

**AIRBORNE AND GROUND BASED MEASUREMENTS OF
VOLATILE ORGANIC COMPOUNDS USING PROTON
TRANSFER REACTION MASS SPECTROMETRY IN TEXAS AND
MEXICO CITY**

A Dissertation

by

EDWARD CHARLES FORTNER

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

December 2006

Major Subject: Atmospheric Sciences

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Approved by:

Chair of Committee,	Renyi Zhang
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ABSTRACT

Airborne and Ground Based Measurements of Volatile Organic Compounds Using
Proton Transfer Reaction Mass Spectrometry in Texas and Mexico City.

(December 2006)

Edward Charles Fortner, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Renyi Zhang

Measurements of ambient volatile organic compounds (VOCs) by proton transfer reaction mass spectrometry (PTR-MS) are reported from recent airborne and surface based field campaigns. The Southeast Texas Tetroon Study (SETTS) was a project within the TEXAQS 2005 field campaign, conducting airborne measurements that investigated the nocturnal Lagrangian transport of industrial plumes downwind of the Houston, Texas metropolitan area. On the evening of July 26-27, a polluted air mass with elevated mass 43, mass 45 and mass 57 VOCs along with elevated O₃, CO, and NO_x was tracked from the Houston metropolitan area to an area northwest of Shreveport, LA, a distance of over 200 miles. This campaign demonstrated that the PTR-MS is capable of tracking a VOC plume over large distances and these measurements indicate that transport of VOCs, particularly light alkenes and their oxidation products, out of the Houston metropolitan area may need to be considered by areas downwind of the Houston area when they are determining how to attain their air quality goals.

During the MILAGRO field campaign in March 2006 VOCs were measured by PTR-MS instrumentation on a rooftop in the urban mixed residential and industrial area

north northeast of downtown Mexico City. Diurnal profiles of weekday and weekend/holiday aromatic VOC concentrations clearly show the influence of vehicular traffic during the morning rush hour time period and during the afternoon hours although a separate late afternoon peak is not seen. Plumes of toluene elevated as much as 216 parts per billion by volume (ppbv) and ethyl acetate elevated as much as 183 ppbv above background levels were observed during the late night and early morning hours. These plumes indicate the probability of significant industrial sources of these two compounds in the region. The high levels of toluene measured by our PTR-MS exceed levels that would be predicted by examination of the Mexico City Metropolitan Area (MCMA) emission inventory and when these VOC measurements are integrated with measurements conducted throughout the MCMA a better understanding of both the overall spatial pattern of VOCs in the MCMA as well as its variability will be attained.

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The body of research described herein is composed of field measurement campaigns where a large amount of cooperation between research groups is needed in order to obtain the most useful results. The assistance of Dr. Ray Valente of the Tennessee Valley Authority, and Dr. Carl Berkowitz and Dr. Rahul Zaveri of the Pacific Northwest National Laboratory during the TEXAQS 2005 campaign is appreciated. During the MILAGRO campaign, Dr. Berk Knighton of Aerodyne and Montana State University, and Dr. Phil Stevens of Indiana University provided useful discussions as well as some preliminary data. Argonne National Laboratories graciously provided preliminary wind data for the MILAGRO campaign. I would also like to thank the Texas Commission on Environmental Quality and the Texas Environmental Research Consortium for their funding of the TEXAQS 2005 project.

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1. INTRODUCTION

The body of research which will be discussed herein centers upon the use of a Proton Transfer Reaction Mass Spectrometer (PTR-MS) to conduct airborne and surface based measurements of Volatile Organic Compounds (VOCs). The airborne measurements were conducted over the Dallas, TX and Houston, TX metropolitan areas and the rural areas downwind of these metropolitan areas during the summer of 2005. The surface measurements were executed in March 2006 in Mexico City Mexico. The PTR-MS method is an extension of Chemical Ionization Mass Spectrometry (CIMS) whereby a neutral species is ionized by a reagent ion to yield a product ion, which is analyzed by a quadrupole mass analyzer for species identification and abundance determination [Fortner *et al.*, 2004].

The presence of VOCs in the atmosphere is important for a number of reasons. VOCs react with nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$) leading to the production of O_3 through photochemical processes. The oxidation products of VOCs may have a low enough volatility to allow for partitioning onto existing particulate matter, contributing significantly to fine particle mass as secondary organic aerosol (SOA) [Schauer *et al.*, 2002]. Ozone and SOA have detrimental health effects and have adverse consequences to Earth's climate [Finlayson -Pitts and Pitts, 2002]. Many VOCs are also toxic creating

This thesis follows the style of *Journal of Geophysical Research*.

health concerns regardless of reactions that may later occur. There are a wide variety of sources of VOCs to Earth's atmosphere ranging from natural to anthropogenic in origin [Hewitt, 1999]. There are hundreds of different VOCs with residence times varying from minutes to months and there is a high degree of spatial and temporal variability in VOC concentrations. Accurate online measurements of speciated VOCs which are able to depict spatial and temporal changes in a way that point measurements cannot achieve is the goal of atmospheric trace gas measurements by PTR-MS.

The methodology of PTR-MS along with some of the difficulties in species quantification based on PTR-MS measurements will be discussed followed by reports on measurements conducted recently at the aforementioned locations. Finally, potential future uses of PTR-MS in these two locations will be addressed along with ways that the speciation of VOCs might be improved to facilitate more useful measurements in the future.

2. METHODOLOGY

The development of PTR-MS for online quantification of VOCs in air was pioneered 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 more clearly demonstrate the overall magnitude, spatial and temporal dimensions of VOC plumes.

2.1 Instrument Description

The Ionicon Compact PTR-MS was used in both the TEXAQS 2005 and MILAGRO field campaigns. A brief description of the PTR-MS system follows because it is useful to be familiar with the basic construction of the PTR-MS system in order to better comprehend the methodology used for PTR-MS measurements. The PTR-MS system consists of an ion source to produce positive reagent ions, a drift tube where the ion-molecule reactions take place, and a quadrupole mass spectrometer where the reagent and product ions are detected.

The ion source is a hollow cathode discharge. Pure water vapor flows through the hollow cathode at a flow of 4-10 standard cubic centimeters (sccm). A positive charge is applied to the hollow cathode creating an intense source of H_3O^+ ions. The only other ions generally produced by this hollow cathode discharge are O_2^+ ions which are a potential contamination. Adjustments to the current applied to the hollow cathode and the water vapor flow passing through it can usually limit the O_2^+ ion to $< 2\%$ of the H_3O^+ ion as we achieved for the duration of both campaigns described in this paper. While the majority of this water vapor flow is pumped out of the system a small amount of flow along with the ions created by the hollow cathode discharge pass through a pinhole inlet with an applied voltage into the drift tube region of the system.

The drift tube is a sealed chamber of alternating stainless steel and teflon rings. The stainless steel rings are connected in a series circuit by resistors that run between them. The proton transfer reactions between the reagent ion and the product ion occur in this region. A charge is applied to the rings enhancing ion flow. The ions are then guided down the length of the drift tube, through a pinhole which also has an applied voltage, into the spectrometer.

The sampled ions are then focused with ion optics inside the CIMS, analyzed with a quadrupole mass filter and detected by a multiplier. The multiplier is connected with a preamplifier, which converts the raw signal into TTL pulses, allowing them to be processed by a personal computer.

