

Project H74A

**Ground-based Measurements of Volatile Organic Compounds (VOCs) and Nitrogen
Reservoir Species during TexAQS II – 2006**

Final Report

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EXECUTIVE SUMMARY

The purpose of this HARC funded research (H74A) is to conduct ground-based measurements of volatile organic compounds (VOCs) and nitrogen species (HNO_3 and N_2O_5) during TexAQS II - 2006. This project includes two tasks: (1) measurements of VOCs using proton transfer reaction mass spectrometry (PTR-MS) at the Aldine site and at the University of Houston Moody Tower. A commercial version of PTR-MS (Ionicon Analytik Ges.m.b.H, Innsbruck, AUSTRIA) was used for measurements of pre-selected highly reactive VOCs (HRVOCs). The species measured with PTR-MS included alkenes and aromatics (such as propene, butenes, toluene, isoprene and etc). (2) Measurements of nitrogen-containing compounds such as HNO_3 , N_2O_5 , and NO_3 were made using ion drift-chemical ionization mass spectrometry (ID-CIMS) at the University of Houston Moody Tower. The VOC measurements will help to verify and update the VOC emission inventory, and the measurements of nitrogen containing species will provide an opportunity to assess the nighttime nitrogen chemistry and its role in the O_3 chemistry. The ultimate objective of the measurements is to facilitate decision-makers in the revision of the State Implementation Plans (SIPs) with up-to-date VOC emission inventory and more detailed nitrogen nighttime chemistry.

We originally proposed to measure VOCs at one level, and particulate matter at three levels from the Williams Tower. However, an agreement for space rental on the Williams Tower could not be reached. Consequently, the research plan was changed to a 3-week campaign carried out during the month of September to provide continuous observations of hydrocarbons, aerosols, and selected trace gases at the Deer Park, Aldine, and Bayland Park air monitoring stations, in collaboration with the Pacific Northwest National Laboratory (PNNL) team led by Dr. Carl Berkowitz. The scientific goals involved the characterization and aging of hydrocarbons and aerosols within the Houston Ship Channel plume, and describing these changes as the plume moves across Houston.

Our field project was divided into two parts. (1) From Aug. 17 to Sep. 9, as part of the TRAMP (TexAQS II Radical Measurement Project), both the PTR-MS and the ID-CIMS were deployed at the University of Houston Moody Tower (Lat 29.71667, Lon -95.33333, Elev 70 m) to measure VOCs, HNO_3 and N_2O_5 . (2) From Sept. 14 to Sept. 30, the PTR-MS was relocated to the TCEQ Aldine site (Lat 29.901111, Lon -95.32611, Elev 18 m) to participate in the Houston Triangle Project, while the ID-CIMS continued the VOC and HNO_3 measurements at the Moody Tower. In addition, the PNNL team deployed an aerosol mass spectrometer (AMS) at the Aldine site from Sept. 15 to 28 to monitor aerosol chemical compositions. After the TRAMP campaign ended on Sept. 30, the PTR-MS remained at the Moody Tower from Oct. 1 to 14. Some extra VOC data were collected.

During the campaign, we detected fourteen individual or group of VOCs, including acetonitrile, propene, acetaldehyde, butenes, acetone, acetic acid, isoprene, methyl vinyl ketone (MVK) + methacrolein (MACR), methyl ethyl ketone (MEK) + methylglyoxal (MGLY), benzene, toluene, C2-benzenes, C3-benzenes, and monoterpenes. Propene and butenes were identified as the major alkene species observed during the campaign and showed influences from the Houston Ship-Channel area and its petrochemical industries. Aromatic VOCs were dominated by automobile emissions. The benzene/toluene ratio was 0.15 indicating the gasoline

benzene content has dropped significantly since TexAQS 2000 [Karl et al., 2003]. Isoprene and monoterpenes showed evidence of both biogenic and industrial sources. VOCs observed at Aldine correlated well with organic aerosol measurements, suggesting that oxygenated VOCs might participate in secondary organic aerosol formation.

The HNO_3 detection limit of the ID-CIMS was 30 pptv for 10 s integration time. The HNO_3 diurnal profile followed the solar cycle and the daily high mixing ratios ranged from 0.2 to 2 ppbv in the early afternoon. Occasionally, nighttime peaks were also observed, which could be originated from either $\text{N}_2\text{O}_5 + \text{H}_2\text{O}$ heterogeneous reactions or transported aged plumes. Preliminary analysis showed that both O_3 and HNO_3 time series had similar trends and followed each other very well, consistent with the production mechanism of HNO_3 during the daytime.

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1. Introduction

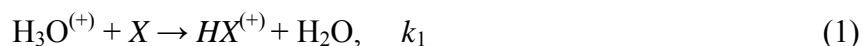
The purpose of this HARC funded research (H74A) is to conduct ground-based measurements of VOCs using proton transfer reaction mass spectrometry (PTR-MS) and nitrogen species (HNO_3 and N_2O_5) using ion drift - chemical ionization mass spectrometry (ID-CIMS) during TexAQS II - 2006. It is well established from the TexAQS 2000 study that both VOCs and NO_x (NO and NO_2) play key roles in the O_3 photochemical production process in the Houston area. In order to develop an effective control strategy to reduce O_3 production, it is crucial to know their concentrations and evolving processes in the atmosphere. The proposed VOC measurements will help to verify and update the VOC emission inventory, and the proposed measurements of nitrogen-containing species will provide an opportunity to assess the nighttime nitrogen chemistry and its role in O_3 chemistry. The ultimate objective of these measurements is to facilitate decision-makers in the revision of the State Implementation Plans (SIPs) with up-to-date information.

This project includes two tasks: (1) measurements of volatile organic compounds using proton transfer reaction mass spectrometry at the Aldine site and at the University of Houston Moody Tower. A commercial version of PTR-MS (Ionicon Analytik Ges.m.b.H, Innsbruck, AUSTRIA) was used for measurements of pre-selected highly reactive VOCs (HRVOCs). The species measured with PTR-MS include alkenes, aromatics (such as propene, butenes, toluene, isoprene and etc.), and oxygenated VOCs. (2) Measurements of nitrogen-containing compounds such as HNO_3 , N_2O_5 , and NO_3 were made using ion drift-chemical ionization mass spectrometry at the University of Houston Moody Tower.

We originally proposed to measure VOCs at one level, and particulate matter at three levels from the Williams Tower. However, an agreement for space rental on the Williams Tower could not be reached. Consequently, the research plan was changed to a 3-week campaign carried out during the month of September to provide continuous observations of hydrocarbons, aerosols, and selected trace gases at the Deer Park, Aldine, and Bayland Park air monitoring stations, in collaboration with the Battelle team led by Dr. Carl Berkowitz. The scientific goals involved the characterization and aging of hydrocarbons and aerosols within the Houston Ship Channel (HSC) plume, and describing these changes as the plume moves across Houston.

2. PTR-MS Methodology

The principle that PTR-MS utilizes is the detection of a neutral molecule X according to the proton transfer reaction



where $\text{H}_3\text{O}^{(+)}$ is the reagent ion, $\text{HX}^{(+)}$ is the protonated product ion, and k_1 is the ion-molecule reaction rate constant. The abundance of the neutral species X can then be quantified from the equation

$$[\text{HX}^{(+)}] = k[\text{H}_3\text{O}^{(+)}][X]t \quad (2)$$

where

$$t = l/U_{\text{ion}} \quad (3)$$

and l is the length of the drift tube while U is the reagent ion drift velocity in the drift tube. The reagent ion drift velocity U is determined by the equation

$$U = uE \quad (4)$$

where u is the ionic mobility of the ion and E is the voltage gradient in the drift tube. The ionic mobility is determined by

$$u = u_0(760/P)(T/273) \quad (5)$$

where P and T are the pressure and temperature within the drift tube and u_0 is the reduced ionic mobility taken from the literature. The proton transfer reaction is very efficient for hydrocarbons and oxygenated VOCs with a proton affinity greater than that of water (165.5 kcal mol⁻¹). The method of employing PTR-MS to quantify atmospheric VOCs has been thoroughly discussed by Lindinger et al. and de Gouw et al.

