** Top: observed and calculated OH reactivity on 6 and 7 September, 2006 at Moody Tower during TRAMP. Bottom: calculated percentage contribution of the measured species to OH reactivity.

### 3. Work in Progress

Extensive evaluation of the data obtained at Moody Tower during TRAMP 2006 is completed yet. We are still working on post-campaign instrument calibrations, tests, and validation. A recent calibration of our primary calibrator at NIST indicates that our OH and HO<sub>2</sub> sensitivity in GTHOS should be lower by a factor of ~1.3-1.8 than what we thought. OH reactivity data measured by MAOHR should remain the same. We are very close to the validation of our calibration and will submit our final data when we finish the validation. Once we get all data from other groups, we will conduct some box model calculations using Regional Atmospheric Chemistry Mechanism (RACM) and compare the modeled OH and HO<sub>2</sub> to the observations. Using the complete suite of the data collected at Moody Tower, especially NMHC, OVOCs, CO, NO<sub>x</sub> data, we will calculate OH reactivity based on the OH reactant concentrations and their rate coefficients. Calculated OH reactivity will then be compared to the observed OH reactivity to examine the agreement and to reveal certain missing OH reactivity.

### 4. References

- Faloona, I.C., D. Tan, R.L. Leshner, N.L. Hazen, C.L. Frame, J.B. Simpas, H. Harder, M. Martinez, P. Di Carlo, X. Ren, and W.H. Brune, A laser induced fluorescence instrument for detecting tropospheric OH and HO<sub>2</sub>: Characteristics and calibration, *J. Atmos. Chem.*, **47**(2), 139–167, 2004.
- Kovacs, T.A. and W.H. Brune, Total OH loss rate measurement, *J. Atmos. Chem.*, **39**, 105–122, 2001.

### 5. PI Contact Address

W. Brune, [brune@meteo.psu.edu](mailto:brune@meteo.psu.edu), phone: 814-865-3286, fax: 814-865-3663

## 2.5 Texas A & M (PI: R. Zhang)

### VOCs and HNO<sub>3</sub> Measurements at the UH Moody Tower

Renyi Zhang

Texas A&M University

#### 1. Instrumentation

- Measured Parameters:
  - gas-phase VOCs and HNO<sub>3</sub>
- Measurement Instrument/Technique:
  - Ion-Drift CIMS (Fortner et al., 2004) & Proton Transfer Reaction Mass Spectrometry
- Deployment period:
  - Aug 17 – Oct 15, 2006

#### 2. Preliminary results

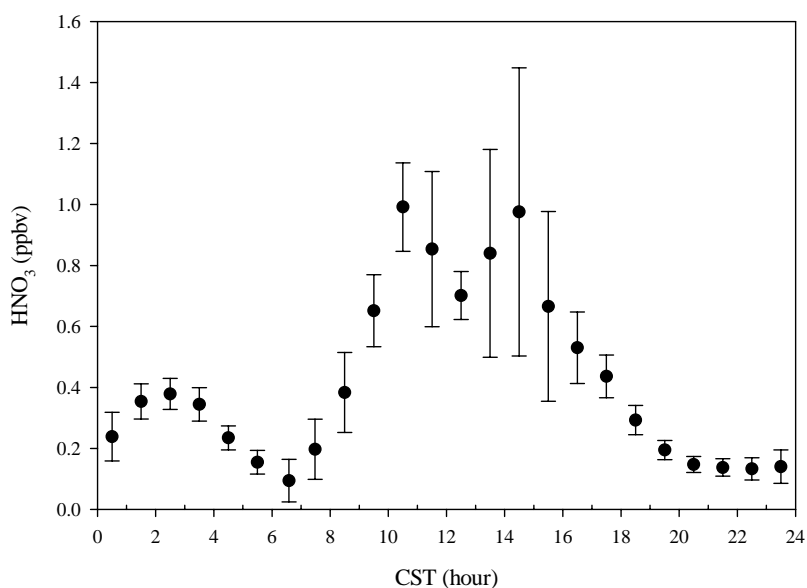


Figure 1. Hourly averaged HNO<sub>3</sub> diurnal profile.

HNO<sub>3</sub> was measured continuously by the ID-CIMS from Aug 20 to Sep 7 and Sep 24 to 27 at UH Moody Tower. All HNO<sub>3</sub> data has been fully processed through proper QA/QC procedures including inlet spike tests, calibrations with commercial permeation source, and verification of the permeation rate. The daily variations of HNO<sub>3</sub> concentration are depicted in Figure 1, an hourly averaged diurnal profile. The most prominent feature is the small peak at 2:30 AM, when no photochemistry could occur. There are two possible explanations. One is that it was formed locally through heterogeneous reactions and the other is that aged air masses were brought back from the ocean. Daytime HNO<sub>3</sub> followed the solar cycle and was consistent with its role in the photochemical processes. The peak value was less than 1.5 ppbv, which implied that the O<sub>3</sub> production might be NO<sub>x</sub> limited.

**VOCs** were continuously measured by a compact PTR-MS from Aug 17 to Oct 15 at UH except the period from Sep 13 to Oct 1, when the PTR-MS was participating in the Houston Triangle Project. More than twenty VOC species were detected and identified. Propene was the major alkene species detected during this project and we believe it originated from the ship channel area because its high concentration peaks correlated with easterly wind. The record propene peak was about 1.1 ppmv observed in the morning of Aug 20. Unlike alkenes, aromatic VOCs were more correlated with the traffic conditions. Figure 2 is the hourly averaged diurnal profiles of benzene, toluene, C2-benzenes, and C3-benzenes. The peak time concurred with the morning rush hour. However, no significant afternoon peaks were observed, which was possibly caused by stronger photochemical reactivity and higher boundary layer in the afternoon.

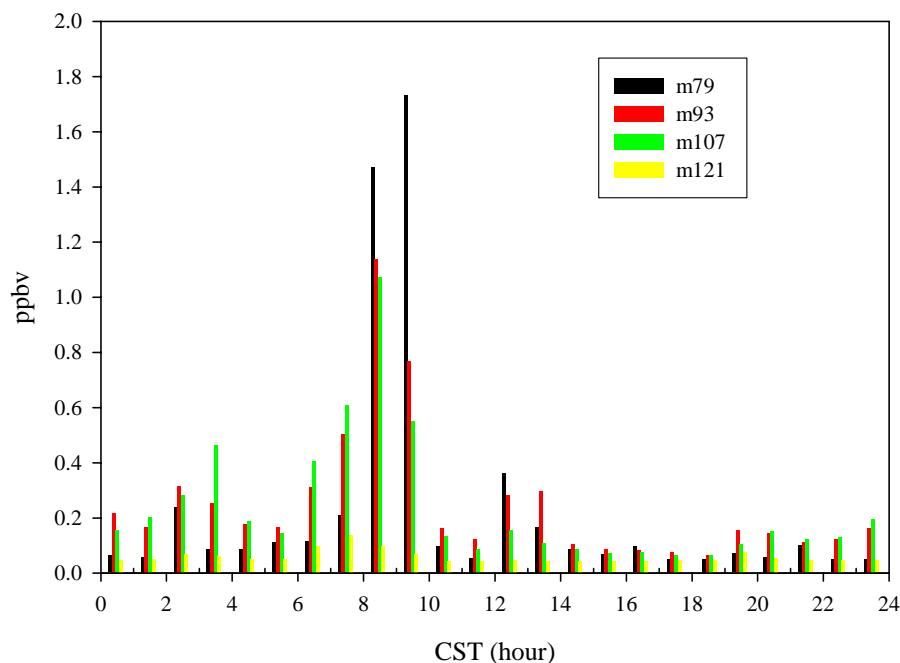


Figure 2. Hourly averaged aromatic VOCs measured from Aug 17 to Sep 1 at UH. m79, m93, m107, and m121 are benzene, toluene, C2-benzenes, and C3-benzenes respectively.

### 3. Work in Progress

We are analyzing and characterizing the oxygenated VOCs measured at UH.

### 4. References

Edward C.E., J. Zhao, R. Zhang, Development of Ion Drift-Chemical ionization Mass Spectrometry, *Anal. Chem.* **76**, 5436-5440, 2004.

### 5. PI Contact Address

Renyi Zhang, [zhang@ariel.mct.tamu.edu](mailto:zhang@ariel.mct.tamu.edu), phone: 979-845-7656, fax: 979-862-4466.

## 2.6 Texas A & M (PI: D. Collins)

### Measurement of aerosol size distributions, hygroscopicity, and transformation rate

Don R. Collins and Crystal C. Reed

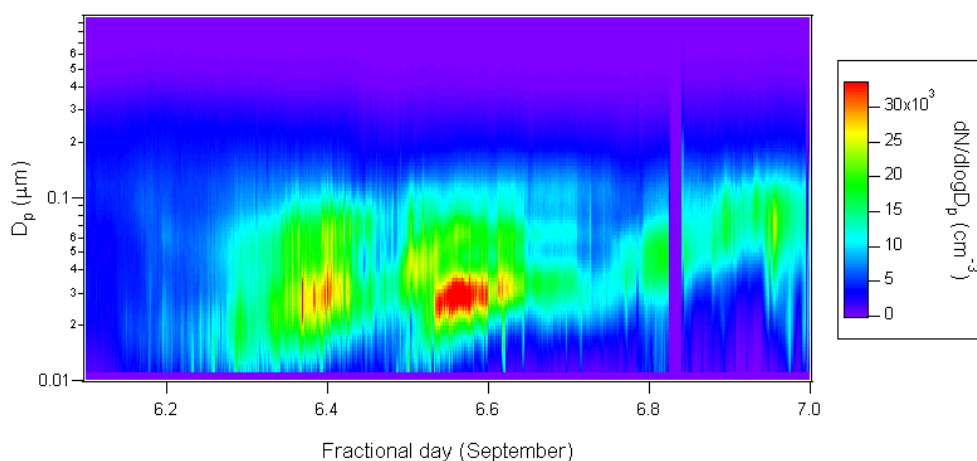
Texas A&M University

#### 1. Instrumentation

- Measured Parameters:
  - Particle size distributions:  $0.01 \mu\text{m} < D_p < 0.7 \mu\text{m}$
  - Size resolved hygroscopicity:  $0.013 \mu\text{m} < D_p < 0.4 \mu\text{m}$
  - Particle growth rate
- Measurement Instrument/Technique:
  - Tandem differential mobility analyzer (TDMA) / Aerosol Chambers for Evolution Studies (ACES)
- Deployment period:
  - Aug 15 – Sep 30

#### 2. Preliminary results

As has been observed during prior field studies in the Houston area, particle number concentration was typically dominated by particles less than  $0.05 \mu\text{m}$ , while volume concentration was dominated by accumulation mode particles. Also consistent with previous measurements, hygroscopic growth factor distributions were generally bimodal, with a less hygroscopic mode believed to be primarily comprised of primary organic and soot particles and a more hygroscopic mode comprised of sulfate-containing particles. Particles formed through nucleation events or directly emitted were observed to grow over a time scale of a few hours. An example of this type of growth event is shown in the figure below, which presents measured aerosol size distributions on September 6.



**Figure 1:** Submicron aerosol size distributions measured on September 6.

### 3. Work in Progress

We will process all ambient size distributions and hygroscopic growth factor distributions within the next month or two. These data will be combined with similar measurements we made at three other locations in Houston during the latter part of September and with complementary measurements made at the Moody Tower. After we have finished processing the ambient aerosol measurements we will focus on the chamber experiments. As a first step in that analysis, we will evaluate the influence of any contaminants on the observed particle growth rates.

### 4. PI Contact Address

Don Collins, [dcollins@tamu.edu](mailto:dcollins@tamu.edu), phone: (979) 862-4401, fax: (979) 862-4466

## 2.7 Texas A & M (S. Brooks)

### Size Distributions and Size-Select Hygroscopicity of Atmospheric Aerosols

PI: Dr. Sarah D. Brooks

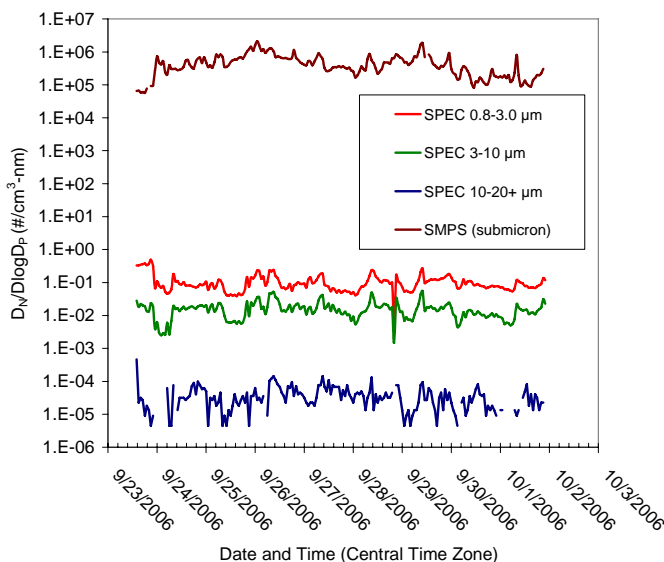
Texas A&M University

#### 1. Instrumentation

- Measured Parameters:
  - Aerosol size distributions 10 nm to 20  $\mu\text{m}$  diameter, single particle hygroscopicity.
- Measurement Instruments/Technique:
  - SMPS, GRIMM 1.108 Spectrometer, Streaker Impactor Sampler
- Deployment period:
  - August 18 – October 12, 2006

#### 2. Preliminary results

Aerosols commonly present in the urban atmosphere span more than two orders of magnitude in size and also vary in their composition and ability to take up water and form cloud droplets. To obtain time resolved size distributions over this range, we have deployed a GRIMM Scanning Mobility Particle Sizer (SMPS) and a GRIMM 1.108 Aerosol Spectrometer (SPEC). Taken together these instruments count particles in 53 size bins ranging from 10 nm to 20  $\mu\text{m}$  diameter. Figure 1 shows preliminary data collected with the SMPS and the Spectrometer for a 10 day period. Here we report the total normalized number concentration of submicron particles observed by the SMPS and the normalized number concentrations of larger particles obtained by summing higher resolution SPEC data into three broad size ranges. As expected, our results indicate that the particle counts are dominated by the submicron particles. However, we have also observed significant numbers of large particles, including particles of 10  $\mu\text{m}$  diameters and greater, from the roof of the Moody Tower. (Figure 1).

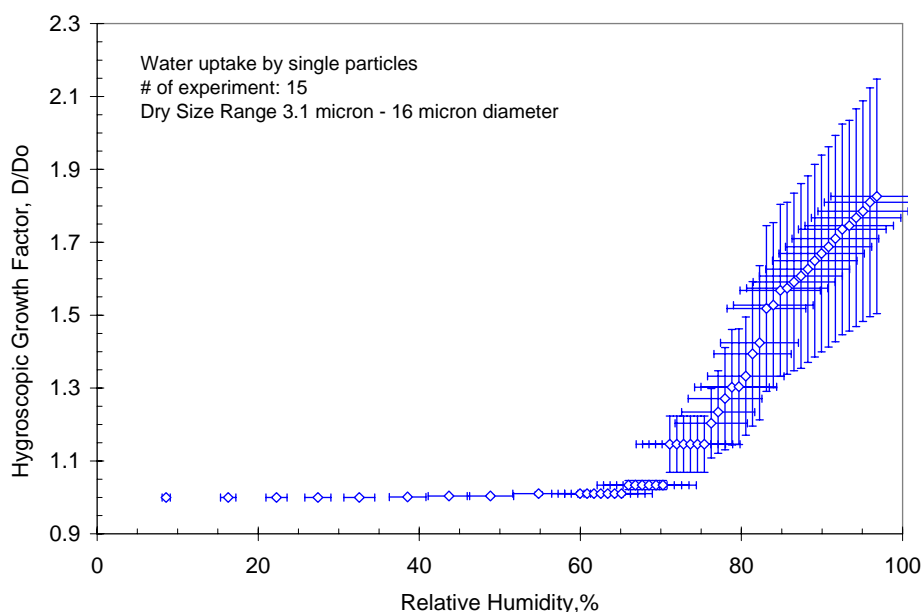


**Figure 1:** Normalized number concentrations for the total submicron particles measured by SMPS (brown) and the 0.8-3  $\mu\text{m}$  diameter (red), 3-10  $\mu\text{m}$  diameter (green), and 10-20  $\mu\text{m}$  diameter (blue) measured by the Aerosol Spectrometer.