2.2 Theory

The principle that ion drift chemical ionization mass spectrometry (ID-CIMS) utilizes is the detection of a neutral molecule X according to the reaction



where A is the reagent ion, X' is the 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

$$[X'] = k[A][X]t \quad (2)$$

where

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

and l is the length of the drift tube, while U_{ion} is the reagent ion drift velocity in the drift tube. The reagent ion drift velocity U_{ion} is determined by the equation

$$U_{ion} = uE \quad (4)$$

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.

For VOC detection, H_3O^+ is primarily used as the reagent ion and the proton transfer reaction



occurs in the drift tube. 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). Table 1 depicts some common species in air including VOCs and their proton affinities.

2.3 E/n Ratio

When conducting PTR-MS measurements a parameter of the highest importance is referred to as the E/n ratio,

$$E/n = x(Td) \quad (7)$$

where

$$Td = 10^{-17} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \quad (8)$$

and

$$E = \text{Voltage applied to drift region/length of drift region} \quad (9)$$

$$n = \text{molecules/cm}^3 \text{ of the carrier gas.} \quad (10)$$

The adjustment of this ratio influences the kinetic energy of the ions in the drift region. As this ratio is increased fragmentation of product ions increases and the formation of water clusters $(\text{H}_3\text{O}\cdot\text{H}_2\text{O}^+)_n$, $n=1,2,\dots$ is more effectively suppressed. When conducting PTR-MS measurements fragmentation of product ions should be suppressed as much as possible because this fragmentation complicates the speciation and quantification of both the original product ion mass and those masses it fragments into. Water clusters should also be suppressed because they may react with VOCs and they complicate the quantification of all VOCs with the exception of those that have been tested individually and found to not react with these water clusters.

Table 1. Some common species in air including VOCs and their proton affinities.

Substance	Formula	Mass	Proton Affinity (kcal/mol)
Oxygen	O ₂	32	100.6
Nitrogen	N ₂	28	118
Carbon Dioxide	CO ₂	44	129.2
Ethene	C ₂ H ₄	28	162.5
Water	H ₂ O	18	165.2
Formaldehyde	CH ₂ O	30	170.4
Benzene	C ₆ H ₆	78	179.3
Propene	C ₃ H ₆	42	179.6
Acetaldehyde	C ₂ H ₄ O	44	183.8
Acetonitrile	C ₂ H ₃ N	41	186.2
Toluene	C ₇ H ₈	92	187.4
Acetone	C ₃ H ₆ O	58	194.1
Dimethyl Sulfide (DMS)	C ₂ H ₆ S	62	198.6
Isoprene	C ₅ H ₈	68	198.9

During both field campaigns discussed herein an E/n ratio of 115 Td was utilized. At this ratio the water clusters were maintained at less than 10% of the H_3O^+ signal strength and fragmentation of most VOCs was limited. The water cluster strength was found to vary with humidity ranging from 2-9.5% of the H_3O^+ signal. It should be noted here that there is a great deal of variability between different PTR-MS instruments regarding the level of water clusters at a certain specified E/n ratio. *Lindinger et al.*, (1998) report using an E/n ratio of 120-140 Td in order to keep water clusters at less than 10%. A study of relative humidity dependence on water cluster formation conducted by *de Gouw et al.*, (2003a) determined no effect at 120 Td and a small effect at 110 Td with a maximum water cluster value of approximately 13% when the partial water pressure exceeded 40 millibars.

If it is necessary to use a lower E/n ratio for some specific purpose, perhaps to measure just one VOC that fragments at a higher E/n ratio, it is possible as long as that VOC has previously been calibrated with a known response to different levels of water clusters. Provided that only the first water cluster ($H_3O \cdot H_2O^+$) is present the equation

$$\text{Normalized ion signal} = 10^6 i[RH^+] / (i[H_3O^+] + X_R(i[H_3O^+ \cdot H_2O])) \quad (11)$$

may be used [*de Gouw et al.*, 2003b] where product ion signals are normalized to a standard reagent ion signal of 10^6 counts s^{-1} due to varying reagent ion signals. The ion signals of product ions, H_3O^+ , and ($H_3O^+ \cdot H_2O$) are represented by $i[RH^+]$, $i[H_3O^+]$ and $i[H_3O^+ \cdot H_2O]$ respectively and X_R is a factor determined through calibrations of the VOC

to be quantified which represents both the difference in detection efficiencies of the two reagent ions as well as the difference in the rate coefficients of the $\text{H}_3\text{O}^+ + \text{R}$ and $\text{H}_3\text{O}^+\cdot\text{H}_2\text{O} + \text{R}$ proton transfer reactions. This calculation has been used in previous field campaigns by research groups [*de Gouw et al.*, 2003b] who encountered water clusters as high as 40% necessitating that they be accounted for. It is desirable if possible to eliminate this potential source of error by limiting the amount of water cluster present to less than 10% as was done in both field campaigns described in this paper. Equation 11 can only be used for species that have been calibrated necessitating that calibration standards be available.

2.4 Instrumental Background Determination

Another important component to consider in any measurements employing PTR-MS is the determination of the instrumental background at all masses. This instrumental background must be subtracted from the signal when measuring ambient air. For the first campaign that this PTR-MS system was involved in, an airborne campaign over Houston and Dallas, TX, zero air (Scott Marrin) was used in place of the normal ambient flow when determining the instrumental background. The flow rate was not changed when switching from ambient to zero air and all of the drift tube parameters such as pressure and voltage tunings remained unchanged. The humidity of the sampled air was changed dramatically, however, as zero air is very dry. Calibrations were performed prior to the field campaign to determine humidity dependence and in most cases very little humidity

dependence was found. Unfortunately, only a limited number of species were calibrated and a background check which did not alter humidity at all would have been preferable.

Another way to determine instrumental background is to pass the ambient air through a catalytic converter en route to its sampling with the PTR-MS. A catalytic converter had actually been constructed in our laboratory prior to the airborne field campaign but was not used in the airborne campaign due to electrical power restrictions on board the aircraft as well as safety concerns. The catalytic converter was constructed of ½" stainless steel tubing stuffed with platinum wool (Shimadzu) and heated to 375° C. The catalytic converter removed the VOCs from the sample air without removing any water vapor thereby maintaining the humidity of the sample air. The catalytic converter was able to handle a flow of up to approximately 500 sccm without decomposing and the PTR-MS inlet flow was variable from 50 200 sccm. The catalytic converter did have a break in period of 24-72 hours after it was first heated before it reached optimum operation levels. After the optimum operation level had been reached the catalytic converter removed VOCs quite effectively and instrumental backgrounds were typically below 500 parts per trillion by volume (pptv) and in a few cases below 100 pptv allowing a significant improvement over the detection limit stated by Ionicon of < 1 part per billion by volume (ppbv). The catalytic converter was used throughout the entire ground based Mexico City campaign.

2.5 PTR-MS Speciation, Limitations and Solutions

When conducting PTR-MS measurements a specific mass is measured not a specific VOC. Ideally there is only one VOC attributable to a certain mass and that will allow for accurate quantification of the VOC. Unfortunately there are only a limited number of masses where this is actually the case. Masses 33, 45, 63 and 105 can be attributed solely to methanol, acetaldehyde, dimethyl sulfide (DMS) and styrene respectively [Warneke *et al.*, 2003]. Mass 121 and mass 137 may be attributed to the sum of a limited number of similar compounds, C₃ benzenes and monoterpenes respectively. All other masses have at least a small degree of either dissimilar species at the same mass or possible fragmentation from higher masses which may complicate quantification.