One of the primary limitations of PTR-MS is the fact that it measures the ions at a particular mass and there may in some situations be more than one species detected at a specific mass. Certain masses such as masses 45 (acetaldehyde), 79 (benzene) and 93 (toluene) can generally be attributed to only one species while other masses such as 43, 57 and 71 are more complicated. These masses have multiple species and while PTR-MS is ideally suited to characterize the dimensions and magnitude of the VOC plume, GC or canister samples may be better suited to speciate the VOCs of these masses, provided GC is capable of measuring all of the different VOC species which is another limitation particular to GC analysis. It should be noted that this limitation of PTR-MS can frequently be overcome if the goal is to measure only one particular VOC rather than cycling through a suite of masses. In the case where only one VOC is measured adjustments can be made to the electric field in the drift tube to affect fragmentation patterns in the drift tube. This frequently limits the PTR-MS to measuring only the VOC which the electric field has been tuned for.

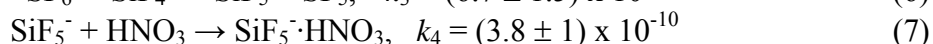
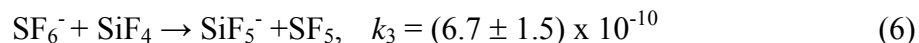
We have developed a catalytic converter to obtain the VOC background at a particular mass and by doing this we have maintained the relative humidity of the sample air. Results indicated that this method worked well in the recently completed MILAGRO (Megacities Impacts on Regional and Global Environment) field campaign where the instrumental background was found to be a factor of 10-100 times less than the ambient condition and humidity did not affect it.

VOC calibration was performed using commercially available VOC standards. The Texas A & M University (TAMU) standard contains 10 compounds (propylene, 1-butene, acetone, isoprene, methyl ethyl ketone, benzene, toluene, m-xylene, alpha-pinene, and 1,3,5-trimethylbenzene) at mixing ratios of 100 ppbv each. The commercial PTR-MS was recently tuning optimized from the MILAGRO field project and calibration correction factors were found to range from .7 to 1.25 during the MILAGRO field campaign where calibrations were conducted in the range of 1-20 ppb of VOC standard using the previously referred to standard.

We also coordinated with other groups exchanging our standards in order to facilitate the calibration of the greatest number of species using the same standards to calibrate multiple instruments. Calibrations were conducted at a minimum of twice weekly and more frequently if conditions warranted. Side-by-side intercomparison of the commercial PTR-MS with the ID-CIMS instrument was accomplished by using the same inlet line to determine relative detection limits and the level of agreement between the instruments. Limited canister samples were also taken and cross comparison with the canisters were conducted after the field campaign. Preliminary data were exchanged with the PNNL PTR-MS groups during the field program in order to better coordinate our efforts at measuring VOCs of interest. Final data were also exchanged upon conclusion of data analysis after the field program. Coordination was done to ensure that data analysis was conducted in the same manner as the other PTR-MS used in the Houston Triangle Project.

3. ID-CIMS Methodology

For HNO_3 detection, the ion-molecule reaction sequence



are used to produce the reagent ion [Huey et al., 1998]. HNO_3 is quantified using [Fortner et al., 2004]

$$[\text{HNO}_3] = [\text{SiF}_5^- \cdot \text{HNO}_3] / (k_4 [\text{SiF}_5^-] \Delta t) \quad (8)$$

The reduced ionic mobility of SiF_5^- in N_2 has not been experimentally determined. We estimated its value on the basis of the literature value for SF_6^- in N_2 , assuming an exponential mass-dependent expression between the masses of the two respective ions. The literature value for the ionic mobility of SF_6^- in N_2 is $1.9 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ [Huey et al., 1995] and we estimated a value of $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for SiF_5^- in N_2 .

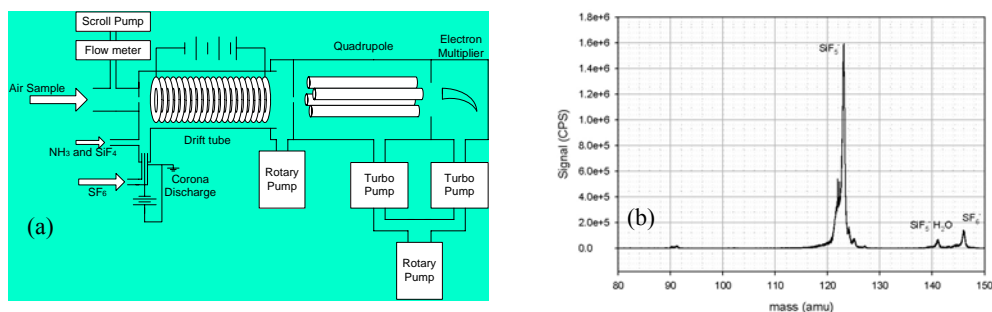


Figure 1. ID-CIMS configuration (a) and reagent ion detection (right) for HNO_3 measurement.

HNO_3 calibration was performed using a permeation source. Fig. 1 shows the ID-CIMS configuration and reagent ion spectra for HNO_3 detection. Fig. 2 depicts HNO_3 calibration using a permeation tube and calibration results. Typical detection sensitivity of the ID-CIMS instrument for HNO_3 is on the order of 30-100 pptv.

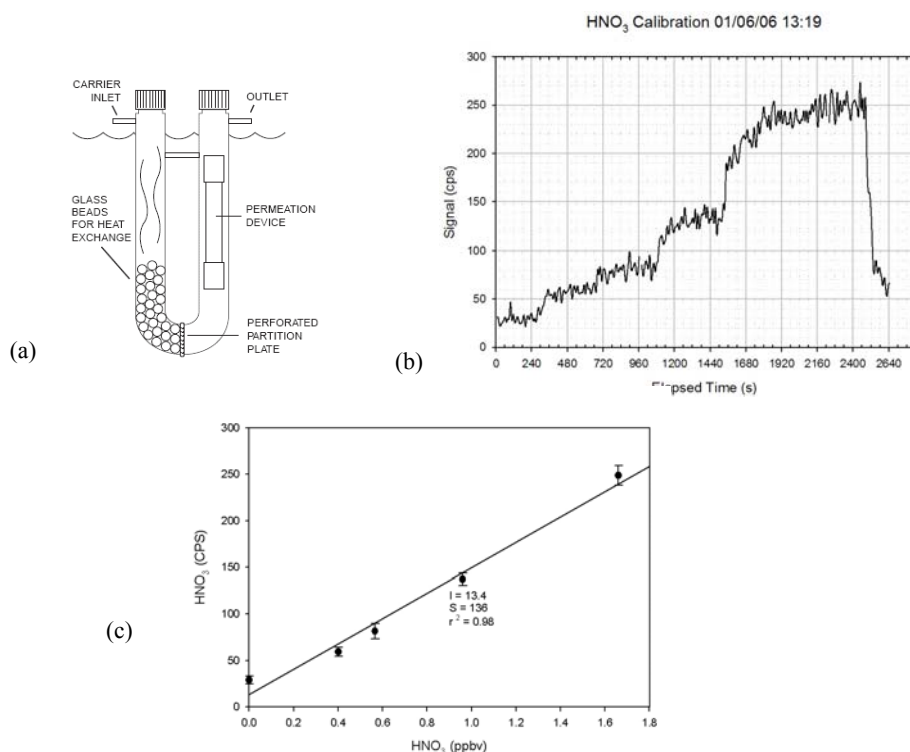
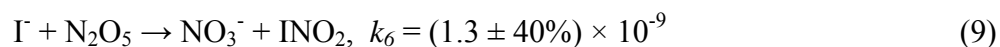


Figure 2. HNO₃ calibration using a permeation tube (a) and some results of calibration (b) and (c).