To further characterize these particles, time-resolved aerosol filter samples are collected using a PIXE Streaker Filter Sampler. The Streaker is designed to produce a time discrete record of aerosols in two size fractions, PM 2.5 and PM 10. The instrument is a low volume sampler (with a flow rate of 1 lpm) and the length of each sampling period is adjustable from minutes to hours. We are currently operating the Streaker collecting discrete samples every 90 minutes. Streaker samples are taken to the Texas A&M Microscope Center for measurements of single particle hygroscopicity and elemental analysis.

### 3. Work in Progress

Single particle hygroscopicity measurements are being conducted on the time resolved impactor samples using an Environmental Scanning Electron Microscope. Also, elemental composition is determined using Energy Dispersive Electron Spectroscopy. The figure below shows the hygroscopic growth factor as a function of relative humidity for aerosols collected from the Moody Tower during the campaign. In the figure, averaged experimental data from 15 single particle experiments is shown. The dry size of particles in these experiments ranged from 3.1 micron - 16 micron diameter. The y-axis error bars indicate the standard error in our measurements, and the x-axis error bars represent experimental uncertainty in the relative humidity measurements. As can be seen, the collected particles were reasonably hygroscopic, taking up significant amounts of water at relative humidities above 70% and increasing to ~180 % of their original size at RHs above 90%. For additional experimental details, see Hiranuma et al.



### 4. References

Hiranuma, N., S.D. Brooks, B.W. Auvermann, and R. Littleton, Using Environmental Scanning Electron Microscopy to Determine the Hygroscopic Properties of Agricultural Aerosols, *Atmos. Environ.*, submitted April 2007.

### 5. PI Contact Address

Sarah Brooks, sbrooks@tamu.edu, phone: 979-845-5632, fax: 979-862-4466

## 2.8 NOAA-ARL (PI: W. Luke)

### Measurement of NO, NO<sub>2</sub>, NO<sub>Y</sub>, CO, and SO<sub>2</sub> During the TEXAQS II Intensive Observational Period (IOP)

PI: Winston Luke (NOAA Air Resources Laboratory)

Collaborator: Barry Lefer, Bernhard Rappenglueck, James Flynn (University of Houston)

#### 1. Instrumentation

- Measured Parameters:
  - NO, NO<sub>2</sub>, NO<sub>Y</sub>, CO, and SO<sub>2</sub>
- Measurement Instrument/Technique:
  - O<sub>3</sub> Chemiluminescence (Reactive Nitrogen)
  - Non-Dispersive Infrared (CO)
  - Pulsed Fluorescence (SO<sub>2</sub>)
- Deployment period:
  - August 15-October 1, 2006

#### 2. Preliminary results

The selective measurement of NO, NO<sub>2</sub>, and NO<sub>Y</sub> (NO<sub>Y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + HNO<sub>3</sub> + HONO + HO<sub>2</sub>NO<sub>2</sub> + PAN + RONO<sub>x</sub> + NO<sub>3</sub><sup>-</sup> + ...) is important for several reasons. First, the measurements allow us to characterize the total load of reactive nitrogen compounds in an air mass; this in turn allows us to estimate the potential for photochemical ozone production and along with measurements of non-methane hydrocarbons (NMHCs) and ozone (O<sub>3</sub>) allow us to determine whether ozone formation in the Houston environs is NO<sub>x</sub> or hydrocarbon limited. The question of reactant limitations on photochemical ozone formation is crucial to the successful implementation of effective emission controls to mitigate high ozone production episodes in non-attainment areas.

Second, the differentiation between NO<sub>x</sub> (NO<sub>x</sub> = NO + NO<sub>2</sub>) and NO<sub>Y</sub> allows us to calculate concentrations of NO<sub>z</sub> (NO<sub>z</sub> = NO<sub>Y</sub> - NO<sub>x</sub>). NO<sub>z</sub> may be thought of as those compounds which are formed from chain termination reactions in the NO<sub>x</sub>-O<sub>3</sub> photochemical cycle, and measuring concentrations of O<sub>3</sub> and NO<sub>z</sub> allow us to calculate the efficiency of ozone production –the number of O<sub>3</sub> molecules produced per NO<sub>x</sub> molecule oxidized. The ozone production efficiency (OPE) is determined by a number of factors, primarily NMHC/NO<sub>x</sub> reactivity ratios, which in turn depends on the specific mixture of the NMHC pool.

Finally, the selective measurement of NO<sub>2</sub>, made by NOAA with an LED-based photolysis system which avoids the interfering photolysis of HONO, HO<sub>2</sub>NO<sub>2</sub>, etc., along with NO<sub>Y</sub>, and ancillary species (HNO<sub>3</sub>, PAN, RONO<sub>x</sub>) allows us to accurately close the NO<sub>Y</sub> budget, to determine the potential abundance of nitrogen bearing moieties which may not otherwise be measured. Because the NO<sub>2</sub> photolysis cell is selective and does not suffer from the interferences associated with thermal or broad-band photolytic systems, these measurements may be used at night to estimate the potential contribution of NO<sub>3</sub>, HONO, and N<sub>2</sub>O<sub>5</sub> to overall NO<sub>Y</sub> levels.

The ancillary measurement of CO and SO<sub>2</sub> allows us to identify the nature of NO<sub>x</sub> emission sources impacting the Moody Towers site. High NO<sub>x</sub> associated with high concentrations of CO may be correctly attributed primarily to automobile emissions, while correlations with SO<sub>2</sub> indicate an industrial origin. Measurements of SO<sub>2</sub> also provide vital data for determination of aerosol production rates, efficiencies, and pathways in the Houston area.

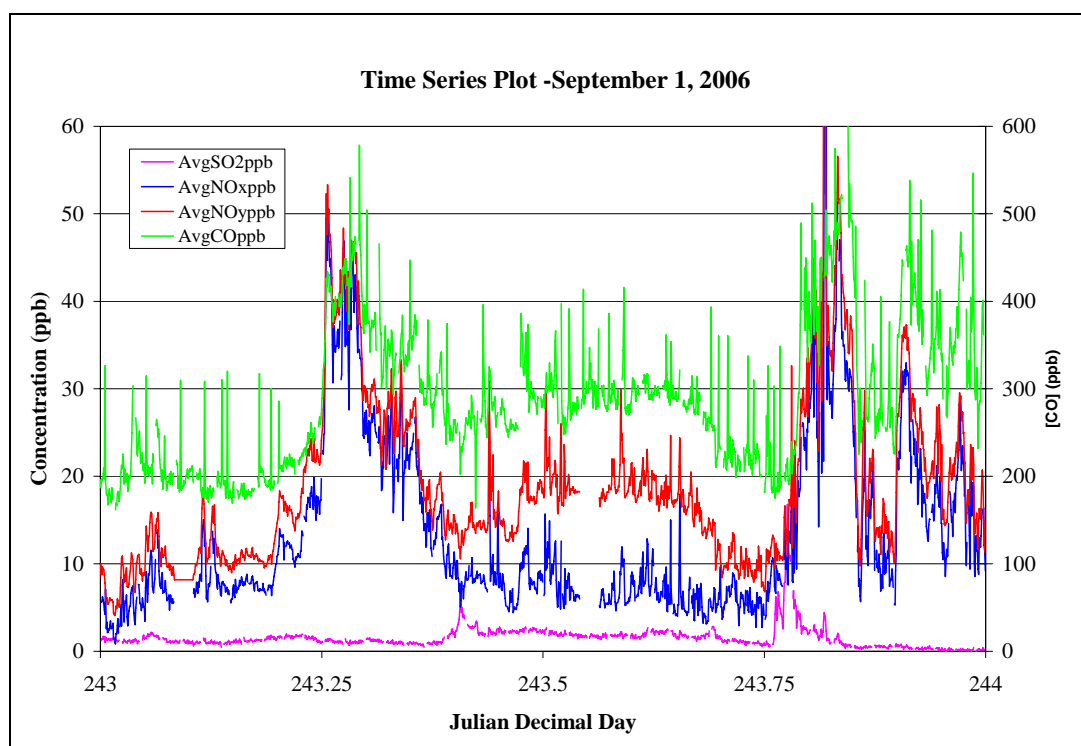


Figure 1 illustrates data collected on September 1. As is often seen in the TEXAQSII data set,  $\text{NO}_Y$  levels peak with the morning and evening rush hours, although petrochemical flares also contribute. Note that in the morning and evening  $\text{NO}_X$  constitutes almost all the  $\text{NO}_Y$ , but in mid day the concentration of  $\text{NO}_Z$  (probably  $\text{HNO}_3$ ) increases as the ozone photochemical cycle is at its most efficient. Note the close correlation between  $\text{NO}_Y$  and CO in the rush hour periods, implicating vehicular emissions. On this day  $\text{SO}_2$  concentrations were rather low.

### 3. Work in Progress

Efforts are underway to reduce the data collected at the Moody Towers and to produce a QA'd data set. Data analysis and interpretation will follow subject to the availability of extramural support.

### 4. PI Contact Address

Winston Luke; [Winston.Luke@noaa.gov](mailto:Winston.Luke@noaa.gov); phone 301-713-0971

## 2.9 NOAA-ARL (PI: S. Brooks)

### Airborne Mercury Speciation on the Moody Tower Rooftop, University of Houston

PI: Steven Brooks

Collaborators: Winston Luke, Mark Cohen

NOAA Air Resources Lab.

#### 1. Instrumentation

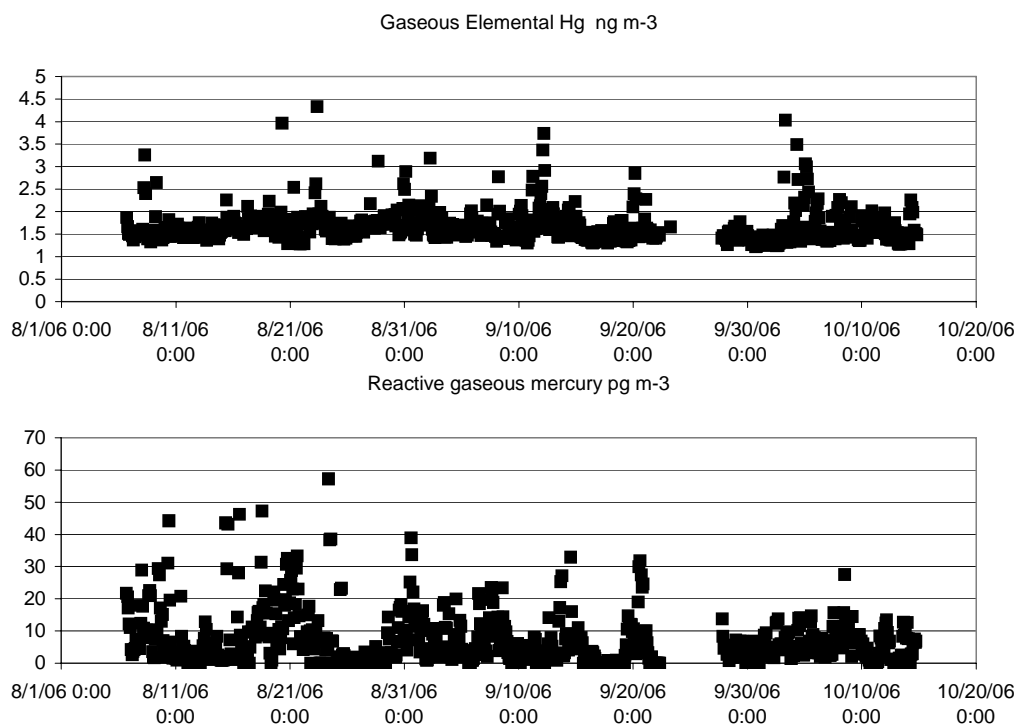
- Measured Parameters:
  - Gaseous elemental mercury, Reactive gaseous mercury, and Fine (<PM<sub>2.5</sub>) particulate-bound mercury
- Measurement Instrument/Technique:
  - Tekran mercury sensors 2537a, 1130, 1135 and 1102
- Deployment period:
  - Aug 6 – October 14, 2006

#### 2. Preliminary results

The dataset showed gaseous elemental mercury in the typical urban range of 1.5 to 5.0 ng m<sup>-3</sup>. Reactive gaseous mercury varied from 0.0 to ~60 pg m<sup>-3</sup> with typical afternoon peaks (~3pm). Fine particulate-bound mercury varied from 0.0 to ~80 pg m<sup>-3</sup> with typical early morning hours peaks (~4am).

Very remarkable items in collected dataset:

1. Particulate-bound mercury levels were extremely high during the early morning hours of 8/31.
2. The air was extremely clean (with respect to all mercury species) on 8/26-28 and again 9/15-18.



**Figure 1:** Mercury species concentrations.

**3. Work in Progress**

Extensive evaluation of the data obtained during the campaign 2006 is not yet completed

**4. PI Contact Address**

Steve Brooks, [Steve.Brooks@noaa.gov](mailto:Steve.Brooks@noaa.gov), phone: 865-576-1233, cell: 304-678-5996, fax: 865-576-1327