Certain masses have been found to only have minor contributions from fragmentation such as masses 79 and 93 which have been found to be attributable to benzene and toluene respectively in past studies [de Gouw *et al.*, 2003b, Warneke *et al.*, 2003]. Mass 59 is attributable to both acetone and propanol, however the mixing ratio of propanol is generally considered to be low enough where it will not interfere substantially with acetone measurements [Warneke *et al.* 2003]. If a significant propanol source is nearby this may complicate measurements but propanol does have a much shorter lifetime than acetone (9 hours versus 5 weeks) which should cause a higher variability in the signal. Mass 107 may be classified as the sum of xylenes, benzaldehyde and ethyl benzenes which is a useful albeit not too specific measurement one can make.

Other masses such as masses 43, 57, 71 and 73 contain multiple species of interest that PTR-MS does detect which we would like to be able to quantify accurately including propene, 1 – butene, methyl tertiary butyl ether (MTBE), methyl vinyl ketone, methacrolein, methyl ethyl ketone and methyl glyoxal. Unfortunately, these masses all suffer from heavy fragmentation of higher masses even at relatively low E/n ratios greatly complicating the ability to accurately quantify these important VOCs.

Another consideration which should be addressed when multiple species are summed at one mass is that different species have different reaction rates with the H_3O^+ ion. When quantifying the mixing ratio of a sum of VOCs at a certain mass a certain reaction rate must be entered and because the magnitude of each individual species is not known there is the potential for error in assessing an average reaction rate based on the theory that each of the respective VOCs found at a particular mass is present in equal amounts. The range in values of these reaction rates vary from approximately $1.5\text{-}4 \times 10^9 \text{ cm}^3 \text{ s}^{-1}$ and some reaction rates have not been measured.

Finally another limitation of PTR-MS is that when using H_3O^+ as the reagent ion there are a few VOCs which are important ozone precursors that we are unable to quantify due to their proton affinity being lower or around the same level as that of H_2O . Ethene cannot be measured using PTR-MS because it has a proton affinity lower than H_2O as is shown in Table 1. Formaldehyde's proton affinity is only slightly higher than that of H_2O so that there is a considerable backwards reaction leading to a reduction in sensitivity when attempting to measure formaldehyde.

There are a number of potential fixes for many of these limitations depending on the desired use of the PTR-MS and the availability of standards to conduct certain experiments before the PTR-MS is used for its field application. If it is desired to measure a certain species standards of that species may be sampled using ambient air which has passed through a catalytic converter as a carrier gas, prior to the campaign or even during the campaign if a break in sampling is possible. Fragmentation patterns of the species which is to be measured may be analyzed and fragmentation patterns of other species thought to contribute to the signal at the desired measuring mass may be analyzed as well provided that all of the necessary standards are available. There may be less interfering species at a mass which the desired measure species fragments into. It may be possible to adjust the E/n ratio to a level where only the desired species is present at the measure mass due to fragmentation of the other species. The isotopic ratio of the desired species may be used to detect and quantify the species at a different mass where there is less interference. Another option may be to use a reagent ion which is more restrictive in the number of VOCs it performs proton transfer with. For instance, if NH_3 is used rather than water vapor as the discharge gas the NH_4^+ ion is produced, which has a proton affinity of $204 \text{ kcal mol}^{-1}$ [Lindinger *et al.*, 1998]. All of these potential corrections to fragmentation quantification problems involve at least a certain amount of preparation as standards must be obtained and the corrections are more easily implemented if there are fewer VOCs which are being measured concurrently using the same instrument.

3. THE TEXAQS 2005 SETTS AND NETPS FIELD CAMPAIGNS

3.1 Introduction

The Houston Galveston metropolitan area is known to have a wide variety of VOC sources particularly in the ship channel region where a large number of petrochemical facilities, synthetic organic chemical manufacturing plants and ship traffic on the channel itself emit a wide variety and large amount of VOCs and NO_x. . In particular with respect to VOCs, lower molecular weight alkenes such as ethene, propene, and butenes have been identified to be most abundant inside these petrochemical source plumes and dominate the reactivity of VOCs as ozone precursors [Kleinman *et al.*, 2002; Daum *et al.*, 2003; Ryerson *et al.*, 2003; Berkowitz *et al.*, 2004]. Results from the 2000 Texas Air Quality Study (TexAQS 2000) have unambiguously established that these highly reactive volatile organic compounds (HRVOCs) from petrochemical industrial sources are linked to rapid and efficient photochemical ozone production in the Houston Galveston area [Daum *et al.*, 2003]. A modeling study [Wert *et al.*, 2003] of daytime ship channel plumes sampled on 1 September 2000 during the TexAQS 2000 study showed that ethene and propene emissions alone could account for elevated O₃ (200 ppbv) and formaldehyde (30 ppbv) encountered some four hours downwind of the source region. During the evening it could be expected that ethene and propene would exist further downstream of their emission point in the ship channel and

thus possibly impact the air quality of areas further away from the Houston metropolitan area.

The Dallas-Fort Worth (DFW) metropolitan area contains approximately 4.8 million residents. This metropolitan area does not have the petrochemical facilities which are present in the Houston metropolitan area and would be expected to have a VOC profile typical of a large city in the USA. The DFW metropolitan area routinely has high temperatures exceeding 90° Fahrenheit during the summer months enhancing photochemistry. As this region attempts to develop a comprehensive air pollution reduction strategy there is a strong motivation to determine the levels of O₃ and the O₃ precursors, NO_x and VOCs, which are transported into the region.

As part of the Texas Air Quality Study 2005 (TEXAQS 2005) the Ionicon compact PTR-MS participated in the Southeast Texas Tetroon Study (SETTS) during the last half of July and the Northeast Texas Plume Study (NETPS) during the month of August. In these projects the PTR-MS was part of the instrument package aboard a Twin Otter research aircraft and sampled during a variety of different missions. The first objective of this project was to demonstrate that the compact PTR-MS could be used to gain valuable information regarding the presence and amount of VOCs over industrial, urban and biogenic sources. Another key objective was to track the evolution of these VOCs dynamically through space and chemically as primary VOCs are converted to oxidation products, particularly in relation to other trace gas (CO, O₃, NO_x, SO₂) plumes.

One of the key goals related to the PTR-MS used in SETTS was to determine if VOCs could be tracked as components in an industrial plume downwind of a point or area source using PTR-MS. The SETTS campaign provided the ability to tag an air parcel with a balloon, referred to as a tetroon, which is described in greater detail in the experimental section. If an air parcel containing HRVOCs that are emitted in the ship channel could be tagged and followed, measurements could then be conducted in a Lagrangian manner using an instrumented aircraft following this air parcel as it advanced downwind of Houston. During the daytime these HRVOCs could be expected to react away fairly quickly, however, at night they might be expected to be able to travel greater distances without chemical evolution. Unfortunately, as mentioned earlier, ethene is not detected by PTR-MS while heavier alkenes are but at masses where interference is possible. The PTR-MS involvement in SETTS focused on the transport of VOC plumes downwind of the Houston Ship Channel at night when plume integrity is preserved due to a lack of convective activity and chemical evolution is suppressed due to a lack of sunlight.