For N₂O₅ detection, the ion molecule reaction



is used to produce the product ion [Zhang et al., 1995]. N₂O₅ is quantified using

$$[N_2O_5] = [NO_3^-] / (k_6 [I^-] \Delta t) \quad (10)$$

The I⁻ reagent ion reacts only with N₂O₅ and creates the product ion, NO₃⁻, but its reaction with HNO₃ is much smaller [Huey et al., 1995].

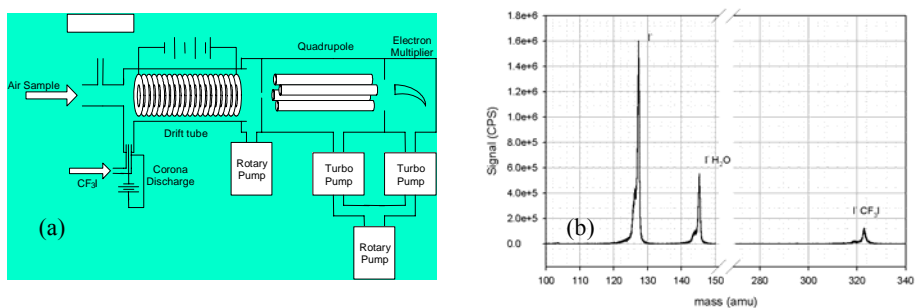


Figure 3. ID-CIMS configuration (a) and reagent ion detection (b) for N₂O₅ measurement.

N_2O_5 calibration was performed using a UV absorption cell. Fig. 3 shows the ID-CIMS configuration and reagent ion spectra for N_2O_5 detection. Fig. 4 depicts N_2O_5 calibration using the UV absorption cell and some results of calibration. Typical detection sensitivity of the ID-CIMS instrument for N_2O_5 is on the order of 20-100 ppt, similar to that of HNO_3 .

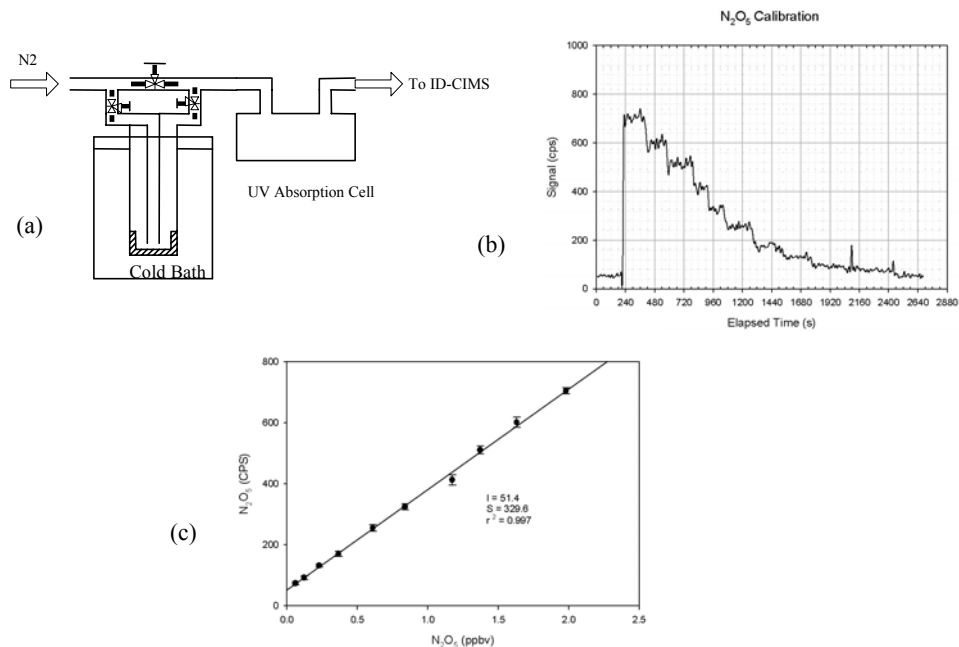


Figure 4. N_2O_5 calibration using a UV absorption cell (a) and some results of calibration (b) and (c).

The sampling inlet was critical for the HNO_3 , NO_3 , and N_2O_5 measurements, especially in an area with a high humidity such as in Houston. A short and heated inlet represented the best solution. Also, a fast pumping speed for the sample flow was needed to minimize the residence time.

4. Instrument QA/QC Overview:

4.1 QA/QC for the VOC data:

The QA/QC procedures for VOC data focused on determining the background signal and calibration factor for each VOC species. The background signal was checked with a catalytic converter, a half-inch OD stainless steel tube filled with Pt coated quartz fiber (Shimadzu Corporation). The advantage of the catalytic converter is that it removes VOC from the ambient air without changing the air humidity. Thus, the background signal could be measured under the same conditions as those of normal measurements. The PTR-MS was calibrated against a suit of working VOC standards generated by mixing commercial certified ($\pm 10\%$ of the labeled value) VOC standards (Spectra Gases Inc.) into the zero air produced by the catalytic converter. The slope of the plot of signals against standard mixing ratios yielded the calibration factor that we used to convert the raw data into real concentrations with an uncertainty no more than 12%. Table 1 lists the averaged calibration factors for propene, acetaldehyde, butene, isoprene, benzene, toluene, and xylene based on calibration data collected at the Aldine site.

VOC	Propene	Acetaldehyde	Butene	Isoprene	Benzene	Toluene	Xylene
Calibration Factor (signal / ppbv)	6.37×10^{-12}	1.22×10^{-11}	8.21×10^{-12}	9.52×10^{-12}	7.90×10^{-12}	8.32×10^{-12}	7.80×10^{-12}

Table 1: Calibration factors used for processing VOCs data collected at the Aldine site.

4.2 QA/QC for the HNO₃ data:

The background HNO₃ signal was checked by passing ambient air through a nylon cloth filter coated with sodium bicarbonate and the HNO₃ standards were generated by a commercial permeation tube. The permeation device used for HNO₃ calibration consisted of a U-shape 1-inch OD, 7-inch long glass tube and a regulated heating jacket wrapped around the glass tube. The U-tube was divided into two symmetrical compartments by a glass grid in the middle. One side housed a 5.0-cm long Teflon permeation tube (VICI Metronics Inc) and the other side was filled with 0.5-cm diameter glass beads. During calibration, the whole device was heated and maintained at 40 °C. About 300 to 400 sccm (standard cubic centimeter per minute) N₂ carrier gas was fed into the side filled with glass beads and warmed up to the same temperature as the entire device before entering the permeation tube side. Right after exiting the permeation device, the concentrated HNO₃/N₂ stream was injected into a 1-inch OD Teflon tube in which it was mixed with a 50 to 200 slpm (standard liter per minute) dilution flow. The concentration of the final HNO₃ working standard ranged between 300 pptv and 2 ppbv.

Although the permeation tube was certified by the manufacturer, due to the “sticky” nature of HNO₃ it was still necessary to verify its effective permeation rate under normal field operation conditions to account for any possible wall loss during the handling of the standards. The verification procedure was similar to the normal calibration process. Instead of introducing the generated HNO₃ standards into the ID-CIMS for calibration, we bubbled the HNO₃ standard through a specific amount of pure water (Resistance > 17 MΩ) for a specific time. The collected HNO₃ solution was then analyzed by ion chromatography (DIONEX), which was calibrated by ultra pure sodium nitrate solutions. The uncertainty with this procedure was usually within a few percent. Our measured permeation rate was 109 ng/min and the claimed value was 116 ng/min. Therefore, we estimated that the uncertainty associated with our HNO₃ calibration was less than 6%.