## 2.10 University of California Los Angeles (PI: J. Stutz)

### Chemistry and Vertical Mixing in the Nocturnal Boundary Layer in Houston

PI: Jochen Stutz,

Collaborator: L. Lawrence, H. Oh, and O. Pikelnaya

Department of Atmospheric and Oceanic Sciences

University of California Los Angeles

#### 1. Instrumentation

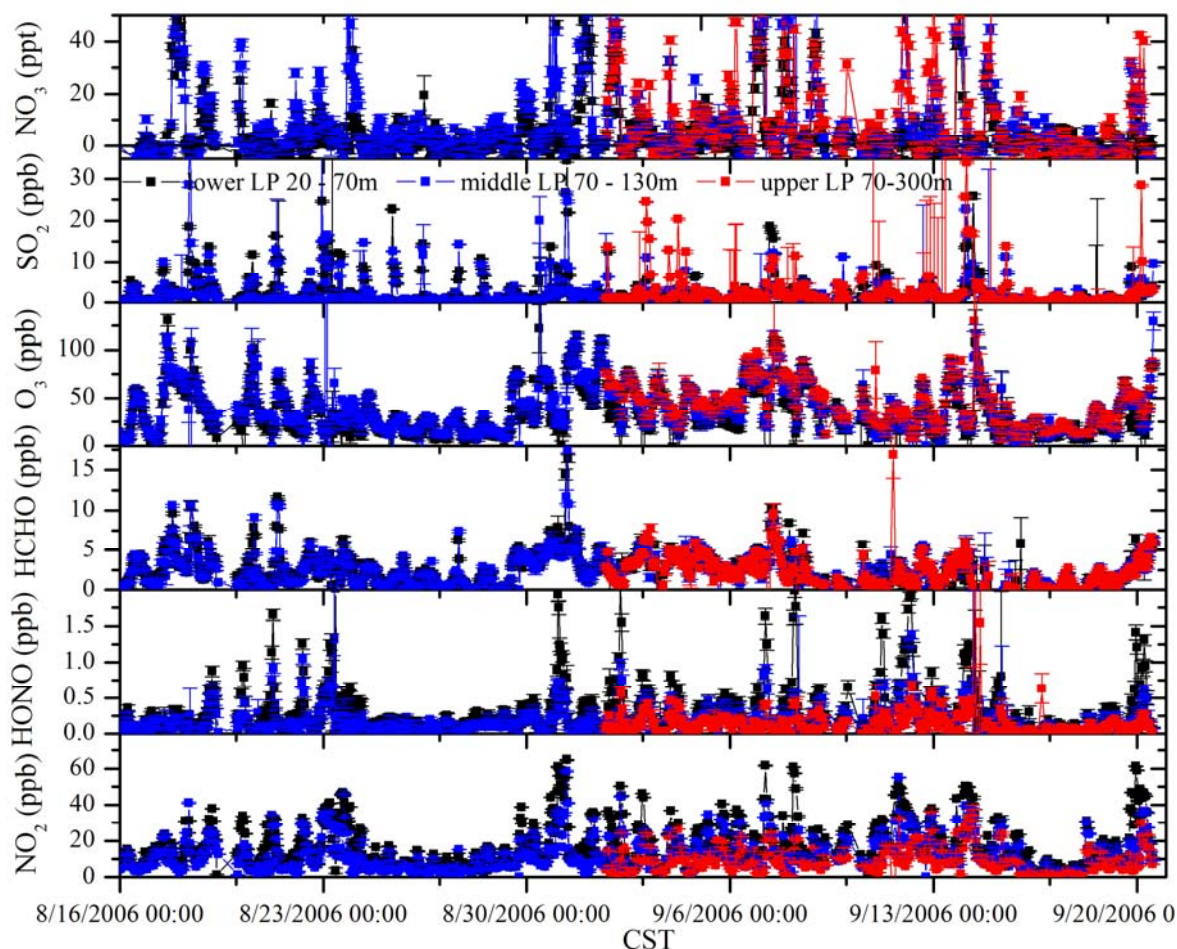
- Measured Parameters:
  - O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, HCHO, HONO and NO<sub>3</sub> on various absorption paths
- Measurement Instrument/Technique:
  - Long-path Differential Optical Absorption Spectrometer: Vertical gradients of O<sub>3</sub>, NO<sub>2</sub>, SO<sub>2</sub>, HCHO, HONO and NO<sub>3</sub> in the lowest 300 m of the boundary layer were performed. Observations were averaged on three light paths between the Moody towers and downtown Houston in the following height intervals: 20 -70m, 70 – 130m, and 70 – 300m
  - Multi-Axis Differential Optical Absorption Spectrometer: Passive absorption measurement using scattered solar light were performed along 8 elevation viewing angles during daytime to measure vertical profiles of NO<sub>2</sub> and HCHO. The viewing direction was approximately parallel to that of the LP-DOAS.
- Deployment period:
  - August 7 – September 20, 2003

#### 2. Results

The goal of UCLA's participation in TRAMP was the study of nocturnal and early morning chemistry and the impact of vertical transport in the stable nocturnal boundary layer (NBL), as well as during the break-up of the NBL in the early morning. Figure 1 shows an overview of the acquired data during the TRAMP experiment. While a detailed interpretation of the data, for example by using chemical transport models of the NBL, has not yet been performed, the following conclusions can be drawn based on the observations:

- Vertical gradients of O<sub>3</sub> and NO<sub>2</sub>, of up to 40 ppb were observed in the lowest 300 m of the NBL during many nights in Houston. The transition from a stable to a well mixed boundary layer in the morning lead to a more even vertical distribution of all trace gases. The cause of the nocturnal gradients is the emission of NO at the ground together with the weak vertical mixing in the NBL (Stutz et al. 2004).
- DOAS data and in-situ O<sub>3</sub> and NO<sub>2</sub> observation at Moody tower (data from U Houston) shows that during most days Moody tower in-situ observations were representative on a large scale. During some nocturnal periods the Moody tower data differed considerably from the LP-DOAS observations, most likely due to the poor vertical, and probably also horizontal, mixing of the various trace gases.
- NO<sub>3</sub> mixing ratios of up to 60 – 100 ppt were observed during some night. The vertical gradients were less pronounced than expected, probably due to a less stable nocturnal boundary layer than observed in other urban areas. A more detailed analysis is necessary to make a more quantitative analysis of these observations.
- HONO mixing ratios of up to 2 ppb as well as vertical concentration gradients were observed during some nights and the early mornings. The HONO photolysis frequencies observed by the University of Houston can be used to quantify the contribution of HONO photolysis to the morning OH formation.

- Vertical gradients of HCHO mixing ratios were observed during certain periods. The cause of these gradients, i.e. direct emission from the ground or transport from a more distant source, remains to be investigated.
- During several occasions plumes of SO<sub>2</sub> were observed. The vertical gradients of the plumes were not consistent. The combination of the LP-DOAS observations with the aerosol LIDAR measurements by PNNL will allow further investigation of these plumes.



**Figure 1:** Overview of long-path DOAS data of various trace gases on three different light paths during TRAMP.

### 3. Work in Progress

The data analysis of the long-path DOAS data is currently being refined. The analysis of the MAX-DOAS observations will be performed in the coming months. The interpretation of the observations will commence after the final data set has been compiled.

### 4. References

Stutz, J., B. Alicke, R. Ackermann, A. Geyer, A. White, and E. Williams, Vertical profiles of NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, O<sub>3</sub>, and NO<sub>x</sub> in the nocturnal boundary layer: 1. Observations during the Texas Air Quality Study 2000, *J. Geophys. Res.*, **109**, doi:10.1029/2003JD004209, 2004.

### 5. PI Contact Address

J. Stutz, [Jochen@atmos.ucla.edu](mailto:Jochen@atmos.ucla.edu), Tel. 310-825-5364, Fax. 310-206-5219

## 2.11 University of California Santa Cruz (PI: P. Chuang)

### Measurement of cloud condensation nuclei behavior of Houston aerosol

PI: Patrick Y. Chuang

University of California Santa Cruz

#### 1. Instrumentation

- Measured Parameters:
  - CCN concentration at different supersaturations, exposure times and temperatures. These measurements are used to derive CCN condensational growth rates.
- Measurement Instrument/Technique:
  - Custom supersaturating column coupled to a phase-Doppler interferometer for drop sizing
- Deployment period:
  - Sept 4– 11, 2006

#### 1. Preliminary results

We have completed our analysis that describes the condensational growth rates of cloud condensation nuclei (CCN). Figure 1 summarizes results from the 5 days (between 9/4 and 9/11/2006) at Moody Towers during which we conducted measurements. The results are reported as relative mass accommodation coefficient,  $a'$ , such that:

$$a' = \frac{a_{meas}}{a_{ammsulf}}$$

where  $a_{meas}$  is the measured mass accommodation coefficient, and  $a_{ammsulf}$  is  $a$  determined by calibration in the laboratory using pure ammonium sulfate particles. Figure 1 shows  $a'$  values relative to the standard deviation  $\sigma$  found in the calibration tests, where  $1 \sigma$  represents a change in growth rate by a factor of 1.5. Particles that grow more slowly than ammonium sulfate calibration aerosol will have  $a' < 1$ , which we report as negative deviations in  $\sigma$ . Overall (Figure 1, bottom right), there is a large fraction of particles which exhibit condensational growth rates much slower than that for ammonium sulfate (see Table 1). There is, however, a tremendous amount of day-to-day variability, which we attribute to different aerosol sources and/or photochemical ages.

Growth rate range	Fraction of particles
$< -6\sigma$	1.2%
$-4\sigma$ to $-6\sigma$	4.8%
$-2\sigma$ to $-4\sigma$	37.8%
$+2\sigma$ to $-6\sigma$	52.4%
$> +2\sigma$	3.8%

**Table 1:** Summary of results from Moody Towers.

The measurements in Houston comprise one of the four sites where such measurements were made during Aug to Sept 2006. The results of this overall campaign will be reported in a manuscript to be submitted in the next few weeks.

## 2. Work in Progress

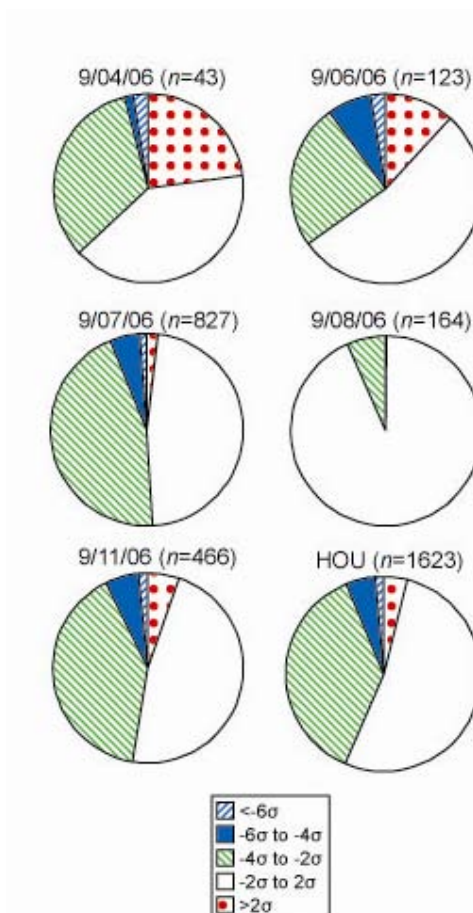
Our next goal is to connect our observations with other Moody Tower PIs (primarily Don Collins, Texas A&M, and Rob Griffin, Univ. New Hampshire, but also potentially others) to synthesize a larger picture of the role of organics in the cloud-nucleating ability of Houston aerosol. The high variability in CCN growth properties observed during this period leads us to believe that significant shifts in other aerosol properties were measured by other investigators. By combining a suite of measurements, we seek a deeper understanding of what controls the aerosol condensational growth rate at this site.

## 3. References

None.

## 4. PI Contact Address

Patrick Chuang, [pchuang@es.ucsc.edu](mailto:pchuang@es.ucsc.edu), phone: 831-459-1501, fax: 831-459-3074



**Figure 1:** Observed values of  $a'$  for five different days in Houston during TexAQS II. See Table 1 for summary values.

## 2.12 Portland State University (PI: D. Atkinson)

### Aerosol Optical Properties

PI: Dean B. Atkinson

Collaborators: Monica E. Wright, Jeremy Parra

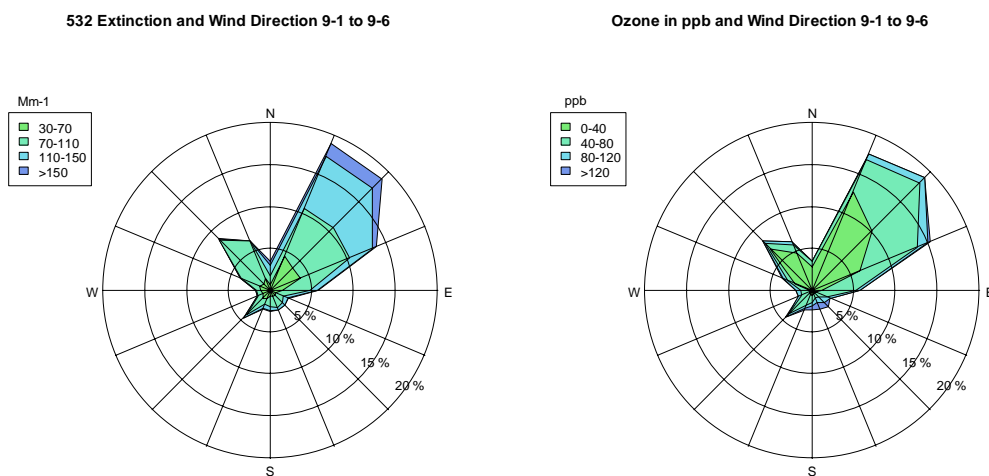
Portland State University

#### 1. Instrumentation

- Measured Parameters:
  - Particle (aerosol) optical extinction and scattering coefficients, derived particle absorption coefficient, aerosol single-scattering albedo, limited data on particle number concentration
- Measurement Instrument/Technique:
  - tandem cavity ring-down transmissometer / nephelometer (CRDTN), TSI Model 3007 condensation particle counter
- Deployment period:
  - August 11, 2006 – September 28, 2006

#### 2. Preliminary results

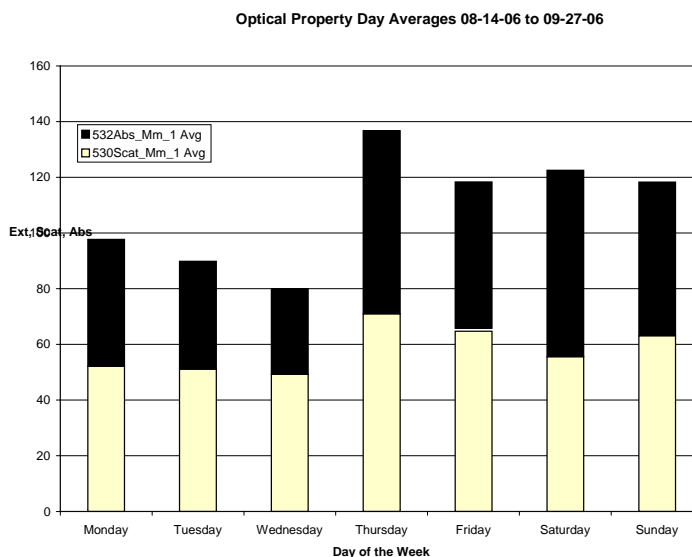
There were a number of likely sources of aerosol particulate matter in Houston during the Moody Tower study period. Our real-time aerosol optical measurements (fine particle extinction, scattering, and absorption coefficients and single scattering albedo) reflected all of the expected sources at various times. There was no clear indication of a single dominant source of PM in Houston from the preliminary data analysis, although the wind roses (Fig. 1) shown below strongly support the notion that much of the particulate, and primary and secondary chemical contaminants originate in the ship channel area. During the data collection, it was clear that emissions from local industries often contributed dramatically, if episodically, to the total light extinction by particles – for example, see Fig.1 of the preliminary report. The influence of mobile particulate sources was clearly reflected, although not as strongly as is typically encountered in Portland, Oregon. This could be due to the elevation of the sampling systems and the consequent dilution of the strong traffic signals usually seen in an urban core at ground level. The differences could also be just a matter of scale, since the level of particle extinction encountered in Houston during the study far exceeded typical levels observed in Portland. While sulfate particle concentrations (from the UNH AMS) and our particle light



**Figure 1** – Wind roses for particulate optical extinction and ozone. The ship channel is to the NE.

scattering levels were highly elevated in many cases, and the influence of power plants was a likely cause (based on the observation by others of elevated SO<sub>2</sub> levels) there were also some indications of longer range transport of PM from sources outside of Houston (perhaps even outside of Texas.) Some of the “possibly long range transport-influenced” events also displayed particles with lower than expected single scattering albedo that could be indicative of the influence of local or distant wildfires observed by others at that time.

Interestingly, the weekly pattern of aerosol optical extinction (and scattering) obtained by constructing daily averages of our highly time-resolved data shows a Monday-Wednesday “weekend” signal as shown in Fig. 2. We did not expect to see this *a priori* but in retrospect, it seems reasonable that traffic and industrial particulate loading would not be significantly lowered on Saturday and Sunday – sporting events and other recreational activities seemed to produce nearly as much traffic on these days as on the weekdays, and the major industries appeared to be operational 24/7/365. The low levels of PM on Monday, Tuesday, and Wednesday are not as easy to rationalize. Confirmation of these results by examination of other “traffic” sensitive data sets should probably be followed by creation of a hypothesis for this effect.