The NETPS campaign was conducted primarily to study the evolution of power plant plumes downwind of the DFW metropolitan area and how these plumes interacted with the urban pollution plume generated within the metropolitan area. While VOCs are not typically associated with power plant plumes it was still determined to be beneficial to have online VOC measurements both upwind and downwind of the DFW metropolitan area.

3.2 Experimental

Three missions were conducted in support of SETTS from July 21-28 with the PTR-MS providing online VOC measurements continuously throughout these missions. The SETTS missions involved launching a tetroon which carried sensors providing information regarding GPS location, temperature, pressure and moisture. The tetroon also contained a modem which transmitted data to the Twin Otter research aircraft and a control team on the ground. This tetroon would then travel along with the parcel of air into which it was launched thereby tagging that air parcel. On the second and third missions a second tetroon was launched which would make altitude deviations upwards or downwards to determine the wind shear above and below the primary tetroons flight path. Twin Otter flights then conducted transects perpendicular to the tagged air parcel and the urban plume. A diagram depicting the concept of operations for SETTS is shown in Figure 1. The base of operations for the Twin Otter aircraft was the Lone Star Executive Airport located near Conroe Texas approximately 30 miles north of Houston Texas.

The PTR-MS instrument was installed in the Twin Otter aircraft at the Twin Otter Research Aircraft facility located in Grand Junction CO from July 11-17 prior to the SETTS campaign. The PTR-MS instrument is composed of a square metal casing which contains a quadrupole mass spectrometer, turbo pumps, inlet pump, drift tube, ion source, power supplies and an Ethernet control box. A 1/16" inner diameter (ID) silcosteel coated inlet tube protruded outwards from the front of the metal casing 4' and

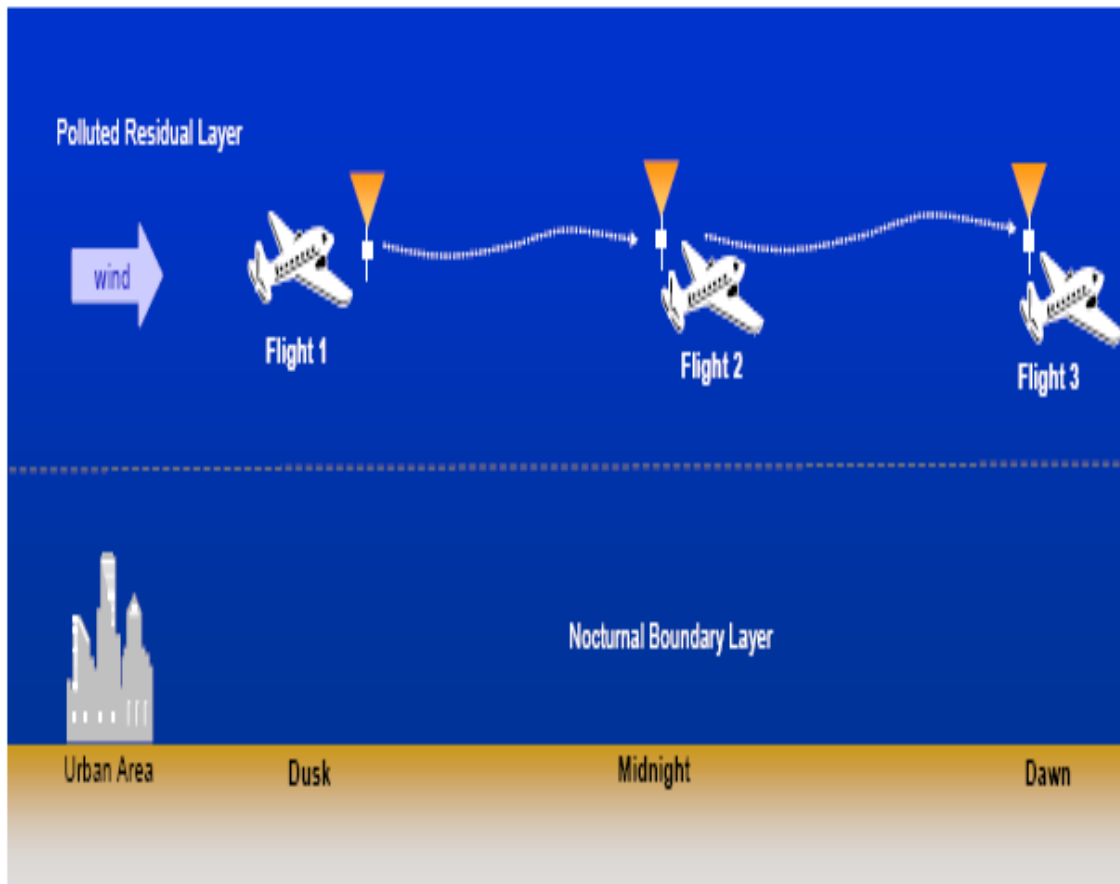


Figure 1. Conceptual drawing depicting the overall mission strategy for the SETTS project. Figure courtesy of Zaveri *et al.* 2005.

was surrounded by a temperature controlled flexible hard plastic sleeve heated to 40° Celsius during measurements. An additional 18" of Teflon tubing (1/16" ID) lead from the inlet plate to the silcosteel coated tubing. Residence time in the inlet was less than 2 seconds. A laptop computer connected to the PTR-MS instrument facilitated in-flight control of the PTR-MS by an instrument operator allowing for in-flight adjustments to the suite of species being measured.

Calibrations of the PTR-MS system were conducted either at the end of the flight day or once every other day during extended no-fly periods. The mixing ratio of the calibrated gases was varied between 2 – 20 ppbv. The calibrations were conducted through the inlet plate of the aircraft post-flight. A custom mix calibration gas cylinder (Spectra) containing methanol, propene, acetaldehyde, 1-3 butadiene, trans-1-butene, cis-2-butene, isoprene, benzene, toluene and m,o and p xylenes was used. Calibrations were done using zero air as the carrier gas as well as ambient air to determine the effects of relative humidity as well as possible interferences not detected using zero air. The PTR-MS system was found to be stable with respect to calibration factors over the course of the field program. A calibration curve was created based on the sum of over 20 calibrations completed through the duration of the field program and has been applied to the SETTS and NETPS field data. For trace gases that were not calibrated an average calibration curve was applied based on the performance of the calibrated gases. It should also be noted that the PTR-MS inlet system uses a pressure controller so that a constant pressure is maintained in the drift tube regardless of altitude eliminating any altitude dependence in the data.

Background checks were conducted approximately hourly while in flight to determine the instrumental background at measured masses. Zero air was passed through the PTR-MS system using a perfluoroalkoxy (PFA) tee which was connected 2" inside of the inlet plate. During data analysis the background was determined to be the average of the cycles accumulated during the specific background check at each mass with a typical background check lasting approximately 15 cycles. Backgrounds were found to vary with time and so at any given time the background applied was the average of the backgrounds determined before and after that measurement.

During measurements the PTR-MS was operated with a drift tube pressure of 1.98 millibars. An E/n ratio of 115 Townsend was kept in the drift tube. This E/n ratio was found to be the lowest possible without incurring any relative humidity dependence while limiting the water cluster $\text{H}_3\text{O}\cdot\text{H}_2\text{O}^+$ at mass 37 to 5-7 % of the primary reagent ion signal H_3O^+ at mass 19. The instrument operated exclusively in single ion mass (SIM) mode while measuring although brief checks of the overall mass spectrum were made periodically to check for any mass peaks of interest. While in SIM mode the instrument cycled between 5-8 masses at 2 seconds per mass allowing for a time resolution of 10-16 seconds.