5. Measurements of VOCs at the Aldine Site

We have performed VOC measurements using PTR-MS at the Aldine Site, in conjunction with the Houston Triangle project conducted by the PNNL team led by Dr. Carl Berkowitz. The Houston Triangle project corresponded to an extensive field campaign for VOC and aerosol monitoring in Houston, Texas at three sites surrounding the urban Houston and the HSC, as part of the 2006 Texas Air Quality Study (TexAQS II). The three locations were Deer Park (south of HSC), Aldine (north of HSC), and Bayland Park (west Houston). The Aldine site is located in Harrison County, northwest of the Houston Ship Channel, latitude 29°54'04” north, longitude 95°19'34” west, and elevation 18 m. Fig. 5 shows the pictures of the Aldine site and the instruments stationed there. The primary measurements included anthropogenic and biogenic VOCs and their degradation products by PTR-MS, aerosol chemical compositions by AMS, and

aerosol size, distribution and hygroscopicity by TMDA at each location, in addition to routine chemical and meteorological data. The research objectives consisted of assessment of conversion and interaction between VOCs and secondary organic aerosols (SOAs) to better understand SOA formation and characterization of VOCs and aerosols to better understand VOC and aerosol emission sources.



Figure 5. The instruments at the Aldine site: (top left) the trailer, (bottom left), PTR-MS, and (right) AMS.

Results from the 2000 Texas Air Quality Study (TexAQS) have unambiguously established that highly reactive volatile organic compounds from petrochemical industrial sources are linked to rapid and efficient photochemical ozone production in the Houston Galveston area [e.g., Daum et al., 2003]. In particular, lower molecular weight alkenes such as ethylene, propylene, and butenes are identified to be most abundant inside petrochemical source plumes and dominate the reactivity of VOCs [Daum et al., 2003; Ryerson et al., 2003; Berkowitz et al., 2004]. Those field measurements also indicate that measurement-inferred emissions of the lighter alkenes are substantially higher than reported by current inventories [Karl et al., 2003; Ryerson et al., 2003; Wert et al., 2003]. Hence one of the most critical elements to quantify ozone formation in photochemical models and to implement SIP for cost-effective ozone control strategies lies in better assessments of the emission sources and inventories of HRVOCs from the industrial sources [Lei et al., 2003; Zhang et al., 2004]. In recognition of this need the HARC Contract # H48.T3.2004 TAMU T2 was awarded to facilitate the purchase and use of the Ionicon Compact Proton Transfer Reaction Mass Spectrometer (PTR-MS) in ground and airborne field studies in Texas.

PTR-MS is a unique method for online quantification of VOCs in air developed by Lindinger et. al. [1998] and co-workers at the University of Innsbruck. Proton-transfer reactions of hydronium ions (H_3O^+) are employed to ionize VOCs and the resulting product ion is then detected by mass spectrometry. VOCs directly emitted from natural and anthropogenic sources

as well as their oxidation products may be quantified simultaneously by PTR-MS. Desirable features that PTR-MS offers which differentiate it from GC-MS systems and canister samples are a fast time response of seconds or less and the ability to continuously monitor VOCs and receive real time data that clearly shows the magnitude and spatial dimensions of VOC plumes.

VOCs observed at the Aldine site included light C3-C4 alkenes, aromatic compounds and oxygenated VOCs (OVOCs). Biogenic VOCs were occasionally detected during night. Propene and butene were major products as well as raw materials in the petrochemical industry. Aldine is about 20 miles to the northwest of the ship channel area thus some industry influence is expected at the Aldine site. However, no significant increase of propene and butene was detected at Aldine during the campaign. Fig. 6 shows the diurnal profiles of propene and butene averaged between Sep 14 and 28. Daily averaged propene and butene were about 5.9 and 8.0 ppbv, respectively. Both propene and butene started to decrease after sunrise (around 6 am), reached minimum around noon, and increased gradually in the afternoon and evening. This anti-correlation with solar cycle might result from a combined effect of photochemical reactivity and planetary boundary layer (PBL) height.

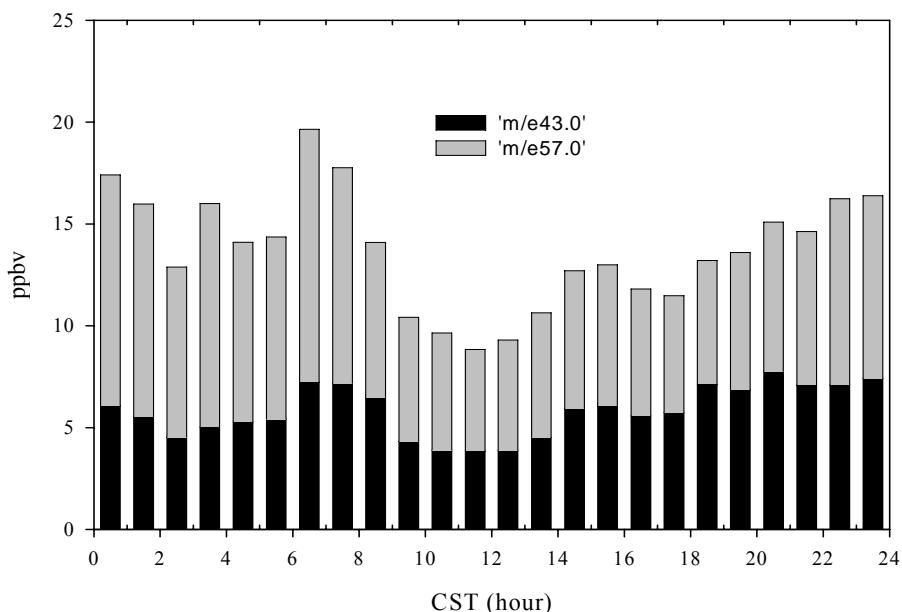


Figure 6. Diurnal profiles of propene (m/e 43) and butene (m/e 57) averaged between Sept. 14 and 28.

Aromatic VOCs observed at the Aldine site showed a signature of fresh auto vehicle emissions. Fig. 7 represents the diurnal profiles of benzene, toluene, and C2-benzenes. The daily average concentrations of benzene, toluene, and C2-benzenes were 0.08, 0.56, and 0.39 ppbv, respectively. The peak between 6 AM and 9 AM coincided with the rush hour traffic. The daily profiles also anti-correlated with solar cycle because oxidation by OH radicals was the major sink for aromatic VOCs. Another feature of the profiles was that the benzene to toluene ratio was very low (0.15), which indicated that the plumes were freshly emitted and the gasoline consumed on the road was nearly benzene free.

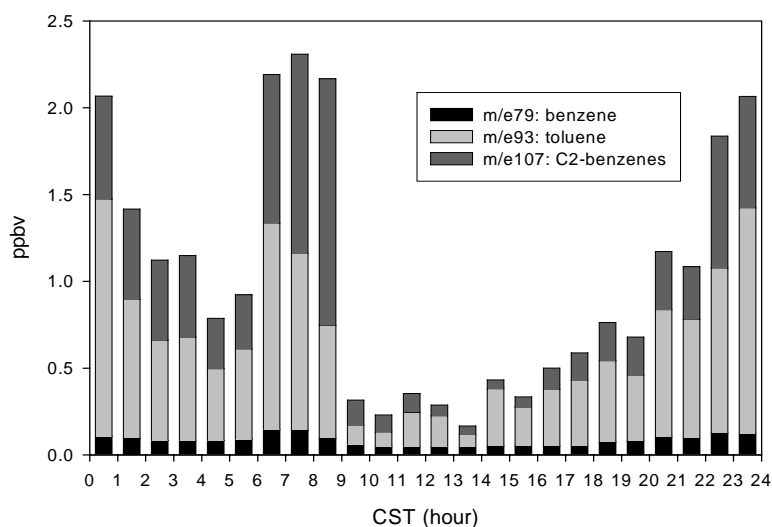


Figure 7. Diurnal profiles of benzene (m/e79), toluene (m/e93), and C2-benzenes (m/e107) averaged between Sept. 14 and 28.