**Figure 2** – Bar graph showing the aerosol optical properties measured during the campaign, averaged to days of the week – *i.e.*, all data from a day averaged and all of those days from the study (usually 5 or 6) averaged. The yellow (bottom) bar is the particle scattering coefficient, the black (top) bar is the particle absorption coefficient, and the sum (the height of the bar) is the particle extinction coefficient (all three in Mm<sup>-1</sup>) – measured directly in the CRDT/N.

We also note from Fig. 2 that on average; nearly half of the total light extinction by particles is provided by light absorption. That is to say, the single scattering albedo is quite low on average for this period. Given that global average single scattering albedo is generally near 1.0, perhaps 0.97 – corresponding to nearly all extinction from scattering, this raises some interesting questions about the radiative effects of aerosols in and around cities. It also implies that there will be a lot of dilution of this aerosol by particles having higher albedo before it reaches the remote troposphere (if it is homogeneously distributed.)

### 3. Work in Progress

Because of the large quantity of data involved, the analysis of our data set (let alone comparison/correlation with other data sets) proved to be difficult. We have thus initiated development of a web-accessible database product that can import the ICARTT compatible file types and organize the many measurements of the campaign. Among the functions of this new product are: data type tabulation by Primary Institution and Principal Investigator, flexible data averaging (to any desired integration time), data merging, and ready download in standard file types for post-processing and presentation. Second tier objectives for the database project will include more advanced statistical analysis and presentation including wind roses and linear and non-linear time correlations, as well as geospatial encoding and analysis of data from locations other than Moody Tower. Using this database, we have been able to readily create wind roses and hourly and daily

averages for our data as shown above. As data is added to the database, inter-set comparisons will be facilitated. Results of these analyses will certainly be ready by the August update to this report.

We still intend to use our particle light scattering and absorption measurements to produce predicted fine particle mass density ( $\mu\text{g m}^{-3}$ ) and light absorbing carbon mass density as hourly and daily averages for the study period. Preliminary analysis of this data indicates that Houston may be in danger of exceeding the National Air Quality standards if the levels that we observed are confirmed by filter based measurements and are representative of the levels observed during the rest of the year (perhaps not likely to be true.)

#### 4. References

J. D. Smith and D. B. Atkinson, "A Portable Pulsed Cavity Ring-Down Transmissometer for Measurement of the Optical Extinction of the Atmospheric Aerosol", *Analyst*, **126**, 1216, (2001).

#### 5. PI Contact Address

D. B. Atkinson, [atkinsond@pdx.edu](mailto:atkinsond@pdx.edu), phone: 503-725-8117, fax: 503-725-9525

## 2.13 University of New Hampshire (PI: R. Griffin)

### Measurements of Size-Resolved Mass Concentrations of Aerosol Species using an Aerosol Mass Spectrometer, Cascade Impactors, and Filter Sampling

### Measurement of Total Aerosol Number Concentration using a Condensation Particle Counter

PI: Robert Griffin

Collaborators: Luke Ziemba, Casey Anderson, Eric Fitz, and Jack Dibb

(University of New Hampshire)

Additional Collaborators: Sonia Kreidenweis (Colorado State University), Athanasios Nenes (Georgia Institute of Technology)

#### 1. Instrumentation

##### a.) Measured Parameters:

- Size-resolved mass concentrations of ammonium, nitrate, sulfate, chloride, and organic aerosol in sub-micron particles
- Measurement Instrument/Technique:
  - Aerodyne quadrupole aerosol mass spectrometer (Q-AMS)
- Deployment period:
  - August 15 – September 28, 2006 with breaks during August 17-20 and September 16-18, 2006 due to instrumental issues; other breaks in data occurred during times of instrument calibration and maintenance

##### b.) Measured Parameters:

- Size-resolved (8 stages up to approximately 10 micron) mass concentration of organic carbon aerosol at a resolution of 2-3 days (day or night only for most samples)
- Measurement Instrument/Technique:
  - Andersen cascade impactors
- Deployment period:
  - August 15 – September 28, 2006

##### c.) Measured Parameters:

- Fine (sub-2.5 micron in diameter) and coarse (2.5 – 10 micron in diameter) aerosol composition (fine inorganic and organic; coarse inorganic) at varying resolution up to 24 hours
- Measurement Instrument/Technique:
  - University Research Glass Versatile Air Pollutant Sampler (filter sampler)
- Deployment period:
  - August 15 – September 28, 2006

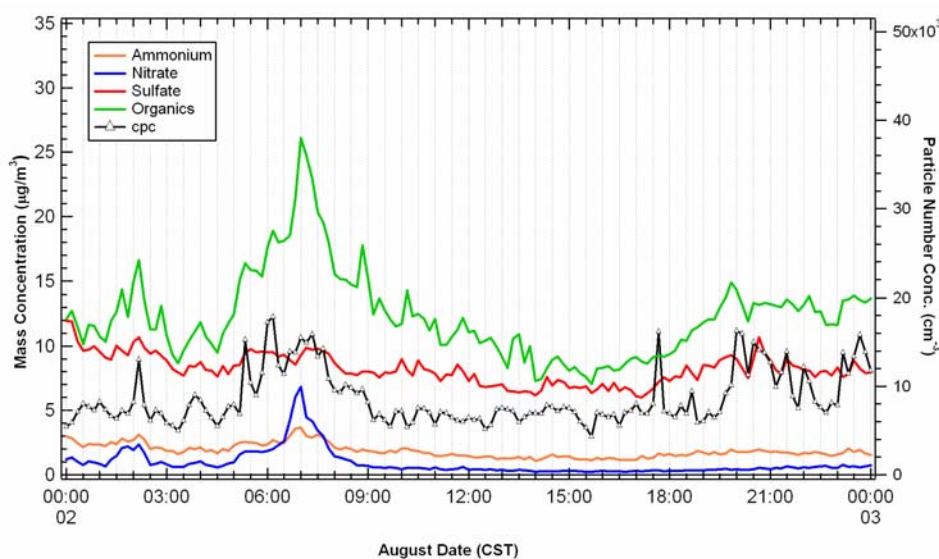
##### d.) Measured Parameters:

- Total number concentration of particles greater than 7 nm in diameter
- Measurement Instrument/Technique:
  - TSI condensation particle counter (CPC)
- Deployment period:
  - Same dates as Q-AMS

## 2. Preliminary results

As an example, mass concentrations of aerosol species on August 2, 2006 generated using the Q-AMS are shown in Figure 1. Particle number concentrations are also exhibited in this figure. It should be noted that Q-AMS data have not yet been corrected for instrumental collection efficiency, which will be done using inorganic filter data (specifically, sulfate). Filters have been extracted, and the extracts have been analyzed using ion chromatography. These data have yet to be finalized, however; it appears that only small correction factors will be necessary. Generally, mass concentrations on this day are dominated by organic material and sulfate aerosol. Ammonium aerosol and sulfate aerosol concentrations are relatively flat over the course of the day. Organic aerosol concentrations show a large increase in the morning and again late in the day. Total number concentrations appear to track those of organic aerosol species.

An interesting feature on this day is the large spike in nitrate aerosol that appears to be associated with unprocessed, primary organic aerosol (POA) material (defined based on particle size and mass spectra). This increase corresponds to a rapid decrease in gas-phase nitric acid and increases in gas-phase nitrous acid and bulk water soluble organic carbon (WSOC). No contemporaneous change in particulate WSOC was observed. These data potentially indicate the uptake of nitric acid and heterogeneous formation of nitrous acid associated with POA. This phenomenon was observed on other days during the campaign, generally during the morning rush hour.



**Figure 1:** Total aerosol number concentration (CPC) and mass concentrations of sub-micron ammonium, nitrate, sulfate, and organic aerosol (Q-AMS) measured at Moody Tower on August 2, 2006.

## 3. Work in Progress

Continued evaluation of the data obtained during the Moody Tower campaign will focus on the aforementioned sources of nitrate aerosol, the distribution of organic aerosol between primary and secondary sources, identification of the influence of chlorine chemistry, and the relationship between sulfate aerosol, sulfur dioxide, and aerosol size distributions. Impactor data will focus on diurnal profiles in the chemical nature of organic aerosol including water solubility. Inorganic filter data will identify the size distribution of nitrate aerosol. Portions of the quartz fiber filters used to collect carbonaceous aerosol have already been provided to Dr. Sonia Kreidenweis to investigate absorption properties and Dr. Athanasios Nenes to investigate surface tension properties of organic material.

## 4. PI Contact Address

Robert Griffin, rob.griffin@unh.edu, phone: 603-862-2021, fax: 603-862-2124

## 2.14 University of New Hampshire (PI: J. Dibb)

### Measurements of Nitric and Nitrous Acids by Automated Mist-Chamber Samplers Coupled to Ion Chromatographs

PI: Jack Dibb

Collaborators: Casey Anderson, Sallie Whitlow, Eric Scheuer, Luke Ziemba, Eric Fitz, and Robert Griffin  
(University of New Hampshire)

Additional Collaborators: Jochen Stutz (UCLA), Barry Lefer, Bernhard Rappenglueck, James Flynn (U Houston)

#### 1. Instrumentation

Samples are collected into a dense mist of ultrapure water, generated by the flow of the sample stream through the mist chamber devices. Syringe pumps inject the sample into the ion chromatograph immediately after each collection interval. At Moody Tower two independent systems were operated to alternately collect and analyze samples over 5 minute intervals.

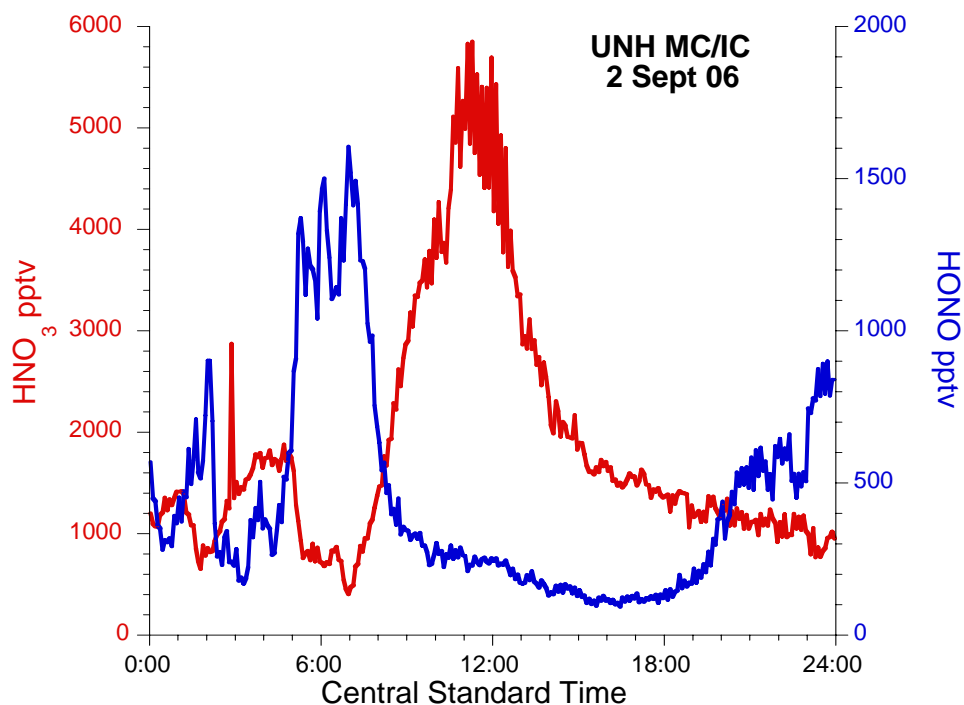
We operated from 18 August through 28 September. The data record has gaps of approximately 2-hour duration about every second day, for maintenance and calibration. Also, just before noon on 10 September heavy rain penetrated the instrument enclosure and caused failure of the UPS. Normal operations resumed at noon on the following day

#### 2. Preliminary results

Our technique actually determines the concentrations of nitrate and nitrite in the mist chamber solution. It is well established that nitric acid ( $\text{HNO}_3$ ) overwhelmingly dominates the signal in nitrate, with no significant interferants in the atmosphere. On the other hand, soluble nitrite has been shown to include contributions from several nitrogen oxides (e.g., pernitric acid, and perhaps organic nitrates) in addition to nitrous acid (HONO). In very cold and dry conditions like those at the South Pole and Summit, Greenland in March, HONO may account for less than half the measured nitrite. Comparison to the Long Path DOAS measurements of HONO made by Jochen Stutz and his team at Moody Towers indicates that in Houston during August and September, our measurement of soluble gas phase nitrite is essentially all HONO and we report it as such.

Measurements of  $\text{HNO}_3$  and HONO on 2 September are presented as an example of our data. This day is representative of a moderately polluted day within our data set. Peak mixing ratios of  $\text{HNO}_3$  near 6 ppb in the early afternoon reflect production from the daytime reaction of  $\text{NO}_2 + \text{OH}$ , and are correlated with the temporal evolution of  $\text{O}_3$  (as measured by U Houston). (For reference, maximum  $\text{HNO}_3$  exceeded 10 ppb several days in this study.) Mixing ratios of  $\text{HNO}_3$  are lower at night, but still appreciable, suggesting significant production via  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ . Rapid photolysis of HONO constitutes a very strong sink, so sustained mixing ratios of several hundred ppt throughout the day indicate continuous production from enhanced levels of  $\text{NO}_x$  in Houston. Higher HONO after sunset reflects shutdown of the photolytic sink.

The early morning peak of HONO (near and after sunrise) coincides with rush hour and extremely elevated  $\text{NO}_x$  (approaching 100 ppb some mornings, as shown by U Houston). However, OH is relatively low at this time of day, so the source of the  $> 1$  ppb enhancement of HONO within about an hour is intriguing. It is probably not coincidental that  $\text{HNO}_3$  decreases by about 1 ppb over the same interval. We suspect that a significant fraction of the rush hour burst of HONO (observed many days of the study) is due to heterogeneous reaction of  $\text{HNO}_3 + \text{H}_2\text{O}$ . Urban surfaces may provide suitable substrate, but the simultaneous enhancement of aerosol nitrate observed by Rob Griffin and Luke Ziemba with the AMS (on this, and other, days) suggests that the boundary layer aerosol may also participate. It should be noted that we also sampled on the NOAA research vessel during this study and saw similar anticorrelated variations of nitric and nitrous acid in early morning several days. Preliminary data from an AMS on the ship also suggests a link to spikes in aerosol nitrate and organic aerosol.



**Figure 1:** Time series of HNO<sub>3</sub> and HONO measured on Moody Tower 2 September, 2006.

### 3. Work in Progress

We intend to investigate the morning HONO/HNO<sub>3</sub>/p-NO<sub>3</sub><sup>-</sup> interaction with Dr. Griffin and his team. Combining our in situ observations of HONO with the profiles from Dr. Stutz's long-path DOAS (employing multiple light paths at different elevations) may provide insight into the impact vertical mixing on the composition of air in and near downtown Houston throughout the day (and over the duration of the study). In addition, we expect to work closely with Dr. Lefer and Dr. Rappenglueck of U Houston, and Dr. Brune of Penn State to assess whether the day time chemistry of HO<sub>x</sub>, O<sub>3</sub> and nitrogen oxides at the Moody Tower site is consistent with current understanding of homogeneous gas phase chemistry. Our gas phase data are in final form, we are waiting for final QA/QC on the DOAS and AMS results for further analysis.