3.3 Results and Discussion: SETTS

In order to avoid convective activity which could damage the tetroons as well as thoroughly dilute the urban plume SETTS missions were executed during evening hours.

The three tetroon flights all produced a clear and unambiguous track of the movement of ozone downwind of Houston. The movement of VOCs was more difficult to detect and while many peaks of interest were measured during all three missions the only mission where a plume involving multiple hydrocarbon species was tracked throughout the duration of the mission was the third mission. A brief overview of the PTR-MS involvement in the three missions follows.

The first tetroon flight occurred on the evening of July 21. An initial flyover of the Houston Ship Channel was completed on this mission before the Twin Otter shifted its focus to characterizing the downwind urban plume in support of the tetroon. Mass 43 and mass 57 mixing ratios, as well as O_3 and NO_y mixing ratios provided courtesy of the Tennessee Valley Authority (TVA), from this ship channel transect are depicted in Figures 2 and 3. Figure 2 depicts measured mixing ratios relative to time while Figure 3 depicts the measured mixing ratio in relation to distance along this linear transect. This transect was conducted at 2000' approximately 3 miles north of the Houston Ship Channel. A very pronounced peak of mass 57 can be seen along this transect with a lesser rise in mass 43. A rise in O_3 of 20 ppbv above the background O_3 is also seen within this plume. Mass 57 is attributed to the sum of butenes as well as MTBE and possibly octanal and butanal fragmentation while mass 43 is attributed to propene as well as many pentene fragments and other compounds which are discussed in the "Speciation of Masses" section later in this section.

As the flight began to do transects downwind of Houston the PTR-MS signal, for the most part, was dominated by mass 45 which is attributed to acetaldehyde. One brief

mass 45 peak of approximately 40 ppbv was sighted in an elevated O_3 plume at 2000' just east of the Waco region at around 04:00 local time.

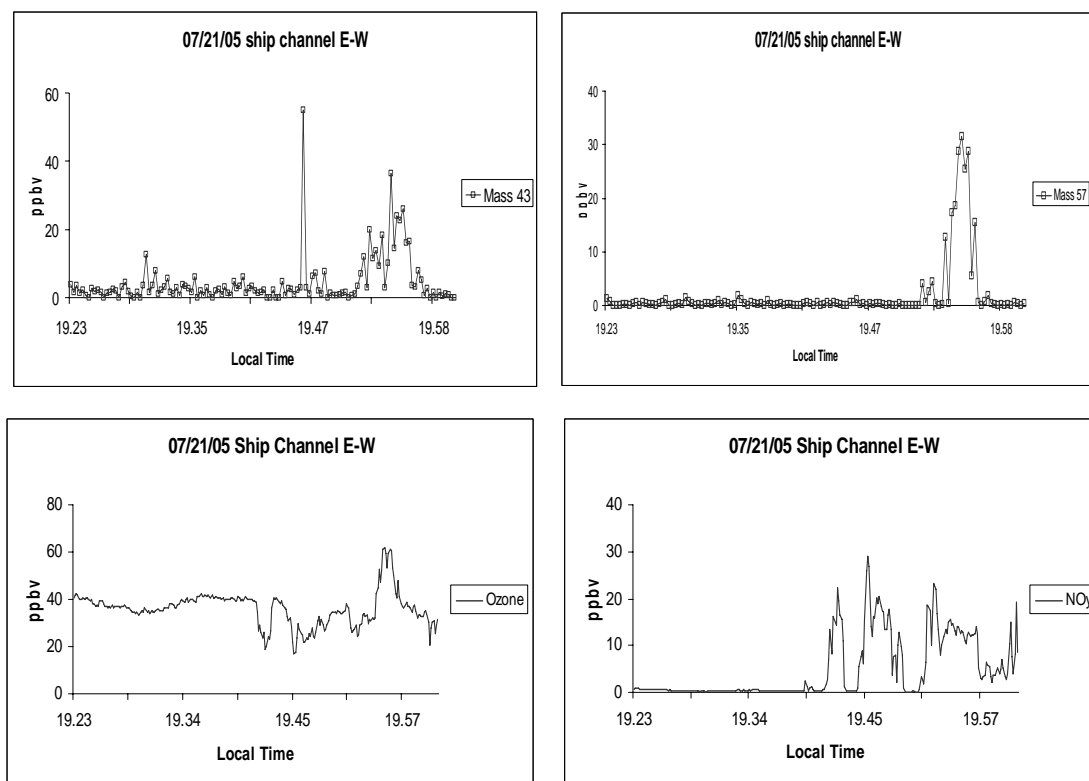


Figure 2. Mixing ratios of masses 43 and 57 along with O_3 and NO_x data provided courtesy of TVA obtained during the 07/21 ship channel transect.

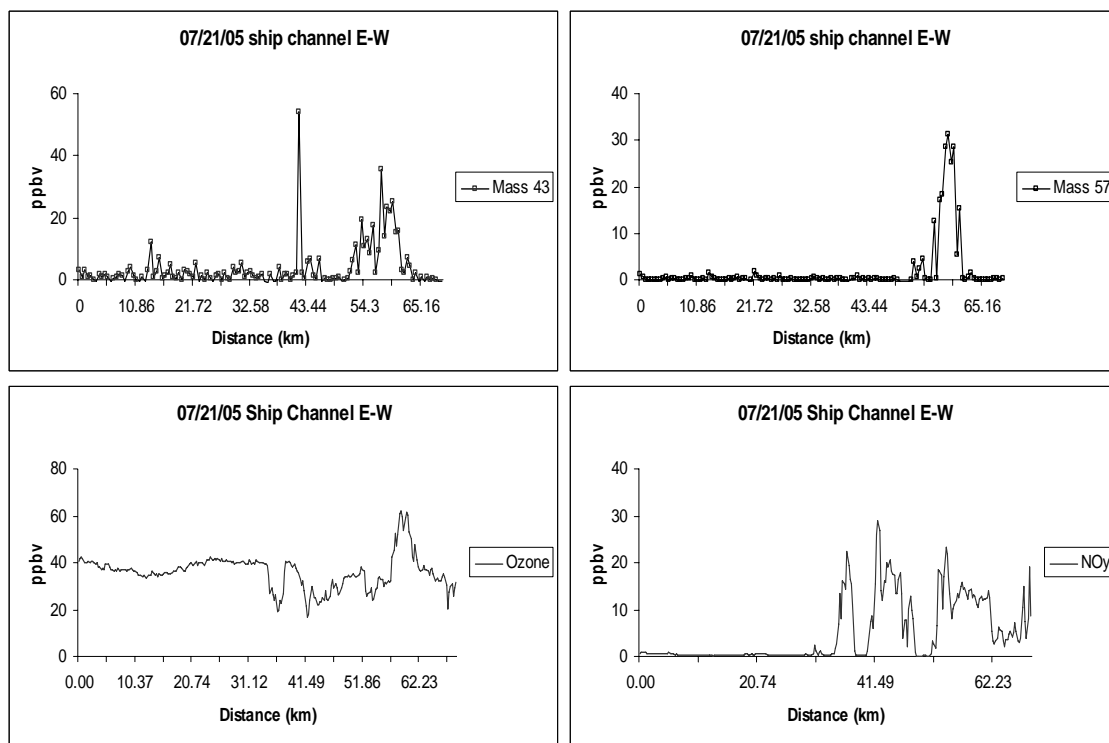


Figure 3. Mixing ratios of masses 43 and 57 along with O₃ and NO_x data provided courtesy of TVA obtained during the 07/21 ship channel transect displayed relative to distance.