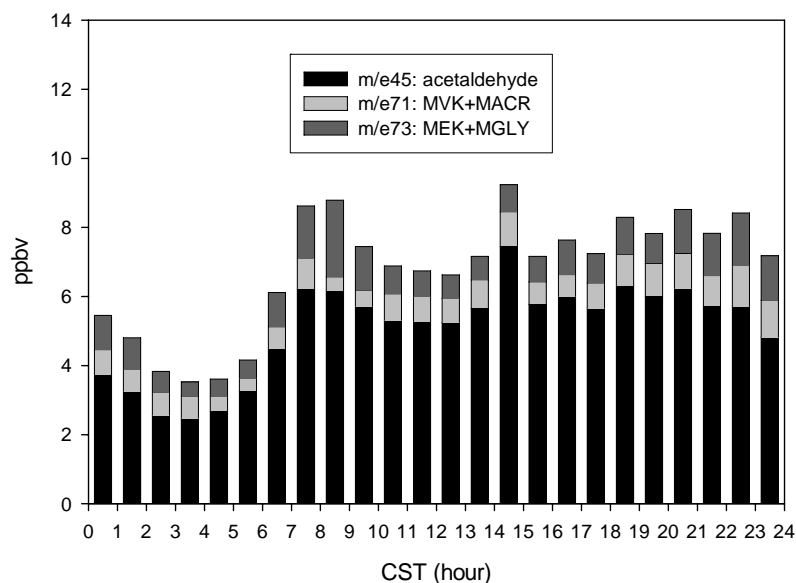


Figure 8. Diurnal profiles of OVOCs averaged between Sept. 14 and 28.

Fig. 8 shows the diurnal profiles of acetaldehyde, MVK, MACR, MEK, and MGLY observed at the Aldine site. Acetaldehyde was the major component of OVOCs and increased significantly after sunrise, indicating that it was mainly formed from photochemical processes. Interestingly, the concentrations of MVK+MACR were higher in the late evening than during the daytime, consistent with the nighttime observations of isoprene and monoterpenes. MEK and MGLY showed similar trend as aromatic VOCs, but their peak time was one hour later. This might indicate the major component of mass 73 was MGLY, which was produced from OH oxidation of aromatic VOCs.

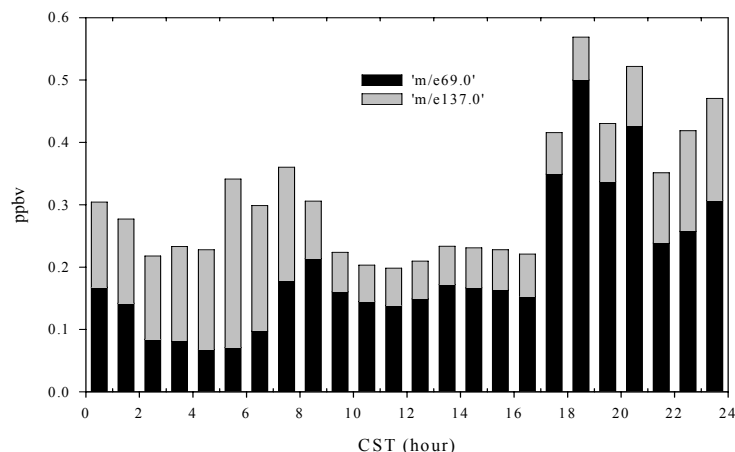


Figure 9. Diurnal profiles of isoprene (m/e 69) and monoterpenes (m/e 137) averaged between Sept. 14 and 28.

Isoprene and monoterpenes are important biogenic VOCs; both are very reactive with hydroxyl radicals (OH) and their emission rates response to environmental stresses, such as the leaf temperature. Isoprene emission also is sensitive to sunlight, in contrast to monoterpene emission. Fig. 9 shows the diurnal profiles of isoprene and monoterpenes observed at the Aldine site. Minimum isoprene and maximum monoterpenes were observed at about 5 am, when there was no emission of isoprene and no sink for the monoterpenes. After sunrise, isoprene emission increased, as did photochemical reactions. From 9 am to 6 pm, monoterpenes were close to the instrument detection limit, and the isoprene concentration was determined by the competition between the emission and OH scavenging. After 5 pm, isoprene emission dominated and its concentration reached the daily maximum. After 8 pm, there was no isoprene emission and the isoprene concentration started to decrease. However, monoterpenes began to build up and reached a maximum at 5 am.

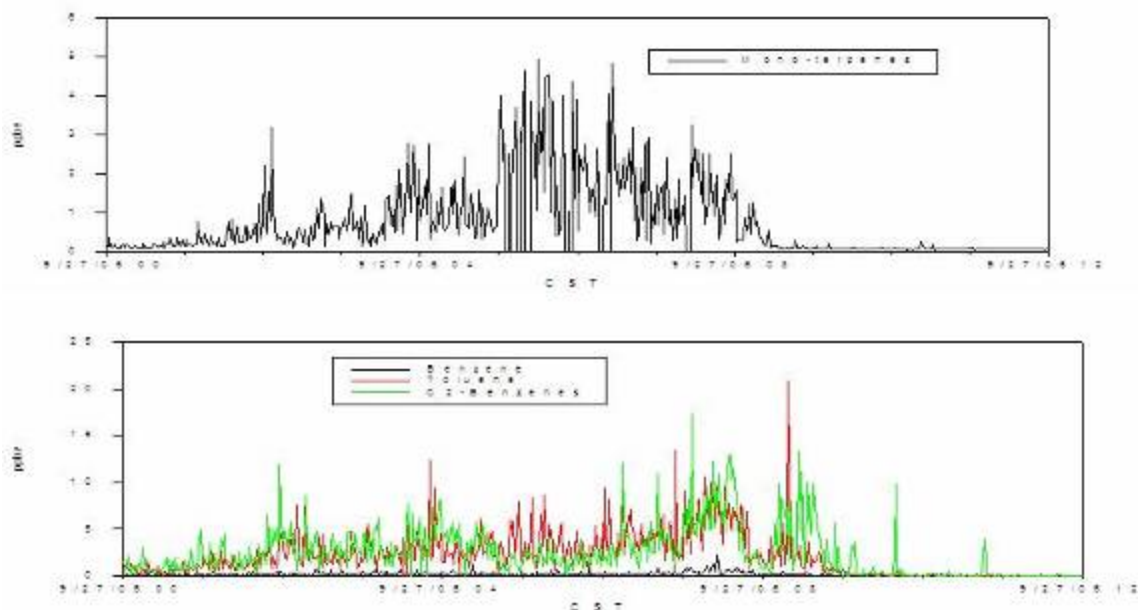


Figure 10. Mono-terpene (top) and aromatic VOCs (bottom) observed on Sept. 27 at Aldine.

On Sept. 27, a mass 137 was observed at Aldine (Fig. 10). Because the mass peak 81, a fragment of mono-terpenes, correlated with the mass 137, we identified this peak as mono-terpenes and estimated its mixing ratio to be near 5 ppbv. During the same period, aromatic VOCs, such as benzene, toluene, and C2-benzenes, were also observed (Fig. 10). Although aromatic VOCs observed during this campaign usually correlated with traffic conditions, this aromatic VOCs event spanned from 2 AM to 9 AM (local time). Thus it could not be explained by traffic conditions alone. Because benzene, toluene, and limonene are used as detergents in the petrochemical facilities, we speculate that we observed a solvent plume originated from the ship channel area.

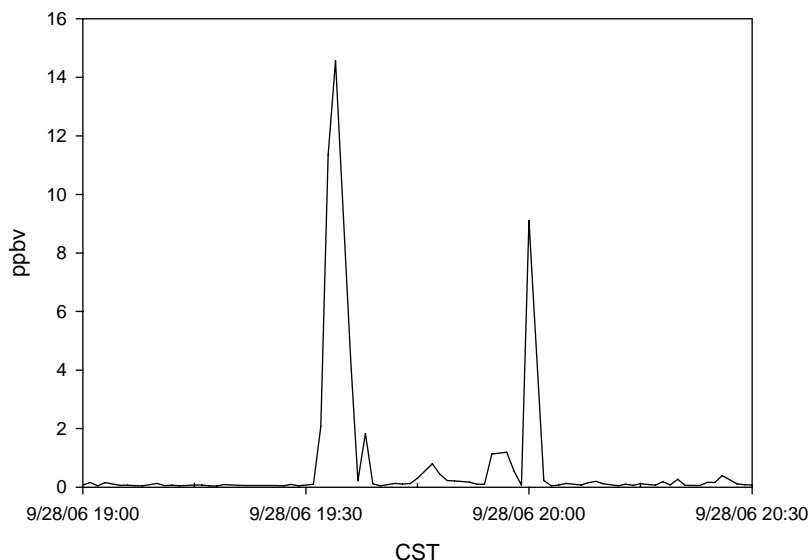


Figure 11. Acetonitrile observed on Sept. 28 at Aldine.