### 4. PI Contact Address

Jack Dibb, jack.dibb@unh.edu, phone: 603-862-3063, fax: 603-862-2124

## 2.15 University of New Hampshire (PI: J. Dibb)

### Measurements of Water Soluble Organic Compounds in both the Gas and Aerosol Phase

PI: Jack Dibb

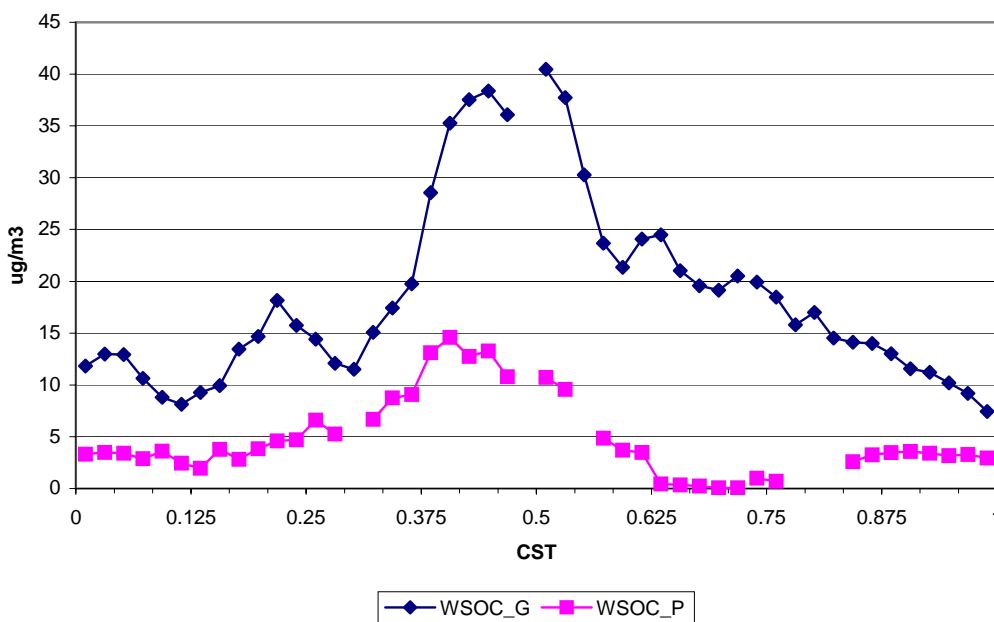
Collaborators: Casey Anderson, Luke Ziembra, Robert Griffin, Sallie Whitlow, Eric Scheuer,  
University of New Hampshire

#### 1. Instrumentation

- Measured Parameters:
  - Water soluble organic carbon gases and aerosols
- Measurement Instrument/Technique:
  - Mist chamber collection and TOC analysis with a Sievers 800 TOC Analyzer
- Deployment period:
  - August 20 – September 27, 2006

#### 2. Preliminary results

Figure 1 shows a time series of the total mass of water soluble organic gases (WSOC\_G) and aerosols (WSOC\_P) for the 7th of September. The morning shows a small peak in the water soluble gases at 5 am that upon comparison with wind direction data appears to be a primary plume from the ship canal. Rush hour traffic also influences concentrations at this time of day. Levels of water soluble organic compounds remain moderate until 7 am, but gas and aerosol concentrations increase rapidly as the sun rises. The gas peak of 40 ug/m<sup>3</sup> at noon is very high, much higher than measurements we have made at other locations. This pattern in the concentration of water soluble organics compares well with the AMS derived organic aerosol mass loadings collected and analyzed on this day by PI Robert Griffin. The midday peak appears to be due to oxidation of primary organic emissions, which increases the solubility of the organic compounds.



**Figure 1:** Mass concentration of water soluble organic carbon gases (WSOC\_G) and aerosols (WSOC\_P) measured at the Moody Tower on September 7, 2006.

### 3. Work in Progress

Further analysis of diurnal trends is ongoing in an effort to ascertain the consistency and average magnitude of the key features shown in Figure 1. Comparison to the AMS derived organic aerosol data will provide a better understanding of the level of oxidation of the organic plumes sampled and whether the organic aerosol mass is primary or secondary in nature. These plumes can then be referenced by wind direction to give an idea of their source. The length of the data set collected should be sufficient to establish levels for background conditions upon which the large anthropogenically influenced plumes can be put into appropriate context.

The water soluble organic carbon data sets are in near final form. Detailed analysis is pending finalization of the AMS data, and the impactor samples collected by Griffin/Ziemba.

### 4. PIs Contact Address

Jack Dibb, [jack.dibb@unh.edu](mailto:jack.dibb@unh.edu), phone: 603-862-3063

## 2.16 Georgia Tech (PI: R. Weber)

### On-Line Measurements of PM2.5 Mass and Bulk Aerosol Chemical Composition

Rodney J. Weber, Rick Peltier

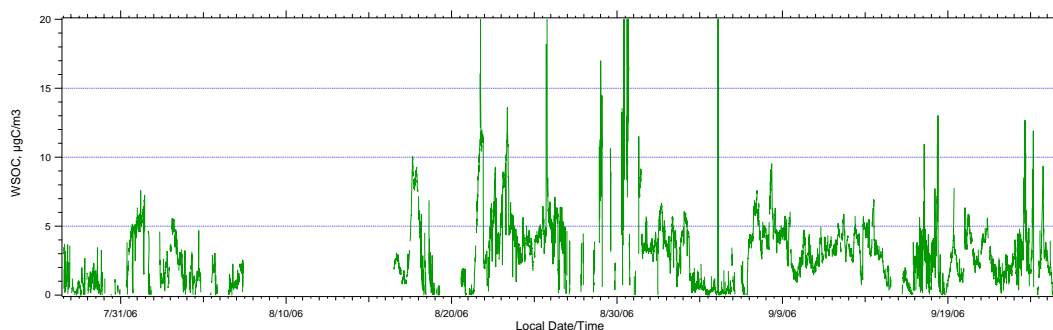
Georgia Tech

#### 1. Instrumentation

- PM2.5 Mass by TEOM (1hr avg.)
- PM2.5 OCEC by Sunset labs (1hr avg.)
- PM2.5 Ions (sulfate, nitrate, ammonium etc at 15 min. avg)
- PM2.5 Water-Soluble Organic Carbon (6 min. avg)
- Deployment period: 7/27/06 to 9/25/06

#### 2. Preliminary results

Our data analysis to this point has been limited to measurements of the water-soluble fraction of PM2.5 organic carbon (WSOC) due to its straight forward analysis [Sullivan *et al.*, 2004]. WSOC is of interest since it has two main sources, biomass burning emissions and secondary organic aerosol formation [Kondo *et al.*, 2006; Miyazake *et al.*, 2006]. To give a general sense of the data coverage and measurement range, the time series of WSOC for the mission is shown below.



#### 3. Work in Progress

Raw data collected during the mission is currently being evaluated and quality assured. Follow this, work will begin on interpreting the results and comparing to identical measurements currently be made from the NOAA WP-3B aircraft.

#### 4. References

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#### 5. PI Contact Address

R. J. Weber, [rweber@eas.gatech.edu](mailto:rweber@eas.gatech.edu), 404-894-1750

## 2.17 Rice University (PI: M. Fraser)

### Atmospheric HCHO by Infrared Spectroscopy

PIs: Matthew P. Fraser, Frank K. Tittel

Collaborators: Gerard Wysoski, Yuri Bakhirkin

Affiliation: Rice University

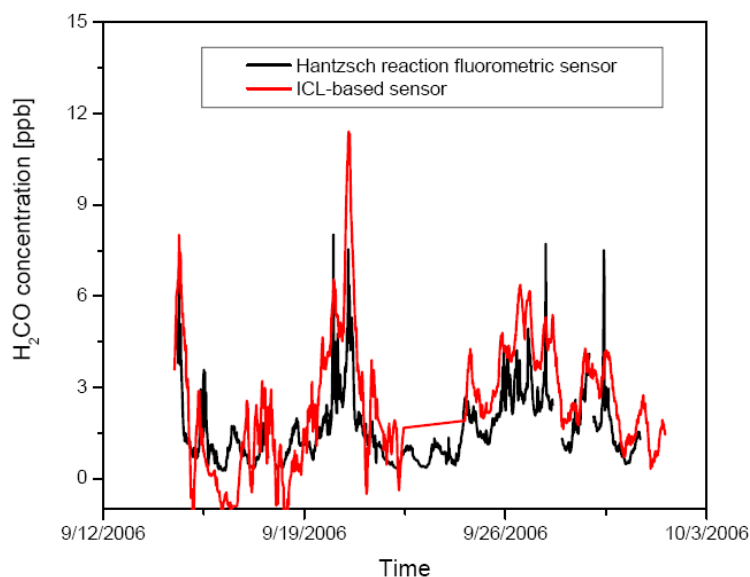
#### 1. Instrumentation

- Measured Parameters:
  - Gas Phase Formaldehyde
- Measurement Instrument/Technique:
  - Infrared Absorption at 3.5 microns
- Deployment period:
  - August 15-October 9, 2006

#### 2. Preliminary results

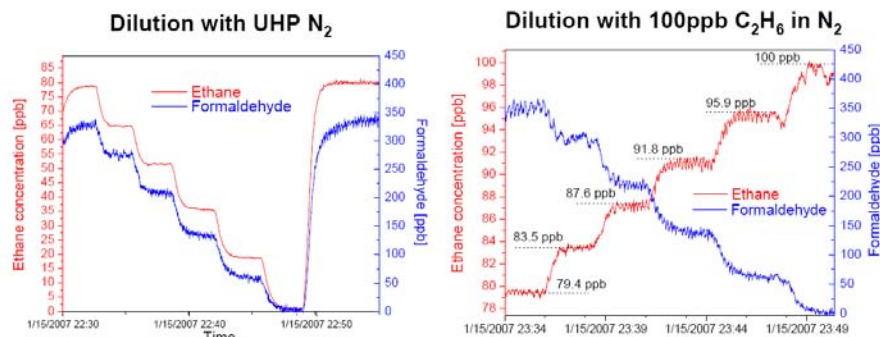
Gas phase formaldehyde measurements were made with time resolution of  $\sim 15$  seconds using a interband cascade laser system to monitor the interference free absorption of HCHO at  $\sim 3.5$  microns. Original plans to simultaneously measure ethylene at 3.3 microns using the same system ran into laser problems and have been delayed. We still hope to deploy the combined HCHO and  $C_2H_4$  system to look at the rapid oxidation of ethylene into formaldehyde in the near future.

The measurements of HCHO provide insight into the relative contribution of secondary formation from the light olefins that dominate ozone photochemistry in the Houston Ship Channel. Some preliminary data comparing the optical technique and the wet-chemical technique conducted by B. Rappengluck from UH are presented below.

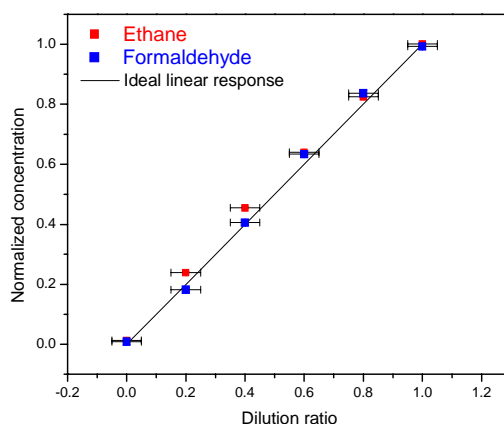


**Figure 1:** Ambient HCHO concentrations measured at Moody Tower by infrared absorption spectroscopy compared to the Hantzsch reaction method from Prof. Bernhard Rappengluck from University of Houston.

For proof of concept for a dual-gas intercascade laser based system, we did laboratory experiments of simultaneous measurements of HCHO and ethane. As ethane has a stronger absorption band than ethylene in the mid-IR, we could quantify ethane down to approximately 0.2 ppbV. The simultaneous measurements showed that there was no cross-talk between the gas channels (Figure 2) and both gases showed linear instrument response for dilution of the mixed gas standard (Figure 3).



**Figure 2:** Laboratory proof of concept for a dual gas optical sensor. HCHO and ethane measured simultaneously in a blended gas standard. No cross talk was observed between channels.



**Figure 3:** Linear response for HCHO and ethane to progressive dilution in laboratory experiments.

### 3. Work in Progress

We are currently working on getting a new laser for quantification of ethylene simultaneously with formaldehyde. We are working with collaborators at UMBC at growing and packaging this laser.

### 4. References

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Bakhrin, Y.; Wysocki, G.; Fraser, M.; Yang, R.; Tittel, F. "Sensitive, real-time interband cascade laser based sensor for ethane monitoring" *CLEO Conference*, Baltimore, MD, May 2007.

### 5. PI Contact Address

Matt Fraser, [mpf@rice.edu](mailto:mpf@rice.edu), phone: 713-348-5883, fax: 713-348-5203

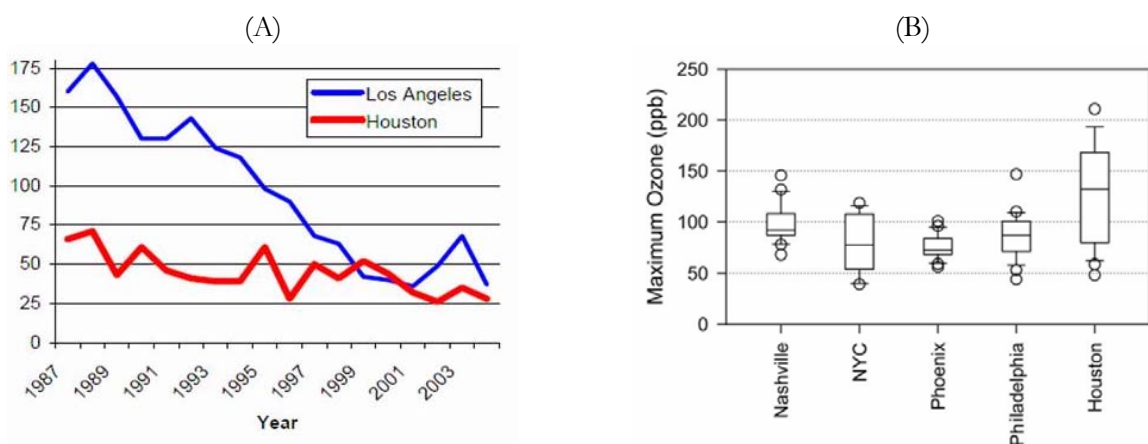
### 3. Supplements to TRAMP

#### 3.1 TRAMP: Nocturnal Mixing from Micropulse LIDAR measurements (TNMPL)

##### 3.1.1 Background

The primary goal of the TNMPL project is to quantify the degree of mixing in the nocturnal urban boundary layer of Houston during the TexAQS II study. In order to address this research need, we propose to set up a ground-based MPL measurement at the UH-Moody Tower during the TexAQS II intensive in August and September 2006. Before considering the broader needs and logistical requirements of this deployment, we will briefly highlight our specific research interests, namely nocturnal mixing and the effect this has on daytime chemistry.

Urban zones represent areas in which significant amounts of gaseous pollutants and particulate matter are released into the atmosphere. The Houston-Galveston Brazoria Area (HGB), located close to the Gulf of Mexico, is the fourth largest metropolitan area in the United States. Among major U.S. metropolitan areas, the HGB is the only one located in a subtropical region with extended hot and humid periods. Solar radiation is intense. Also, conditions with suppressed atmospheric mixing may occur. This specific climatology, along with strong emissions of primary species (carbon monoxide [CO], volatile organic compounds [VOCs] and nitrogen oxides [ $\text{NO}_x$ ;  $\text{NO}_x = \text{NO} + \text{NO}_2$ ]) favor strong photochemical processes. The land-sea breeze system basically determines the distribution of trace gases in the HGB. In addition, the diurnal variation of the planetary boundary layer controls the accumulation of primary emitted species close to the surface and also decouples ozone enriched layers aloft during nighttime. Areas like HGB frequently suffer from severe loadings of a variety of air pollutants. High concentrations of primary toxic species and photooxidants in both the gas and particle phases can result in serious health effects, as well as ecological damage and economic losses. Photochemical smog episodes are common phenomena in the HGB. Comparisons with a number of other major US metropolitan areas indicate that while peak  $\text{O}_3$  levels have decreased significantly in Los Angeles, little improvement in the number of exceedences or peak ozone levels has been observed in the HGB (see Fig. 1). Although several U.S. cities have higher particulate levels than does Houston, the higher levels of a number of hazardous pollutants may exacerbate the health effects of area particles.