On the second tetron flight which occurred the evening of July 23-24 as the first flight of the evening prepared to take off a communication problem delayed the use of the PTR-MS until approximately 45 minutes into the first flight. This led to higher, more variable background readings particularly at lower masses such as mass 43 and mass 45.

Qualitatively peaks in the lower masses can still be seen on this flight, however, quantification of these masses is subject to error due to the background. The Houston Ship Channel airspace was not sampled on this evening.

Two particular transects were noteworthy on this flight. Figure 4 displays a transect which initially was located in a region rich in isoprene oxidation products, methyl vinyl ketone and methacrolein that are detected at mass 71. The transect transitioned from the rural VOC plume into the urban VOC plume as can be seen by the rise in mass 57. During the second flight of the evening at around 23:20 local time Figure 5 shows a plume of elevated mass 71 while flying over the Trinity river valley between the towns of Centerville and Crockett at 2000'. Mass 71 peaks can be attributed to pentenes as well as methyl vinyl ketone and methacrolein, however, in this area there were no other elevated anthropogenic VOC's and the mass 71 signal can be attributed to isoprene oxidation products with confidence.

The third tetraon flight mission was executed on the evening of July 26-27. There were three consecutive overflights of the Houston Ship Channel on this mission. The primary peak of interest on these transects was a mass 57 peak which occurred on all three overflights at roughly the same location (Figure 6). This location was also very close to the location of the pronounced mass 57 peak on the flight of July 21-22. Utilizing GPS data and winds aloft data courtesy of TVA, the location of these peaks was determined to fit within a roughly 3 mile diameter located approximately 5 miles north of the ship channel. Unfortunately, there are many different hydrocarbon emitting

facilities in this area and in order to pinpoint the source a flight closer to the source would be necessary.

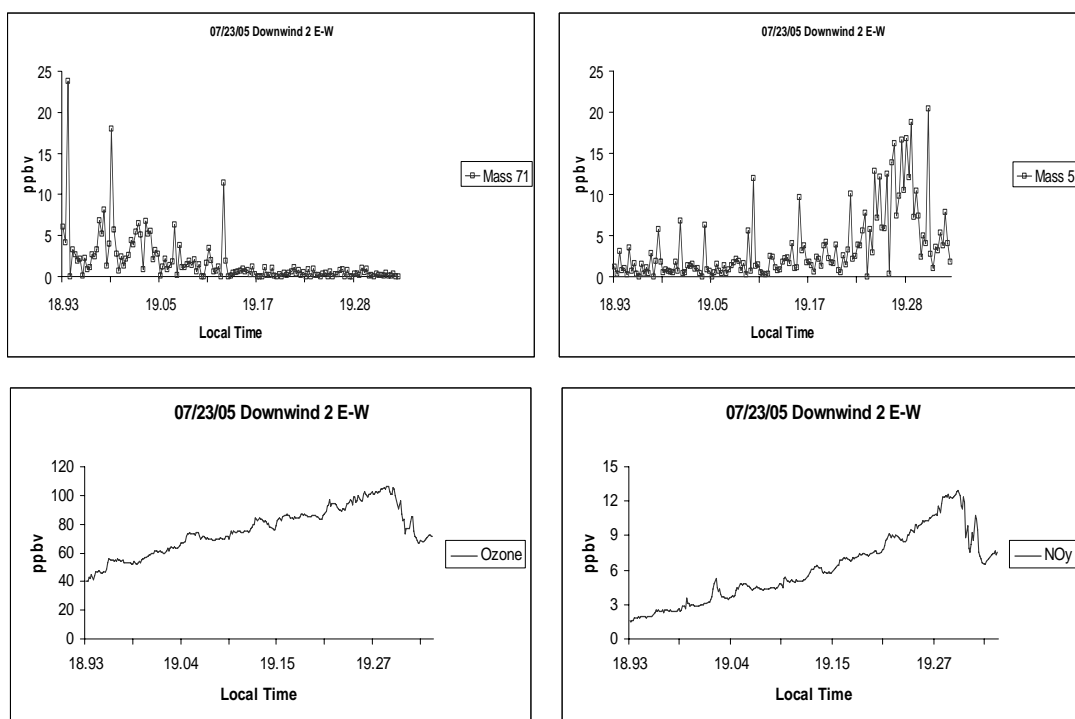


Figure 4. Arc flown approximately 20 miles north of Houston moving east to west at 2000' above mean sea level (MSL). Arc begins in rural heavily forested area and ends after crossing the Houston urban plume.

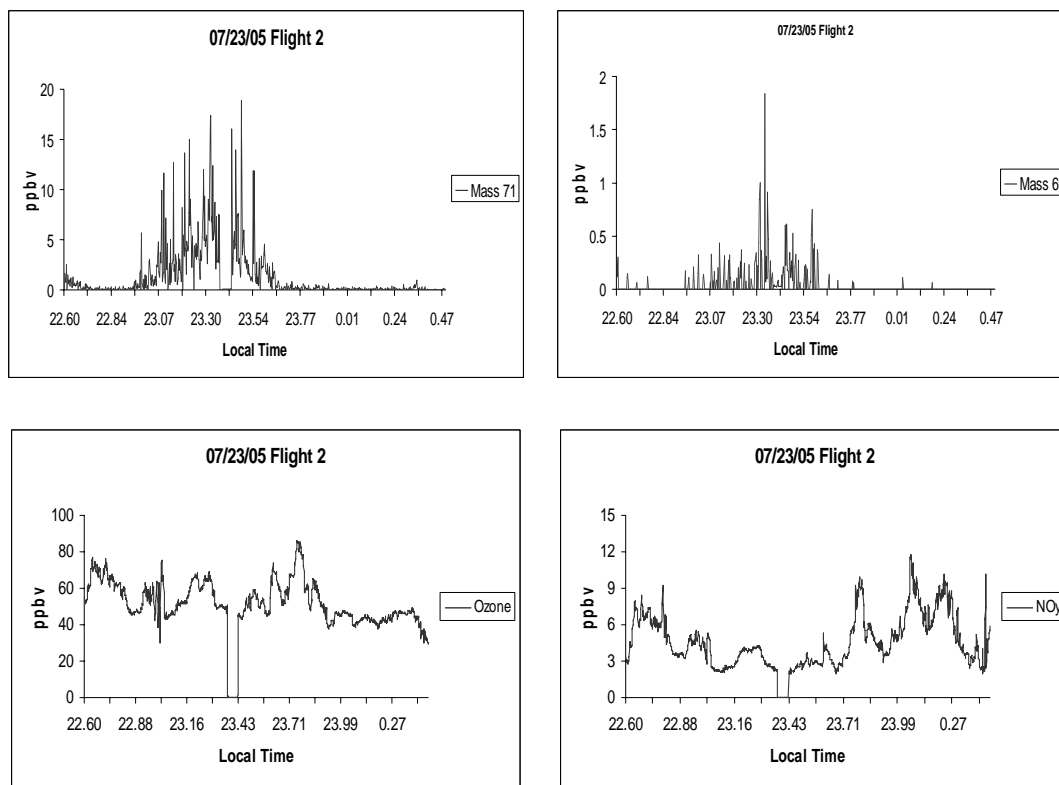


Figure 5. Transect done over forested area showing the presence of mass 69 attributed to isoprene and mass 71 attributed to isoprene oxidation products at night. Altitude of transect was 2000' MSL.