Another interesting observation was the mass 42 peak on Sept. 28 at Aldine (Fig. 11). Because no other significant higher mass peaks were observed, we believe it was acetonitrile, which is considered as a biomass burning marker.

The oxidation products of VOCs are believed to contribute to secondary organic aerosol (SOA) formation. We also explored the correlation between the organic aerosol component and VOCs and their oxidation products. From the late night of Sept. 19 to the early morning of Sept. 21, a significant organic aerosol mass loading was detected at the Aldine site. Meanwhile, the PTR-MS detected elevated monoterpenes, isoprene, and toluene (Fig. 12). We also observed acetaldehyde, methylglyoxal, and methyl ethyl ketone during the same period (Fig. 13). Acetaldehyde is a major oxidation product of alkenes species; although it does not participate in the SOA formation, it can be treated as an indicator of the photochemical oxidation activity. Methylglyoxal is the major oxidation product of isoprene and aromatic compounds and can participate in the SOA formation. Fig. 13 shows a good correlation between the organic aerosol component and these oxygenated compounds, indicating the occurrence of the gas-to-particle partitioning process connecting VOC oxidation to SOA formation.

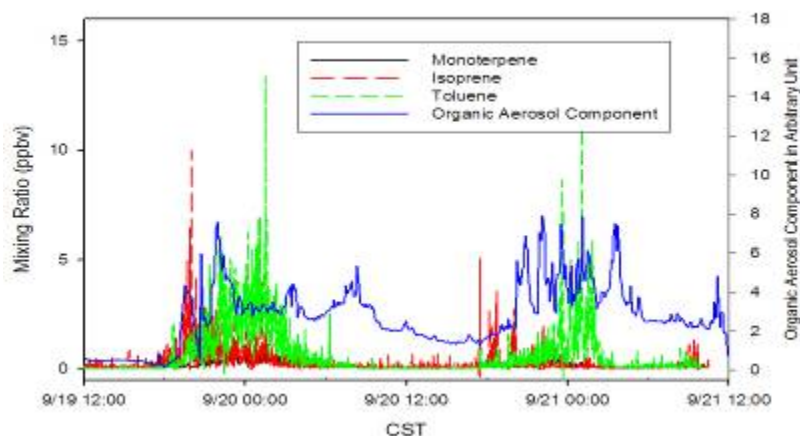


Figure 12. Monoterpenes, isoprene, toluene, and organic aerosol component observed from Sept. 19 to 21 at the Aldine site.

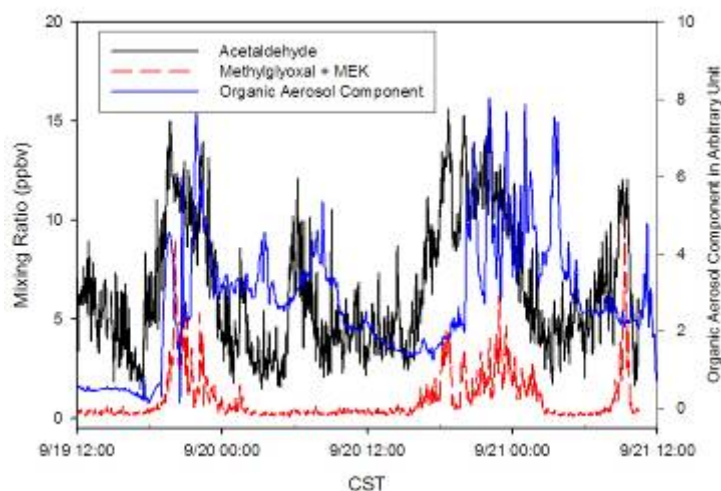


Figure 13. Acetaldehyde, Methylglyoxal, and MEK observed along with organic aerosol component.

6. Measurements of VOCs and Nitrogen-Containing Compounds at the Moody Tower

As part of the TRAMP (TexAQS II Radical Measurement Project), we have also conducted measurements of VOCs and nitrogen-containing species using PTR-MS and ID-CIMS at the University of Houston's Supersite, Moody Tower, during the TexAQS II – 06 intensive. Fig. 14 shows pictures of the ship channel area viewed from the Moody Tower and PTR-MS and ID-CIMS instruments installed inside trailer 2. VOCs, HNO_3 , and N_2O_5 were measured *in situ* using ion drift - chemical ionization mass spectrometry (ID-CIMS). The objective of the TRAMP project was to support the TexAQS II field experiment with a selected ground-based supersite which brought together a broad suite of instrumentation to collect a comprehensive data set and to elucidate fast radical chemistry occurring under high pollution events typical for the HGA. The project addressed the determination and quantification of sources and sinks for radicals in the urban atmosphere of Houston during the TexAQS II field campaign 2006, which is important for a better understanding of the formation processes of secondary species in the Houston area. The study was accomplished by an analysis of radical sources and sinks (and

production and loss rates) as identified by a steady-state time dependant photochemical box model.



Figure 14. The Moody Tower observation site.

Measurements of VOCs at the Moody Tower were performed using both PTR-MS and ID-CIMS. In current photochemical models, HNO_3 formation represents one of the terminating steps for the O_3 production cycle and serves as the major sink of NO_x . However, due to its sticky nature and low concentration, real-time HNO_3 measurement is difficult and not routinely conducted. The HNO_3 measurement is valuable to constrain the photochemical models and verify the simulation results. The daytime nitrogen chemistry has been well studied but the nighttime nitrogen chemistry is not clearly understood due to the limitation of detection techniques. Measurement of N_2O_5 is essential to elucidate the nighttime nitrogen chemistry and quantify the impact of NO_y on ozone formation on the subsequent day. In current atmospheric chemistry models, nitrate radical (NO_3) formed from the oxidation of NO_2 by O_3 is considered as the dominant nighttime free radicals. Similar to OH, NO_3 can also react with VOCs through H-atom abstraction or addition reactions, which can lead to nighttime peroxy radical formation. Self-reactions between peroxy radicals form the peroxides, which can serve as an OH source in the following daytime. NO_3 can also react with NO_2 to form N_2O_5 . Although N_2O_5 is not very reactive in the gas phase, it is taken up by aqueous droplets to form HNO_3 . N_2O_5 can also thermally decompose back into $\text{NO}_2 + \text{NO}_3$. Therefore, N_2O_5 serves as either a sink or a temporary reservoir for NO_3 .

In addition to the ID-CIMS, there are several techniques developed to measure HNO_3 and N_2O_5 , such as the denuder technique, the differential optical absorption spectrometer (DOAS), and the cavity ring down spectrometer (CRDS). The ID-CIMS has the advantages of specific, high sensitivity, and fast response. We found no interference from the major species in the troposphere and achieved a detection limit of 30 pptv with a 10 s integration time. The denuder technique first collects gas-phase HNO_3 into aqueous sample and then analyzes it with an ion

chromatography (IC). In order to achieve an appreciable detection limit, the IC requires a long sampling time (near one hour) to accumulate enough HNO_3 into aqueous phase. Since both nitrate particles and N_2O_5 are soluble in water, they potentially interfere with the IC measurement. Unlike the DOAS, the ID-CIMS is sampling a single air mass with temporal and spatial resolution. Therefore, its data is much more compatible with other trace gas measurements (e.g. NO_x , CO , and O_3) deployed at the same location. The CRDS has been successfully used in the field for NO_3 and N_2O_5 measurements. However, like all the instruments based on optical absorption, it suffers from interference due to aerosol scattering and water vapor absorption. The ID-CIMS is based on a different principle, mass spectroscopy. The ID-CIMS instrument was set up along with a CRDS developed by Dr. Simon North of TAMU, which was funded by the Texas Air Research Center (TARC) to conduct measurements of N_2O_5 and NO_3 during TexAQS II.