**Figure 1:** (A) Annual days exceeding federal one-hour ozone standard [HCPC, 2005]; (B) distribution for the peak ozone concentration observed on aircraft flights in five US cities [Kleinman *et al.*, 2002].

Our understanding of the gas-phase processes forming ozone during the day has improved considerably over the past few decades [Finlayson-Pitts and Pitts, 1997; Seinfeld and Pandis, 1997], and rapid advances are being made in the study of the formation and chemistry of urban aerosol during daytime

smog episodes. It is also becoming increasingly clear that nocturnal chemistry influences the atmospheric composition considerably, both at night and during the following day. [Dentener and Crutzen, 1993], for example, showed that on a global scale nocturnal processes reduce the annual burden of  $\text{NO}_x$  by 50%, lowering global  $\text{O}_3$  levels in their model. Other studies show that nocturnal chemistry can lead to an increase in maximum ozone levels during the next day under highly polluted urban conditions, and influence aerosol and particulate nitrate levels [Dimitroulopoulou and Marsh, 1997; Li et al., 1993; Makar et al., 1998; Riemer et al., 2003]. Airshed models used to design air pollution control strategies do not represent nocturnal processes accurately [Fast et al., 2000]. This severely limits our ability to fight air pollution in cities and on regional and global scales. Despite its importance, the investigation of nocturnal processes in urban areas has received surprisingly little attention. The study of urban nocturnal chemistry poses an exciting challenge. Fundamental aspects, such as the influence of vertical mixing, and the altitude dependence of the nocturnal boundary layer (NBL) composition, require further investigation.

Vertical transport of trace gases plays an important role in cities, where most emissions occur close to the ground. Radiative surface cooling at night suppresses mechanically produced turbulence, leading to surface temperature inversions [Stull, 1988]. Under neutral and weakly stable conditions, trace gases are still efficiently mixed and vertical transport can be described by Monin-Obukov similarity theory [Mahrt et al., 1998; Stull, 1988]. Under strong stabilities mixing is strongly inhibited. Turbulence becomes intermittent and non-turbulent motions become important [Coulter and Doran, 2002; Mahrt et al., 1998]. Vertical mixing in cities is further complicated by the influence of buildings [Doran et al., 2002; Fast et al., 2000]. The description of vertical exchange at night, for example in air quality modeling applications, is a general problem that often leads to an inaccurate description of the chemical composition of the NBL. An additional complication which is often ignored in air pollution models is the vertical transport of reactive gases [Lenschow et al., 1982]. The similarity between the time scale of turbulent mixing and the chemical lifetime of reactive species causes differences in the vertical transport of unreactive and reactive trace gases [Fitzjarrald et al., 1983; Galmarini et al., 1997; Hamba, 1993; Kramm et al., 1991].

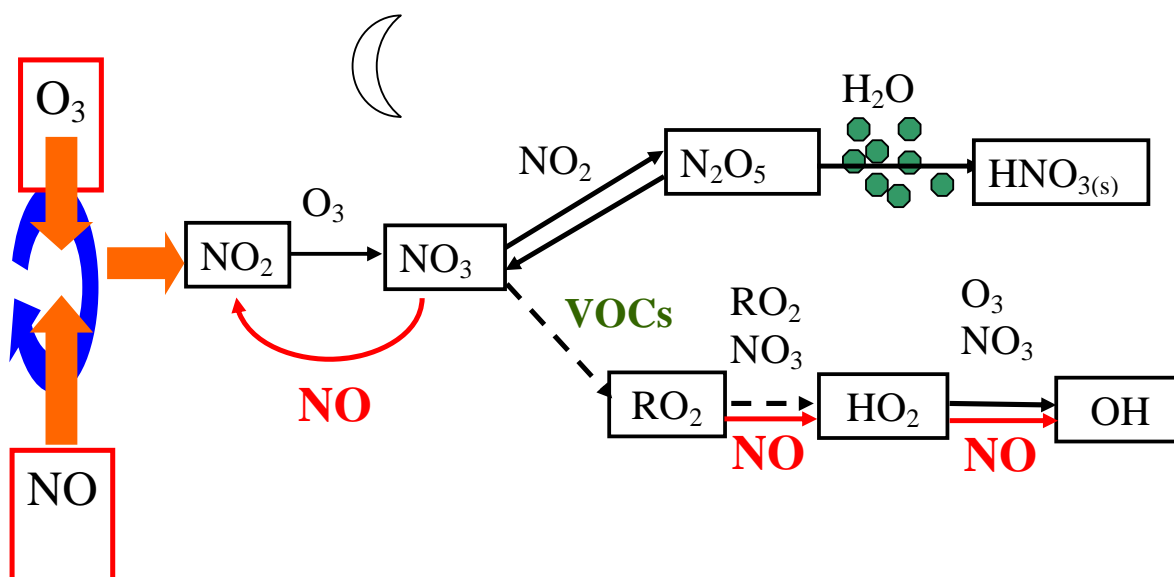
Ozone often develops distinct vertical profiles in the nocturnal boundary layer, with low values at the ground and higher values aloft [Beyrich et al., 1996; Galbally, 1968; Gusten et al., 1998; Pisano et al., 1997; Stutz et al., 2004].  $\text{O}_3$ ,  $\text{NO}$ , and  $\text{NO}_2$  profiles in the NBL are caused by dry deposition [Wesely and Hicks, 2000], the reaction of  $\text{O}_3$  with  $\text{NO}$  emitted by soil and traffic [Pisano et al., 1997], and the magnitude of vertical mixing [Geyer et al., 2004 a]. Observations by DOAS show that  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  concentrations increase with altitude in the NBL due to the higher concentrations of  $\text{NO}$ , VOC's, and aerosol close to the ground [Allan et al., 2002; Fish et al., 1999; Friedeburg et al., 2002; Galmarini et al., 1997; Geyer et al., 2004b; Stutz et al., 2004]. A limited number of airborne observations have suggested significant ozone loss at night as a result of surface reactions on aerosols [Berkowitz et al., 2001]. Reports on the vertical distribution of HONO are not conclusive. In some cases negative gradients show a formation of HONO at the ground [Kleffmann et al., 2003; Stutz et al., 2002b; Vogel et al., 2003; Wang et al., 2003b]. Positive gradients and destruction of HONO have also been observed [Harrison and Kitto, 1994; Stutz et al., 2002b].

The objective of the TNMPL (TRAMP Nocturnal Mixing – Micropulse lidar) Project is to provide observations of the mixing in the nocturnal boundary layer with a ground-based micropulsed lidar (MPL) measurements along two planes (Moody Tower – Williams Tower, Moody Tower – downtown Houston). The TNMPL observations will also provide two separate 2-D “walls” of the daytime and nighttime urban boundary layer height and aerosol optical depths. Consequently, the TNMPL dataset is a critical requirement for the interpretation of the UCLA Differential Optical Absorption Spectroscopy (DOAS) vertical trace gas profile measurements to be collected between the UH-Moody Tower and downtown Houston during the TRAMP campaign. In addition, the TNMPL observations will be useful for many other TexAQS II projects, including: the air quality modelers for validation of urban boundary layer heights and aerosol distributions, comparison to airborne lidar observations, and comparison to in situ aerosol extinction and scattering measurements.

### 3.1.2 Proposal Goals

The project helps to address the quantification of mixing in the nocturnal boundary layer and how this impacts the sources and sinks for radicals in the urban atmosphere of Houston during the TexAQS II field campaign 2006.

Fig. 2 describes radical chemistry occurring during nighttime conditions. The main starting point in the absence of solar radiation is the formation of  $\text{NO}_3$  through the conversion of  $\text{NO}$  to  $\text{NO}_2$  and subsequently to  $\text{NO}_3$  in reactions involving  $\text{O}_3$ .  $\text{NO}_3$  may either react with  $\text{NO}_2$  or a suite of VOCs including aldehydes, alkanes, short lived alkenes, and fast reacting terpenes. This way either nitrogen compounds may be removed through formation of  $\text{HNO}_3$  on particles or  $\text{OH}$  radicals can be produced which in turn interact in fast photochemical reactions during the daytime. Previous observations in Houston [Stutz *et al.*, 2004] showed that up to 50% of the 24h averaged  $\text{NO}_x$  removal occurs through  $\text{NO}_3$  radical chemistry at night, a fact often not considered in air pollution studies. Model calculations also indicate that the two of the dominant factors impacting nocturnal chemistry are the emission strength of  $\text{NO}$  and the magnitude of vertical mixing at night. In many cases uncertainties in the vertical mixing make the quantification of nocturnal radical chemistry challenging.



**Figure 2:** Nighttime radical chemistry

### 3.1.3 Project Plan

#### Micropulse lidar

The micropulse lidar is a compact commercially available eye-safe lidar. It is typically deployed for vertical profiling of the atmosphere and is capable of detecting all significant cloud and aerosol atmospheric structure up to an altitude of 20 km. In support of the TexAQS 2006 campaign, we propose to deploy a micropulse lidar with a computer-controlled scanning mirror to permit scanning of the lidar from vertical to near horizontal along two fixed vertical planes. The lidar, collocated with the DOAS, will be oriented to scan alternately towards Williams Tower and Wells Fargo Plaza Tower (Downtown Houston) to provide boundary layer heights along these vertical planes. The lidar was successfully deployed in a similar configuration in support of the New England Atlantic Air Quality Study (NEAQS-2004) in Indiana, Pennsylvania where it successfully retrieved slant path profiles of optical depth.

The current effort represents a collaboration between Battelle Northwest Division (which runs Pacific Northwest National Laboratory for the U.S. Department of Energy), providing the scanning apparatus and integration support, with Argonne National Laboratories providing the micropulse lidar

and data reduction and analysis, and with the UCLA and the University of Houston providing facilities, logistics, and support.

The micropulse lidar (MPL) transmits an eye-safe green (527 nm) laser beam. It detects backscattered photons with a range resolution as fine as 15 meters on temporal scales as short as a few seconds. Daytime operation typically requires averaging of up to 30 seconds, but nighttime operation permits commensurately less averaging. The scanning mirror apparatus is capable of both slew and fixed position mode and has a maximum scan rate of 10 degrees per second. In practice, we measure repeatedly at several fixed positions alternating from one orientation to the next on a predefined schedule. The scanning apparatus is environmentally sealed incorporating watertight seals and internal heaters to prevent condensation on optics.

### Experimental Design

The combination of the UCLA DOAS, the TNMPL, and UH GPS sondes will provide a suite of information to help constrain the nocturnal mixing critical to understanding urban nighttime chemistry. These measurements will be of use not only to our specific investigations, but to all participants of the Texas 2006 campaign who use mixing layer depth in their analysis of modeling or field observations.

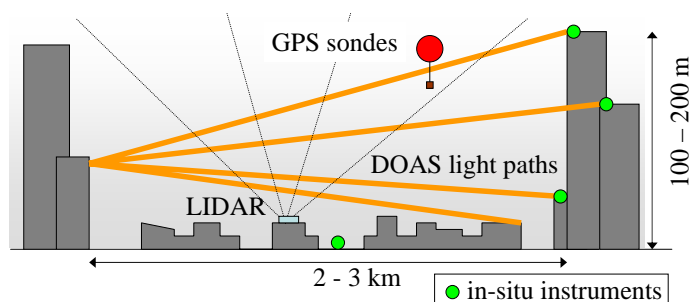


Figure 4: Proposed setup for an urban experiment.

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### 3.1.5 TNMPL Report (PI: C.J. Flynn)

#### H81 TRAMP Nocturnal Mixing from Micropulse LIDAR measurements (TNMPL)

PI: Connor J. Flynn, PNNL

Co-I: Richard L. Coulter, ANL

Co-I: Jochen Stutz, UCLA

Collaborators: Barry Lefer, U Houston, Carl Berkowitz, PNNL

#### 1. Instrumentation

- Measured Parameters:
  - planetary boundary layer heights
- Measurement Instrument/Technique:
  - lidar
- Deployment period:
  - Aug 29 – Sept 29, 2006

#### 2. Preliminary results

Excellent up-time. The lidar operated over 97% of the time. Over 1 GB of lidar profiles were collected. Initial analysis demonstrates good slant angle registration. Preliminary PBL estimates show good qualitative agreement with expected daytime/night time trends. Preliminary PBL estimates for the entire period have been delivered.

#### 3. Work in Progress

All of the routine lidar corrections have been derived and tested. These corrections are described in reference 1 below. The PBL detection algorithm (reference 2) shows promise (see figure below) but is challenged by the complex urban and coastal environment. Adaptations specific to these complex conditions including robust initial screening, localized feature identification (to reject point source contamination), and a variable dilation wavelet filter to account for strong gradients above and below the mixing layer (reference 3) will improve the quality of the lidar retrieved mixing-layer heights. Comparison with other available determinations (sonde profiles, sodar, airborne lidar) will be useful for assessing the data quality. Both of these activities have been accepted for follow-on funding for this fiscal year.

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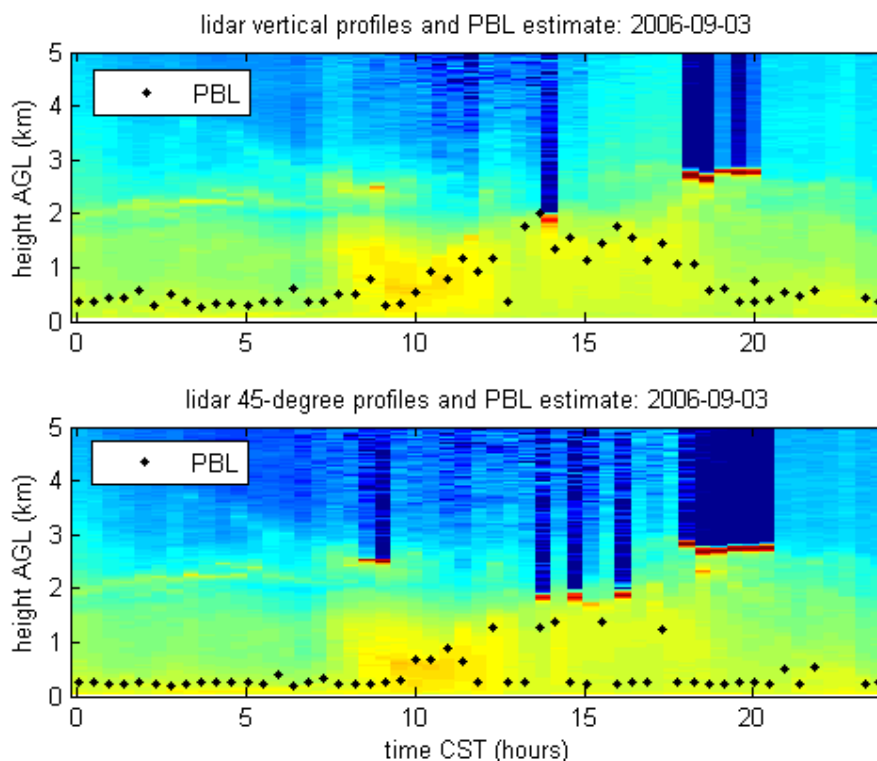
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#### 5. PI Contact Address

Connor J. Flynn, Connor.Flynn@pnl.gov, phone: 5090375-2041, fax: 509-372-6168

## 6. Figure and high-lights



This figure shows fully-corrected lidar profiles collected with the Micropulse lidar in two different orientations. The vertical axis is height above ground level in km. The horizontal axis is time in CST. The color is related to the intensity of lidar backscattering with scattering increasing from blue to yellow to red.