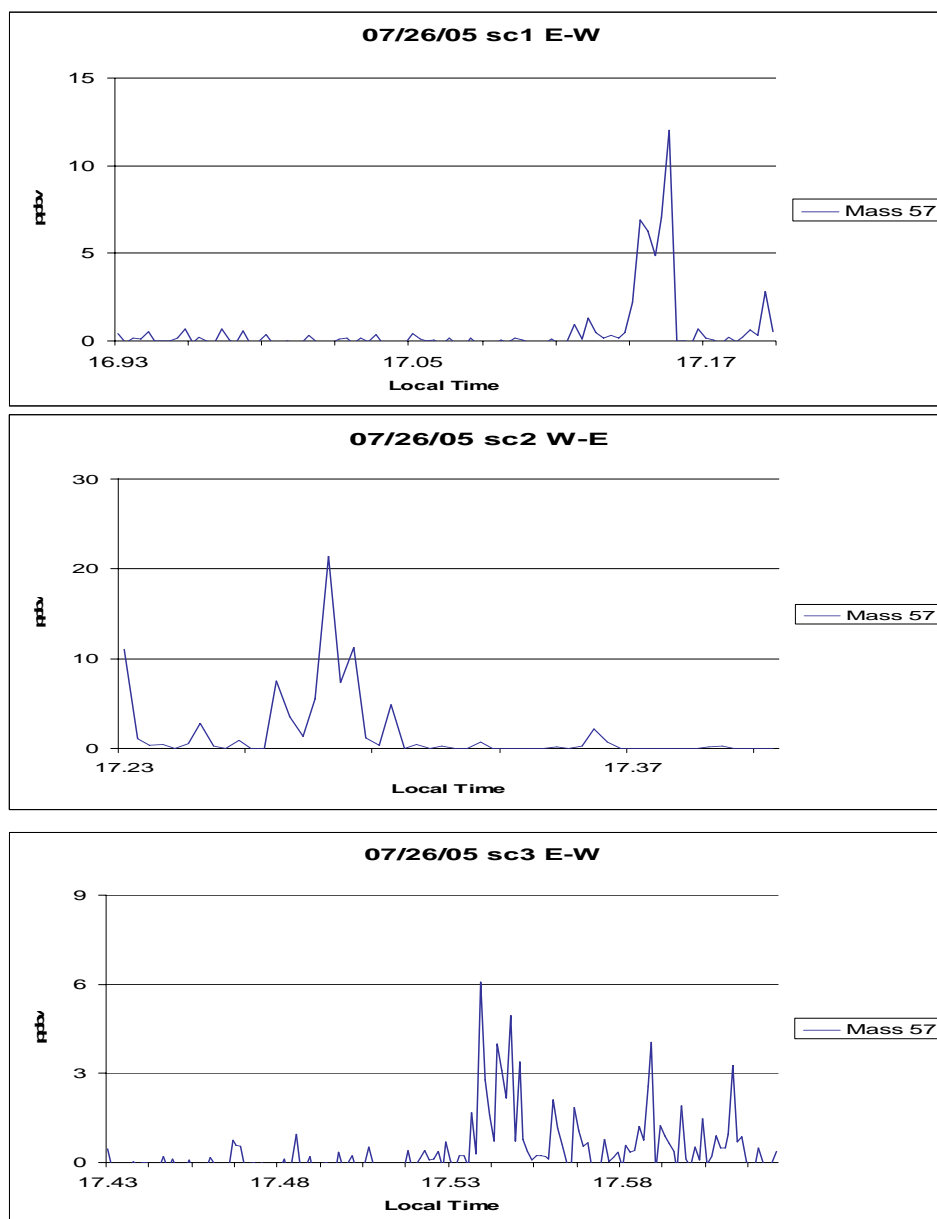


Figure 6. Three consecutive transects flown 3 miles north of the Houston Ship Channel on 07/26 show a mass 57 peak in a similar location during each transect. This location is close to the location of the mass 57 peak found on 07/21. Altitude of all transects shown was 2000' MSL.

Following the ship channel transects eight transects were flown perpendicular to the urban plume downwind of Houston eventually reaching the area between Shreveport LA and Texarkana TX. Figure 7 shows the route flown on this evening with the color coded ozone mixing ratios displayed to illuminate the plumes location. The two tetroons flight paths along with the HYSPLIT models forecast trajectory are also depicted in this figure. The urban plume was evident in all of these arcs observing TVA O₃ and CO data as well as PTR-MS data. The PTR-MS data display elevated mass 43 and mass 45 within the plume through all arcs, while mass 57 was elevated within plumes in all but the final arc.

Figure 8 features scatter plots of masses 43, 45 and 57 measurements taken while the aircraft was in the broad urban plume throughout the evening. Mass 43 can be seen to gradually decline while mass 57 declined at a steeper rate and mass 45 actually displayed a slightly higher mixing ratio during the early downwind plume transects than it had during the ship channel transect. Mass 45 also declined in later transects. It should be noted that while the downwind transects were all within approximately 20 miles of the tetroon the air mass sampled over the ship channel would have been about 50 miles away from the tetroon at the tetroon launch time had it maintained speed and heading. Masses 43 and 57 would be expected to be high in the ship channel region due to propene and butene emissions there. Mass 45 is attributed to acetaldehyde which is primarily formed from propene oxidation. Given any wind at the surface it might be expected for acetaldehyde to have a peak some distance downwind of the ship channel.

Preliminary Data (subject to revision)