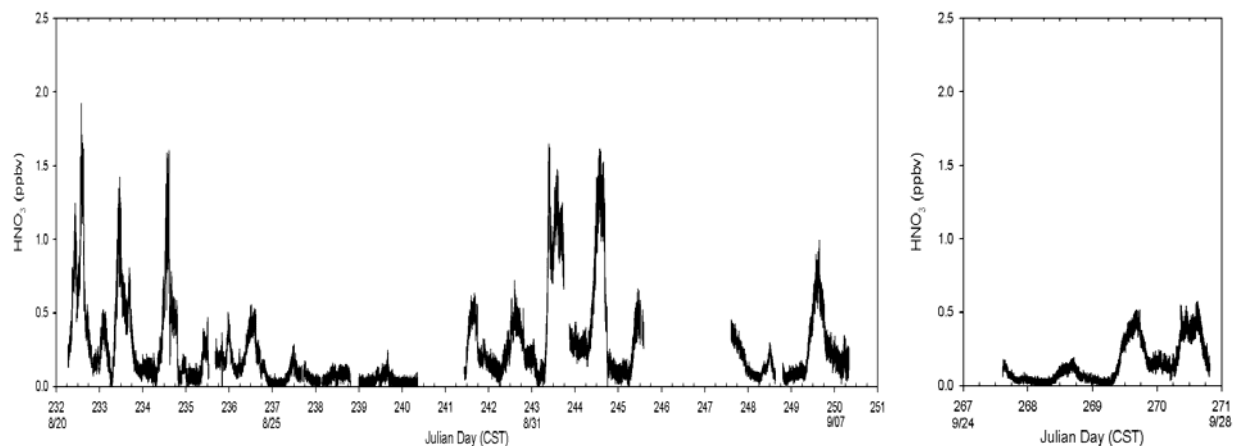


Figure 15. HNO_3 time series from Aug. 20 to Sept. 7 at the Moody Tower.

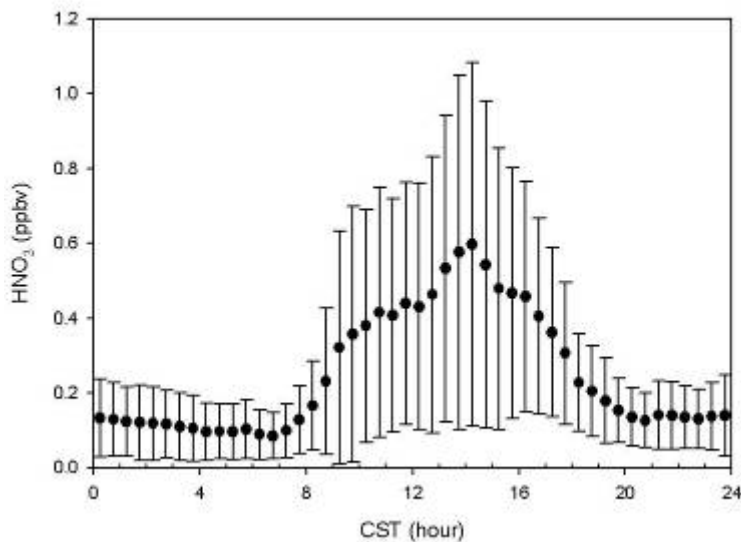


Figure 16. HNO_3 diurnal profile. The error bars correspond to one σ .

We collected nearly twenty days of continuous HNO_3 data during the field campaign. Fig. 15 presents the HNO_3 time series during the periods of Aug. 20 to Sept. 7 (Julian day 232 to 250) and Sept. 24 to 27 (Julian day 267 to 270), respectively. Fig. 16 depicts the HNO_3 diurnal profile averaged during the entire campaign period. Daytime HNO_3 usually peaked in the early afternoon, when the HNO_3 photochemical productivity also reached a maximum. The highest concentration of HNO_3 of 1.9 ppbv was observed on Aug. 20. Nighttime HNO_3 peaks were also observed Aug. 20 (day 232) and 23 (day 235). HNO_3 was relatively higher in August and early September than late September, consistent with the fact that we experienced more high ozone days in the former period than the latter one. The elevated HNO_3 observed during the nights of Aug. 31 and Sept. 26 (day 243 and 269) likely corresponded to the wind reversal weather pattern that occurred several times during the campaign. We speculated that these nighttime HNO_3 events were either produced from NO_3 and N_2O_5 processes or formed during the daytime and transported back from the ocean. We also attempted to measure N_2O_5 during the early part of the campaign, but the concentration was typically below the ID-CIMS to detection limit. The low N_2O_5 concentration occurred because of the nearly complete titration and removal of O_3 by high NO level at night, which inhibited NO_3 formation during most of the nights of field campaign. After Dr. Simon North from TAMU joined the TRAMP team to measure NO_3 and N_2O_5 using CRDS at the Moody Tower, we decided to focus our measurements on nighttime HNO_3 .

Our analysis of VOC measurements focused on two issues, i.e., upset events and high O_3 episodes. In the morning of Aug. 20, we recorded a propene plume (Fig. 17). The plume arrived at Moody Tower around 2 am and disappeared after 9 am. The highest concentration was about 1 ppmv. Because we observed no other VOCs associated with the propene peak, we believed that the m/e 43 peak was mostly composed of propene. Since we also observed an easterly wind that morning, the plume might come from ship channel area. High OH reactivity (Fig. 17 red dots) measured by the Penn. State group also concurred with this propene peak.

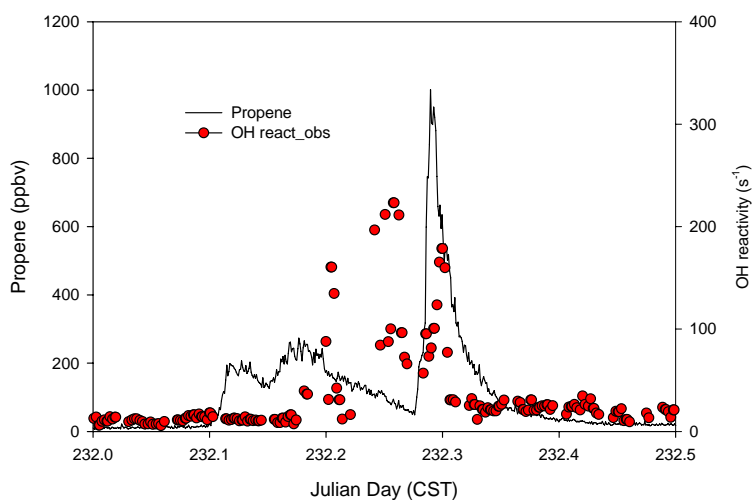


Figure 17. A propylene plume observed in the morning of August 20, 2006 (Julian Day 232). OH reactivity was also showed here as red dots.

In the evening of Oct. 5, the PTR-MS observed another m/e 43 peak of about 180 ppbv and meanwhile only small increase of m/e 57 was observed (see Fig. 18). The record of the PTR-MS's operating parameters indicated the instrument was working properly. In addition,

because no other higher mass VOCs were observed during the same period, we eliminated the possibility of fragmentation. However, according to the discussions with the NOAA group, in addition to propene the m/e 43 peak could also be attributed to vinyl acetate, which is a raw material used by petrochemical industries in the ship-channel area. Therefore, we speculated that the m/e 43 peaks were caused by an upset event of either propene or vinyl acetate.