The top image shows vertically oriented lidar profiles. The bottom image is the vertical projection of profiles collected at 45 degrees from zenith. The excellent correlation between the two images indicates that the angle registration is accurate. Meanwhile the slightly different cloud patterns (red blocks with blue “shadows” extending upwards) indicates the varying scene observed at these two orientations.

The black dots shown in both images represent a preliminary implementation of a wavelet covariance filter algorithm for detection of the planetary boundary layer (PBL). Results for both angles demonstrate the increasing PBL height throughout the course of the solar day. It is not yet clear why the algorithm tends to report more low-level PBL heights for the slant-angle orientation.

## 3.2 PAN Measurements on Williams Tower (PAN-WT)

### 3.2.1 Background

Peroxiacetic nitric anhydride {PAN;  $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ } is a good tracer for the photochemistry involving volatile organic compounds (VOC) and nitrogen oxides ( $\text{NO}_x$ ) and is closely related to the formation of Ozone ( $\text{O}_3$ ). The PAN homologues peroxipropionic nitric anhydride {PPN,  $\text{C}_2\text{H}_5\text{C}(\text{O})\text{OONO}_2$ } and peroxyacrylic nitric anhydride {MPAN,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ } are distinctively related to anthropogenic (PPN) and biogenic (MPAN) VOC precursors.

Direct precursors for PAN are acetaldehyde ( $\text{CH}_3\text{CHO}$ ) and acetone ( $\text{CH}_3\text{COCH}_3$ ). These species are emitted directly from vegetation, but also occur as oxidation products of alkanes, alkenes and aromatics [Altschuller, 1993], including terpenes emitted by forests [Singh, 1987; Altschuller, 1993]. As important individual precursors for PAN have been reported [Seinfeld, 1989, Grosjean et al., 1993, Nouaime et al., 1998; Gaffney et al., 1999]: ethane, ethene, propene, 1-butenes, 2-butenes, 2-methyl-1-butene, i-butene, i-pentane, isoprene, alkylbenzene,  $\alpha$ -pinene,  $\beta$ -pinene, and d-limonene. These species are predominantly emitted by anthropogenic (traffic, industry, liquid petroleum gas) and biogenic sources (both deciduous and coniferous trees).

PPN originates mainly from longer chain anthropogenic hydrocarbons like alkanes (> 5 C-atoms) and alkenes (> 3 C-atoms on at least one side of the double bond) and some biogenic hexene derivatives. Important individual precursors are [Grosjean et al., 1993; Nouaime et al., 1998; Roberts et al., 1998]: propanal, propane, i-pentane, Methyl ethyl ketone (MEK), propylene, 2-methyl-1-butene, and 1-butene. Among the biogenic hexane derivatives are 3-hexenol, 3-hexenal, and cis-3-hexenol which are predominantly emitted after leaf wounding [Fall et al., 1999]. Neither terpenes nor isoprene contribute to PPN formation [Shepson et al., 1992; Altschuller, 1993].

MPAN, however, is formed primarily during the photooxidation of isoprene, which has predominantly biogenic sources such as deciduous trees [Williams et al., 1997; Roberts et al., 1998]. Direct precursor for MPAN is Methacrolein (MACR).

In terms of relative abundance of PAN and PPN, PPN/PAN ratios vary substantially from one category to the next, being 0.12 for carbonyls, 0.16 for aromatics, 0.55 for alkenes, and 0.88 for alkanes [Grosjean et al., 1993]. Thus it is possible to retrieve information about the mix of VOC-emissions. Singh and Salas [1989] as well as Altschuller [1993] observed that PPN/PAN ratios were highest in urban areas and decreased as polluted air masses were transported over long distances indicating that more reactive VOCs contribute to the formation of PPN.

### 3.2.2 Objectives

PAN measurements in Houston would provide a strong test of SIP model predictions. Currently all versions of CAMx modeling for the Houston-Galveston Brazoria Area (HGB) show only a few ppb of PAN, and virtually all reactive nitrogen ( $\text{NO}_y$ ) in these model runs is in the form of nitric acid ( $\text{HNO}_3$ ). Bayland Park on the west side of Houston, in the vicinity of Williams Tower, is one of the areas in the CAMx model where PAN predictions are very low on the worst ozone days. This also corresponds to the low participation of aldehydes in producing new radicals in the models that in turn limits the total amount of OH available to oxidize VOCs.

### 3.2.3 Project Plan

The contractor will procure a PAN/PPN/MPAN GC-ECD instrument from Metcon Inc., Boulder, which is identical to the one to be deployed on Moody Tower and set up and operate the instrument on Williams Tower. Both GCs are advanced versions to the precursor Metcon GC (for details see Volz-Thomas et al., 2002), since these instruments are equipped with two columns and allows continuous measurements of PAN, PPN, and MPAN at a temporal resolution of 10 min.

PANs will be calibrated using established calibration procedures [Roberts et al., 2001; Volz-Thomas et al., 2002; Flocke et al., 2005]. The Metcon GC is equipped with a calibration unit. PAN and PPN calibration is based on photochemical synthesis of PAN and PPN from NO calibration gas and

acetone (for PAN) and propionaldehyde (for PPN) [Volz-Thomas *et al.*, 2002]. We will use the identical NO calibration gas (acquired from Linde) as for the PAN GC at the Moody Tower. It is a certified standard which is traceable to a NIST (National Institute of Standards and Technology) gas mixture. MPAN is calibrated using calibration factors derived from PAN and PPN [Flocke *et al.*, 2005]. A recent PAN intercomparison coordinated by the NCAR in Boulder/CO showed very good agreement among the various participants and measurement devices [Tyndall *et al.*, 2005].

To make best use of the PAN data it will be important to set up this instrumentation at those floors which will be equipped with analyzers for NO<sub>x</sub>, O<sub>3</sub>, and VOC by PNNL, TAMU, and WSU. It is planned to install the PAN GC at two levels at the Williams Tower for two weeks each during the envisaged 4-week campaign. Those levels will include an intermediate floor which will give representative information about the lower boundary layer conditions and the uppermost floor which will give information about nighttime conditions above the inversion layer, and elucidate possible residual layers for PAN due to lower temperatures and less loss mechanisms through the reaction with NO. It is not planned to have PAN measurements at the lowermost floor, since loss mechanism will likely be too strong due to the proximity of strong traffic NO emissions.

Data evaluation for a 4-week campaign will require about 2 weeks. This data will be made available to the TEXAQS-II community and - along with the similar PAN data set obtained at the Moody Tower - will be an important validation tool for air quality models used in SIP applications. In addition, PAN data will be analyzed in terms of ratios among the different PANs and the different VOC precursors, in particular aldehyde compounds, determined by PTR-MS. Also, ratios of PANs and O<sub>3</sub> ratios will elucidate different VOC contributions. Finally, an important study will focus on the atmospheric lifetime considering ambient temperature and NO/NO<sub>2</sub> ratios which will elucidate the velocity of chemical processes and whether PANs may contribute to enhanced O<sub>3</sub> values through the release of NO<sub>2</sub> at high ambient temperatures.

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### 3.2.5 PAN-WT Report (PI: B. Rappenglueck)

#### H78 supplement: Measurements of PANs at the Aldine Site (Houston Triangle Site)

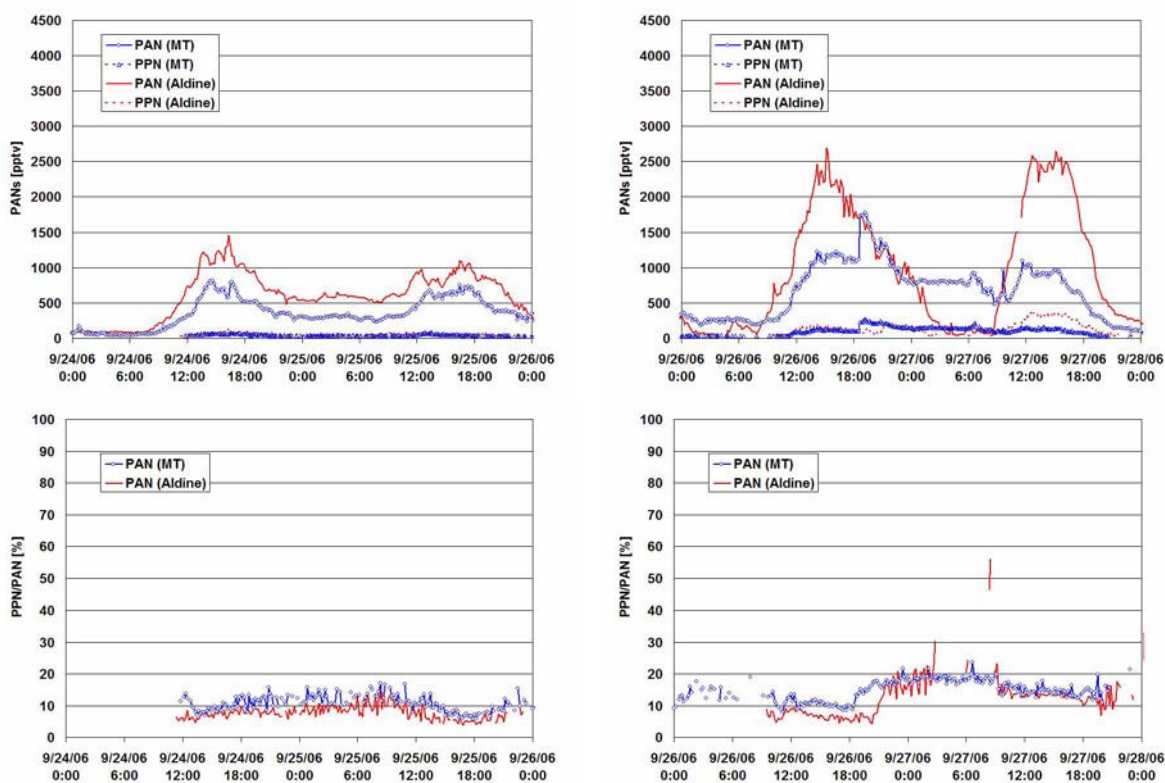
PI: Bernhard Rappenglück (University of Houston)

Collaborators: Rainer Schmitt (Metcon), Michael Leuchner (University of Houston)

#### 1. Instrumentation

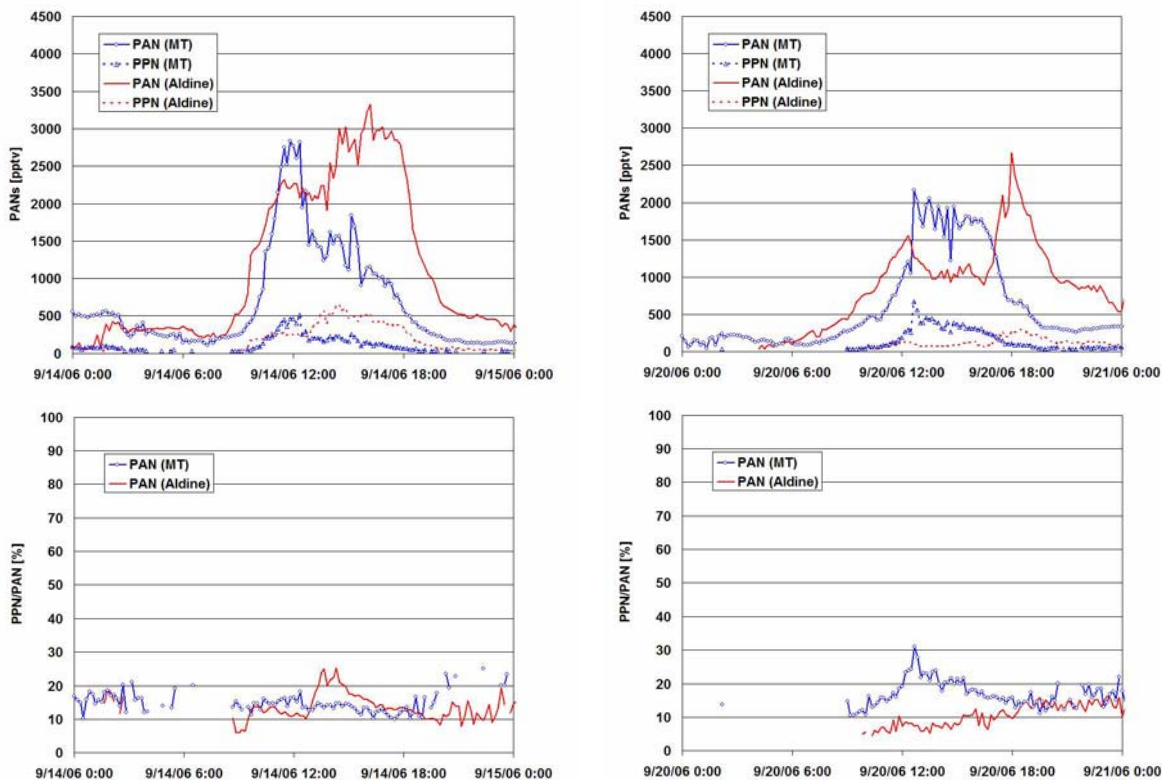
- Measured Parameters:
  - Speciated peroxyacetic nitric anhydrides (PANs)
- Measurement Instrument/Technique:
  - Metcon GC-ECD
- Deployment period:
  - 09/13 – 09/29/06

#### 2. Preliminary results



**Figure 1:** PAN and PPN time series at Aldine and at the Moody Tower (MT) on 09/24-25 and 09/26-27.

Fig. 1 displays preliminary results of the time series for peroxyacetic nitric anhydride (PAN) and peroxypropionic nitric anhydride (PPN) at the Aldine site on selected days. For comparison corresponding results from the Moody Tower are included. As shown in Fig. 1 there is a tendency of higher PAN values at the Aldine site. Usually PPN/PAN ratios are found close to 10%. PPN/PAN ratios may be higher basically due to impact of anthropogenic hydrocarbon precursors. In Fig. 1 slightly enhanced ratios are observed at night.



**Figure 2:** PAN and PPN time series at Aldine and at the Moody Tower (MT) on 09/14 and 09/20.

Fig. 2 shows that diurnal variation of PANs may be different at both sites. Actually, on 09/20 highest PAN values at MT occur in between corresponding maximum values at the Aldine site. For the 09/14 case an increase of the PPN/PAN percentage occurs at the Aldine site shortly around noon when PAN values start to increase. For the 09/20 case the PPN/PAN percentage at the MT site has a maximum at the beginning of the PAN event around noon. A distinctive shift in wind direction and associated different air masses with a change of hydrocarbon composition is most likely the reason for both the change in the diurnal variation of the absolute PAN values and the PPN/PAN fractions.

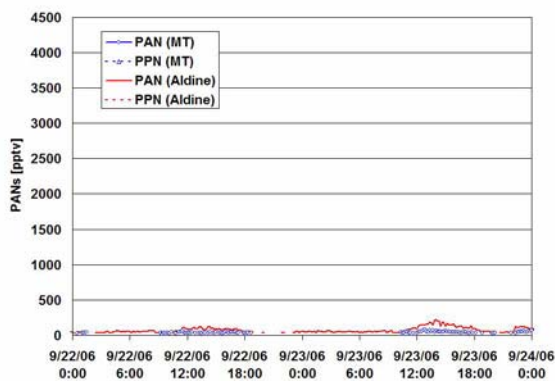


Fig. 3 shows a period with extremely low PAN values at both sites when even PAN falls under the detection limit for various times. This is an indication for background conditions with very limited photochemistry.

**Figure 3:** PAN and PPN time series at Aldine and at the Moody Tower (MT) on 09/22-24.

### 3. Work in Progress

Final evaluation of the PAN data is in process. Both the Aldine PAN data and the Moody Tower PAN data. Still needs to be related to meteorological conditions and examined in terms of anthropogenic and biogenic origins based on concurrent VOC data sets.

### 4. PI Contact Address

Bernhard Rappenglück, [brappenglueck@uh.edu](mailto:brappenglueck@uh.edu), phone: 713-743-1834, fax: 713-748-7906

### 3.3 Vertical Mixing Experiment (VME)

#### 3.3.1 Background

The temporal and spatial dynamics of the trace gas budgets are crucial for the formation of photochemical smog and the deposition of pollutants. Chemical compounds emitted into the atmosphere are continuously being removed from the atmosphere through oxidation, followed by dry and wet deposition processes. Because many photochemically important trace gases are only slightly soluble in water, dry deposition is the dominant removal process. In particular, the deposition of  $O_3$  and  $NO_y$  to the land surface plays a major role in determining air quality. In addition, knowledge of CO and VOC emissions from and deposition onto land surfaces is still rather vague and limits the accuracy of chemical transport models. Better characterization of the emission and deposition of anthropogenic and biogenic trace gases under specific atmospheric stability conditions is critical to refine air quality models.

Micrometeorological methods for flux measurements allow the quantification of surface-atmosphere exchange of trace gases. These methods include the eddy covariance (EC) for trace gas measurements of 10 Hz for analyzers, the disjunct eddy covariance (DEC), or by sampling air parcels separately for up-drafts and down-drafts (conditional sampling). For some species the Relaxed-Eddy-Accumulation (REA) is commonly used. Apart from these approaches profile measurements on micrometeorological towers have been used to address fluxes of biogenic and anthropogenic trace gases in urban areas [e.g. *Steinbrecher et al.*, 2000] and tethered systems have been used for concentration measurements [*Baumbach et al.*, 1993; *Andronache et al.*, 1994; *Baumbach and Vogt*, 1995], but also for flux measurements within the boundary layer [*Zimmerman et al.*, 1988; *Davis et al.*, 1994; *Helmig et al.*, 1998]. In order to obtain surface fluxes based on these measurements mixed-layer gradient methods [*Davis et al.*, 1994; *Helmig et al.*, 1998] and mixed-layer budget methods [*Guenther et al.*, 1996] have been applied. Profile measurements need the knowledge of atmospheric stability functions [e.g. *Schween et al.*, 1997; *Steinbrecher et al.*, 2000] and the inclusion of correction terms for reactive species accounting for reactions with OH and  $O_3$  which otherwise would lead to a bias in flux calculations.

#### 3.3.2 Objectives

The estimation of trace gas fluxes in the metropolitan area of Houston will provide an important input for SIP model predictions, as it will support the development of an improved atmospheric deposition module for the Houston-Galveston Brazoria metropolitan area. During TEXAQS-II trace gas flux measurements will be performed on the campus of the University of Houston (UH) using an integrated approach retrieving data from three different platforms (ground-based, Moody Tower, Baylor University Aztec aircraft) and deriving boundary layer information including atmospheric stability using radiosondes and a tethered system. The determination of fluxes will include  $O_3$ ,  $NO_x$ ,  $SO_2$ , CO and VOCs vertical mixing ratio profiles using approaches like the flux-gradient relationship [*Steinbrecher et al.*, 2000] or mixed-layer gradient method [e.g. *Helmig et al.*, 1998]. This will allow to determine for the first time turbulent fluxes of biogenic and anthropogenic trace gases in the Houston-Galveston metropolitan area and will be critical in the development and implementation of latest deposition parameterizations for regional chemistry transport models. Within this project, the functionality of the CMAQ regional scale chemical transport model will be improved.

#### 3.3.3 Project Plan

In order to obtain information about trace gas fluxes for  $O_3$ ,  $NO_x$ ,  $SO_2$ , CO and VOCs it is planned to include the following measurement platforms:

- ground-based site on UH campus
- Moody Tower site (60 m a.g.l) on UH campus
- Baylor University Aztec aircraft which performing spirals at different altitudes over UH campus

The Moody Tower site as well as the Baylor University (BU) Aztec are equipped with the necessary instrumentation. The UH ground-based site will be equipped with corresponding instrumentation provided by TCEQ. UH will take care of this instrumentation and carry out the set up and maintenance. UH will also carry out data validation. VOCs will be measured online at the Moody Tower and offline using canisters aboard the BU Aztec and on the ground-based site on selected days. These canisters will be provided by UH and will be analyzed using the Moody Tower VOC-GC. In order to take representative values VOC canisters will be sampled for 40 min in coincidence with the online GC sampling period. All other trace gas measurements at the ground-based site and on the Moody Tower will be averaged accordingly. The sampling time aboard the BU Aztec will be about 5 min which is considered to be representative for specific constant flight levels. In addition to the trace gas measurements the following boundary layer measurements will be carried out:

- radiosonde measurements
- tethersonde profile measurements up to 500 ft a.g.l.

This measurement will help to obtain vertical profiles of temperature, potential temperature, relative humidity, wind direction and wind speed. Tethersonde profiling will start from the ground-based and include the height of the Moody Tower site and about 300 ft above this level, while the radio sonde will cover the BU Aztec flight levels. Both systems will yield data meteorological data which is critical for calculating fluxes based on the trace gas measurements in these different levels.

### 3.3.4 Work Plan

It is envisaged to perform trace gas flux measurements on three days. On two days the BU Aztec will be available. The work plan for UH on the ground-based during these days is listed in Table 1. Boundary layer measurements using radiosondes and the tethersonde system will be performed throughout the daytime of these vertical mixing experiment days. Tethersonde measurements will be done in between two radiosonde launchings, specifically after the termination of the radiosondes since tethersonde and radiosonde are using the same frequency.

VOC canister sampling will be done from 7 am until 6 pm. Canisters will be flushed for 15-20 min and filled afterwards for 40 min which coincides with the sampling time of the online GC at the Moody Tower. Sampling at 7 am and 8 am will basically describe the VOC levels prior inversion breakup and will mostly reflect rush hour impacts, which is important to retrieve specific VOC patterns. Also this data will be important as an important input data for air quality modeling. During the daytime between 9 am – 6 pm vertical mixing of trace gases will be determined. Between 9-12 am ground based VOC canister sampling will complement Moody Tower and Baylor aircraft data.

On each vertical mixing experiment day 12 canisters will be sampled on the ground based site and about 5 aboard the aircraft. A total of 36 canisters will be sampled. Another set of 4 canisters will be sampled after the campaign on the Moody Tower to make cross-comparisons with the online GC. Since the 10 canister samples taken aboard the Baylor aircraft are covered by another project, they will not be charged to this supplement. VOC canisters will be analyzed using the GC instrumentation at the UH Moody Tower as soon as possible after VOC collection. A couple of days will be needed in between two extensive days in order to accommodate the analysis and the subsequent preparation of canisters.

After completion of three intensive days UH will take the lead to carry out the trace gas flux calculations using the trace gas and meteorological measurements. Different approaches like the mixed-layer gradient method [Davis *et al.*, 1994; Helmig *et al.*, 1998] and the mixed-layer budget methods [Guenther *et al.*, 1996] will be applied.

Local Time	radiosonde	tethersonde	VOC sampling
7:00	X		X
7:30			
8:00			X
8:30		X	
9:00		X	X
9:30		X	
10:00	X	X	X
10:30			
11:00			X
11:30		X	
12:00		X	X
12:30		X	
13:00	X	X	X
13:30			
14:00			X
14:30		X	
15:00		X	X
15:30		X	
16:00	X	X	X
16:30			
17:00			X
17:30		X	
18:00		X	X

**Table 1:** Work plan for radiosonde, tethersonde and VOC canister sampling on vertical mixing experiment days

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### 3.3.6 VME Report (PI: B. Rappenglueck)

#### H78 supplement: Vertical Mixing Experiment

PI: Bernhard Rappenglück (University of Houston)

Collaborators: Rennee Boudreaux, Craig Clements, Richard Fuller, James Flynn, Barry Lefer, Michael Leuchner, Bridget McEvoy-Day, Leonardo Pedemonte, Ryan Perna (University of Houston)

Max Shauck, Sergio Alvarez, Levi Kauffman, Grazia Zanin (Baylor University)

Martin Buhr (Air Quality Design)

Winston Luke (NOAA/ARL)

Noor Gillani (University of Alabama)

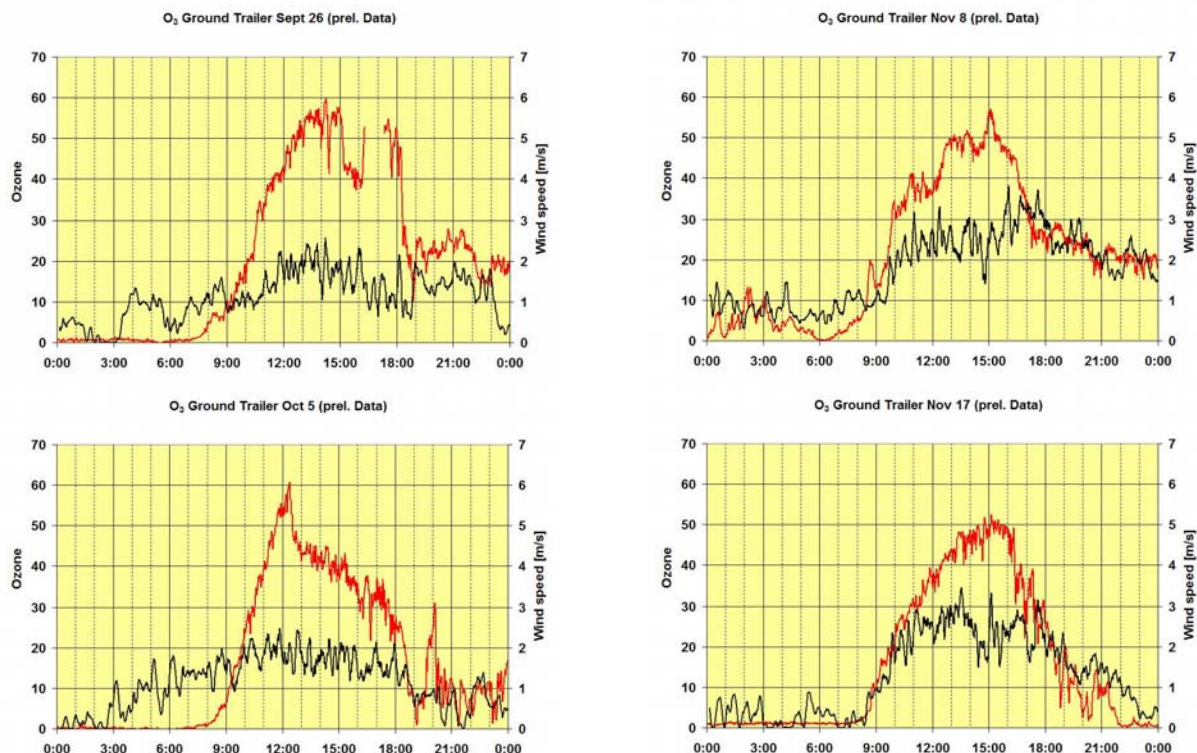
Gary Morris (University of Valparaiso)

#### 1. Instrumentation

- Measured Parameters:
  - O<sub>3</sub>, NO<sub>x</sub>, NO<sub>y</sub>, SO<sub>2</sub>, CO, HCHO, volatile organic compounds (VOCs) and met. data
- Measurement Platforms:
  - Ground-based trailer on University of Houston campus (UHC)
  - Radiosondes (RS), Ozonesondes (OS), Tethersonde (TS)
  - Moody Tower on University of Houston campus (MT)
  - Baylor University Aztec aircraft (BU)
- Measurement Dates:
  - 09/26, 10/05, 11/08, 11/17
- Measurement Instrument/Technique:
  - O<sub>3</sub> UV photometry (UHC, MT, BU, TS), electrochemical concentration cell [ECC] (OS)
  - NO<sub>x</sub> Chemiluminescence (UHC, MT, BU)
  - NO<sub>y</sub> Chemiluminescence (MT [not available on 3<sup>rd</sup> and 4<sup>th</sup> VME day], BU)
  - SO<sub>2</sub> pulsed fluorescence (UHC, MT [not available on 3<sup>rd</sup> and 4<sup>th</sup> VME day], BU)
  - CO gas filter correlation (UHC, MT), vacuum ultraviolet fluorescence (BU)
  - HCHO Hantzsch reaction fluorescent (MT, BU)
  - VOC: GC-FID offline (UHC, BU), online (MT)
  - Meteorological data (UHC, MT, BU, RS, OS, TS)

#### 2. Preliminary results

Four days of the Vertical Mixing Experiment (VME) days have been performed. Only the second day [09/26] included BU flights. Boundary layer measurements using radiosondes and the tethered system were performed throughout the daytime of the 1<sup>st</sup> and the 2<sup>nd</sup> VME day. Radiosondes were launched at 5 am, 7 am, 10 am, 1 pm, 4 pm, and 7 pm. Tethersonde measurements were done in between two radiosonde launchings, specifically after the termination of the radiosondes since tethered and radiosonde were using the same frequency. Vertical soundings were complemented by O<sub>3</sub> sonde launches at 7 am and 1 pm. The 3<sup>rd</sup> and 4<sup>th</sup> VME days were carried out late in the year. Thus vertical soundings were restricted to 7 am to 1 pm. Apart from continuous air chemistry measurements on these days VOC canister sampling were done from 7 am until 6 pm (until 1 pm on the 3<sup>rd</sup> and 4<sup>th</sup> VME days) starting 20 min before the hour. Canisters were



**Figure 1:** Time series of ozone and wind speed obtained on the four VME days.

flushed for 15-20 min and filled afterwards for 40 min which coincided with the sampling time of the online GC at the Moody Tower. On the second VME day the BU aircraft made several spirals over UH campus between 8 am and 12 pm.

Fig. 1 displays preliminary results of  $O_3$  time series on all VME days. Almost all days show low  $O_3$  values during the early nighttime and morning hours which reflects efficient NO titration under low mixing layer heights. In particular the 1<sup>st</sup> and the 2<sup>nd</sup> VME days display a steady increase of  $O_3$  mixing ratios from 7/8 am until noon. Abrupt break-up of the morning inversion layer seems to be absent. On most days maximum wind speed was below 3 m/s, on the 1<sup>st</sup> and the 2<sup>nd</sup> day maximum wind speed was only about 2 m/s indicating limited advection. On these two days there is no clear coincidence of rising  $O_3$  levels with increasing wind speed as observed on the 3<sup>rd</sup> and 4<sup>th</sup> VME days. On the 2<sup>nd</sup> VME BU aircraft performed spirals over UH campus ranging from 200-12,000 ft. The data shows the development of the mixing height from about 1000 ft at 10 am up to 5000 ft at 1 pm, when the mixing layer height was fully developed. During these three hours the mixing layer height gradually increased which was also reflected in the gradual  $O_3$  increase at UHC at a steady rate of about 15 ppb/hr between 8 am and noon.

### 3. Work in Progress

VOC canisters have been analyzed, however extensive evaluation also including other air chemistry and meteorological data obtained for the VME days is not yet completed. QA/QC work is currently being performed for air chemistry data. Tethersonde data is being reprocessed. Once the data is fully available the VME data set will be provided to the newly implemented H87 project. A key issue to be assessed will be the ability of the new Asymmetric Convective Mixing 2 (ACM2) scheme in CMAQ to explain VME observations of CO, ozone, VOC (including formaldehyde), and reactive nitrogen and to compare these results to those of the base case PBL scheme.

### 4. PI Contact Address

Bernhard Rappenglück, [brappenglueck@uh.edu](mailto:brappenglueck@uh.edu), phone: 713-743-1834, fax: 713-748-7906