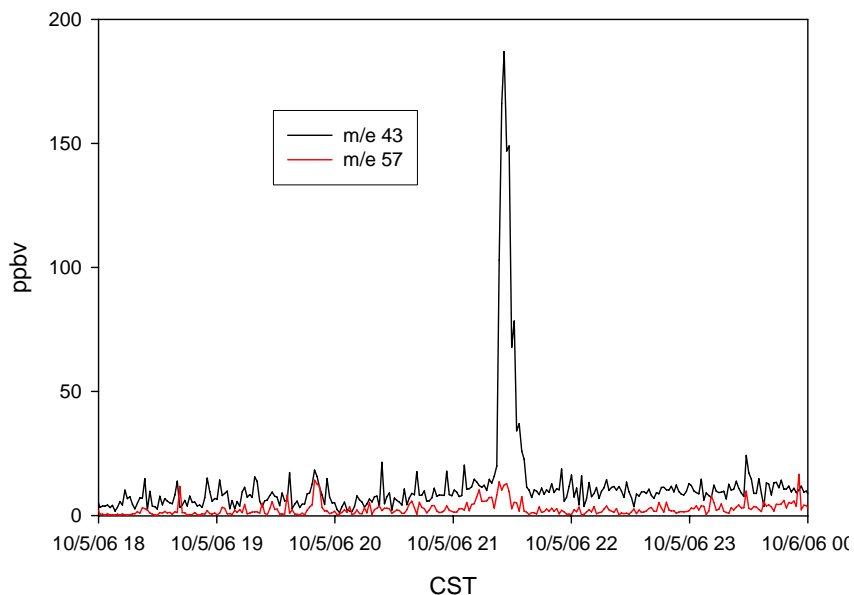


Figure 18. Time series of m/e 43 and m/e 57 in the evening of Oct. 5.

Aromatic VOCs at the Moody Tower showed the signature of traffic sources. Fig. 19 presents the aromatic VOCs observed during the morning rush hour of Aug. 23. Toluene and C2-benzenes were significantly higher than benzene, which indicated that the benzene, a naturally occurring carcinogen, has been effectively removed from the gasoline supplied in the Houston Metropolitan area.

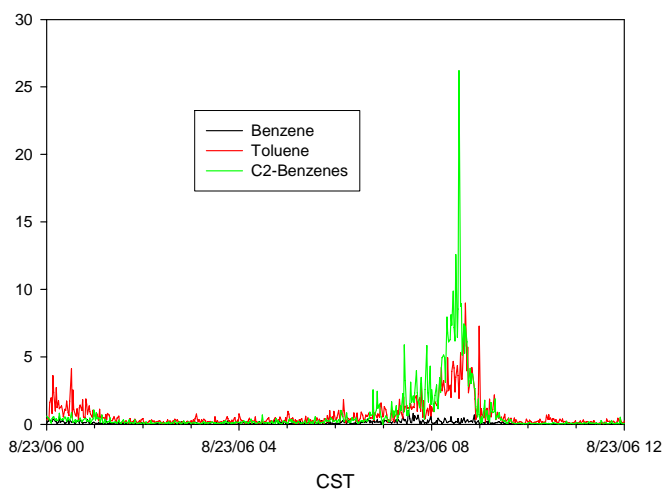


Figure 19. An aromatic VOCs peak observed in the morning of Aug. 23.

The day on Aug. 31 corresponded to a high ozone day, and we observed several prominent VOC peaks. Fig. 20 plots of mass 71 (MVK + MARC), mass 73 (MEK + MG), mass 93 (toluene), and mass 69 (isoprene).

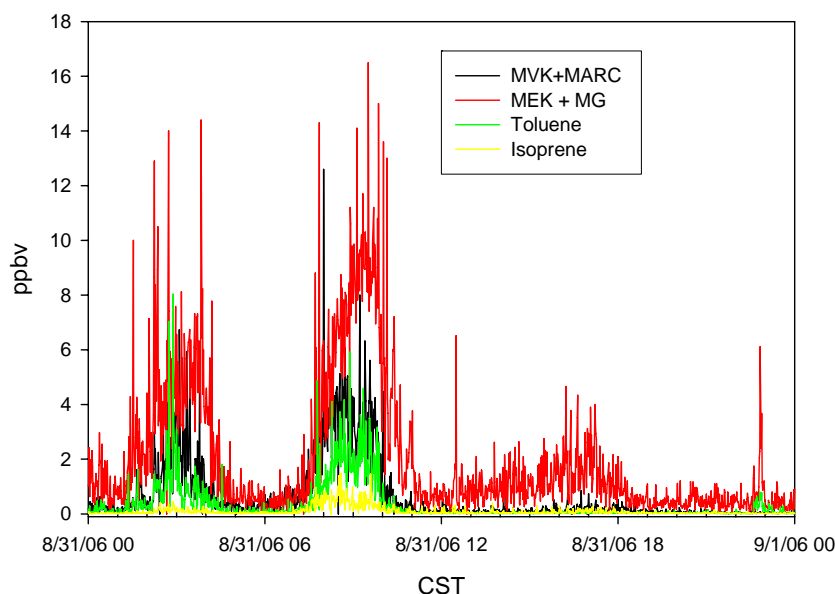


Figure 20. VOCs observed on Aug. 31 at the Moody Tower.

The dominant feature in the VOC measurements on this day was that oxygenated VOCs were significantly higher than their precursors. The first VOC peak was observed around 3 am, when photochemistry was not active. On average, 6 ppbv for MEK + MG, 4 ppbv for MVK + MARC, 2 ppbv for toluene, and less than 0.3 ppbv for isoprene were observed. The second peak was observed around 9 am. Compared with the first peak, no significant increases of toluene and isoprene were found. However, MEK + MG increased by about 6 ppbv, which might be explained by photochemical production. These two peaks clearly shared the same “signature”, i.e., an aged plume. From 1 pm to 6 pm, there were only elevated MEK + MG, which could indicate it was the tail of the earlier plume.

7. Conclusions

As part of the TexAQS 2006 campaign, we participated in both the TexAQS II Radical Measurement Project at UH Moody Tower and the Houston Triangle experiment at the TCEQ Aldine site. We conducted VOC measurements using PTR-MS at both sites and HNO₃ measurements using ID-CIMS at the UH site. Fourteen individual or group of VOC species were identified and quantified during the campaign. Propene and butenes were the most abundant alkenes detected at both sites. Two m/e 43 upset events were recorded at the Moody Tower site on Aug. 20 and Oct. 5, respectively. Both upset events were consistent with TCEQ reports in timing and the local wind direction also pointed to the ship-channel area as the origin. Aromatic VOCs showed signature of automobile emission sources. Benzene/toluene ratio was 0.15 from this campaign, indicating that benzene might have been completely removed from the gasoline supplied at the Houston area. Biogenic VOCs, isoprene and monoterpenes were also

detected during nighttime at both sites. However, monoterpenes might also come from the ship channel area due to the usage of limonene as a cleaning detergent in the petrochemical industries. During the high O₃ episode on Aug. 31, alkenes, aromatic VOCs, and OVOCs were significantly increased, indicating elevated photochemical reactivity. We also detected OVOCs, especially MGLY that correlated with SOA data very well at the Aldine site. Based on laboratory and theoretical studies, MGLY was speculated to participate in the SOA formation through heterogeneous reactions. Thus we might find the evidence in the ambient environment to verify the above speculation.

We also deployed the ID-CIMS at the UH Moody Tower site from August 17 to September 30 to measure gaseous HNO₃. The detection limit of the ID-CIMS was 30 pptv for 10 s integration time. Diurnal HNO₃ profile followed the solar cycle and the daily high mixing ratios ranged from 0.2 to 2 ppbv in the early afternoon. Occasionally nighttime peaks were also observed, which could be originated from either N₂O₅ + H₂O heterogeneous reactions or transported aged plumes. Analysis showed that both O₃ and HNO₃ time series had similar trends and followed each other very well, which was consistent with the production mechanism of HNO₃ during daytime.

Acknowledgements

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