Ozone: July 26-27, 2005

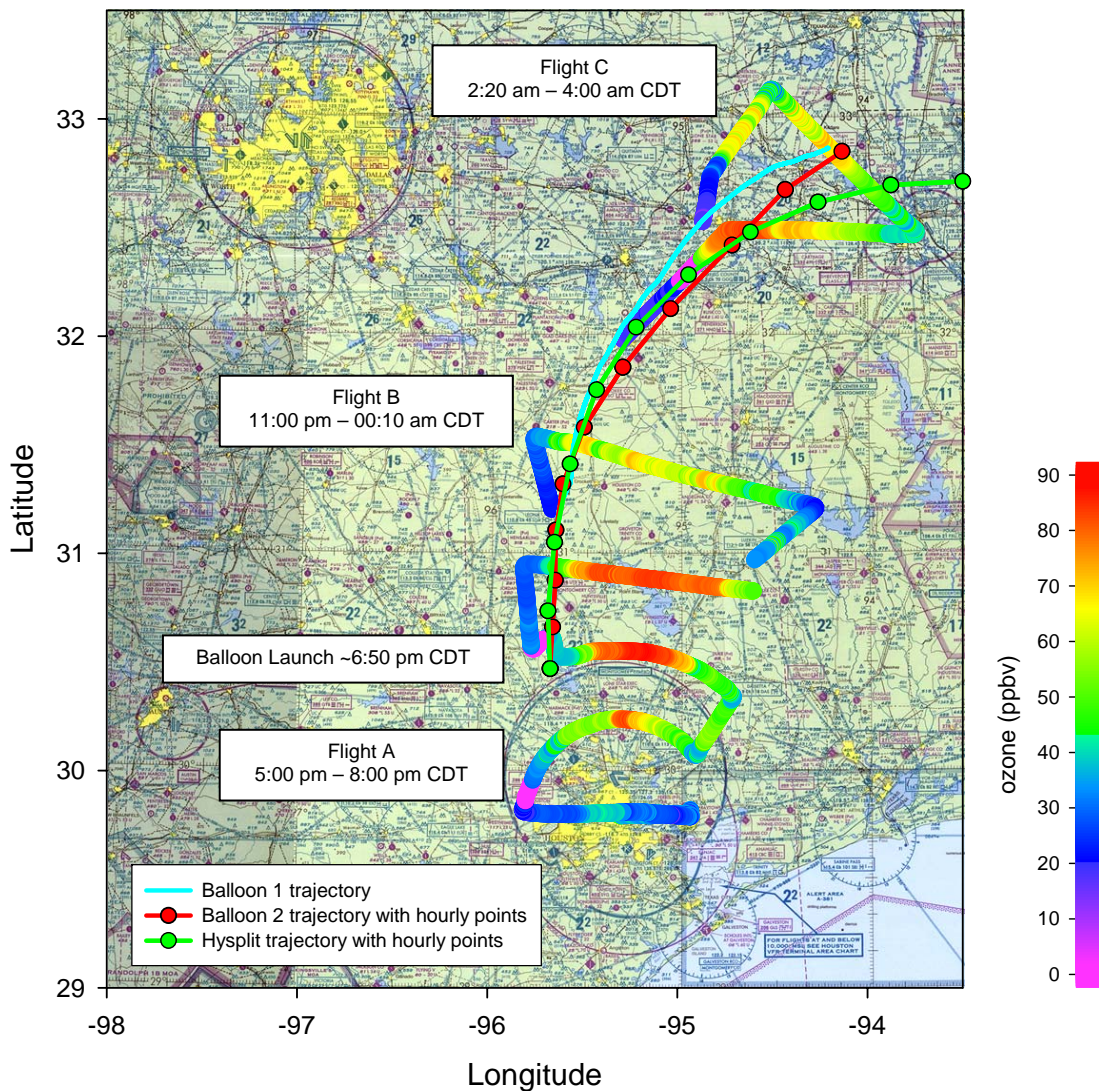


Figure 7. The route flown on the 07/26-07/27 mission is depicted on the map plot with the color coded ozone mixing ratios displayed to illuminate the urban Houston plume. The two tetrons flight paths along with the HYSPLIT models forecast trajectory are also depicted in this figure [Zaveri *et al.* 2005].

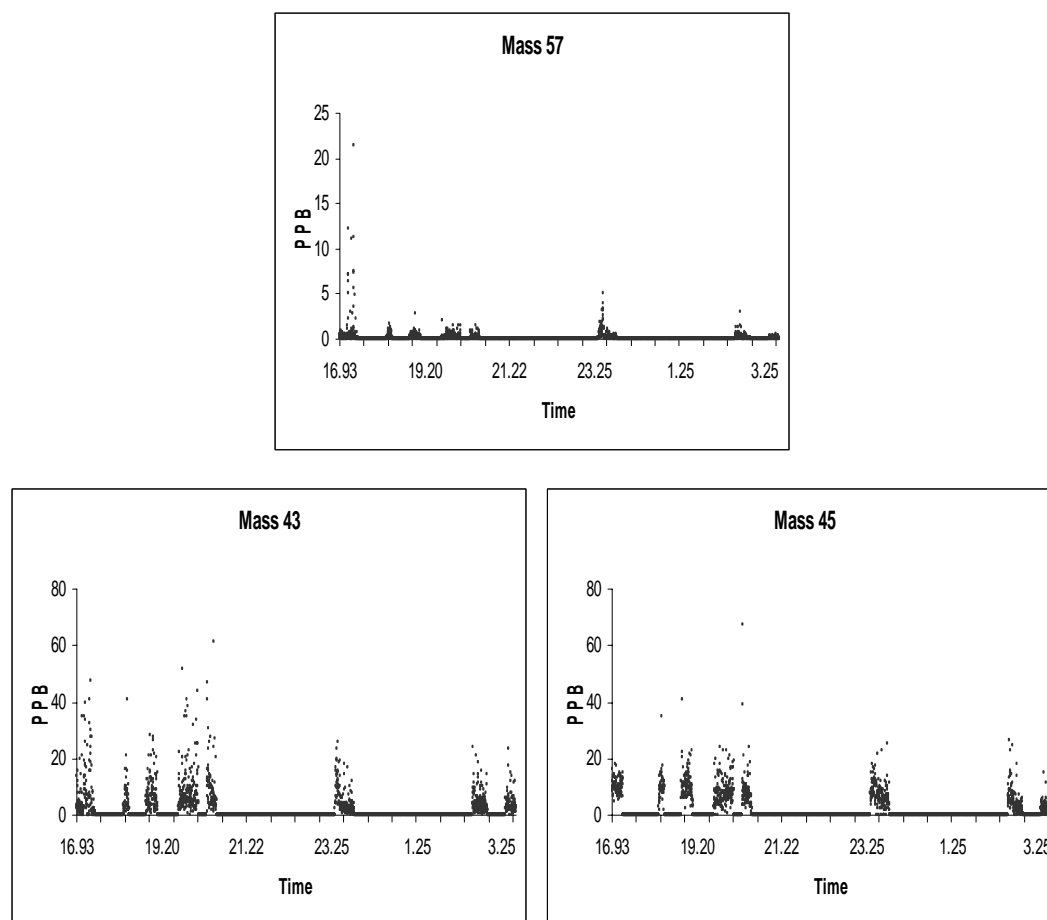


Figure 8. Scatter plots of masses 43, 45 and 57 measurements taken while the aircraft was in the broad urban plume throughout the 07/26-07/27 mission.

Mixing ratios of masses 43 and 57 determined by PTR-MS are shown in Figures 9 and 10 along with mixing ratios of O₃, NO_y and SO₂ determined by the TVA research team. Figures 9 and 10 depict the mixing ratios determined along a ship channel transect flown along a west to east axis approximately 3 miles north of the Houston Ship Channel relative to time and distance respectively. Three ship channel transects were flown on this evening and mass 43 and mass 57 mixing ratios tend to be more elevated at the western end of these transects. The fifth downwind transect was taken approximately 120 miles from the ship channel after the plume had been tracked for 5 ½ hours and is shown in Figures 11 and 12. Pronounced mass 43 and mass 57 peaks of approximately 12 ppbv and 3 ppbv respectively were evident in this transect as well as a broader peak of mass 45 at 10 ppbv. Ozone peaked at approximately 75 ppbv during this transect. Finally concentrations from the seventh downwind transect which was the second to the last transect of the night are depicted in Figure 13. This transect was conducted 200 miles downwind of Houston approximately nine hours after the ship channel transects. Masses 43 and 45 were elevated in the plume to approximately 10 ppbv while mass 57 was generally elevated to 1-2 ppbv although there was a short lived peak of 6-9 ppbv. Ozone was elevated to 85ppbv during this transect.

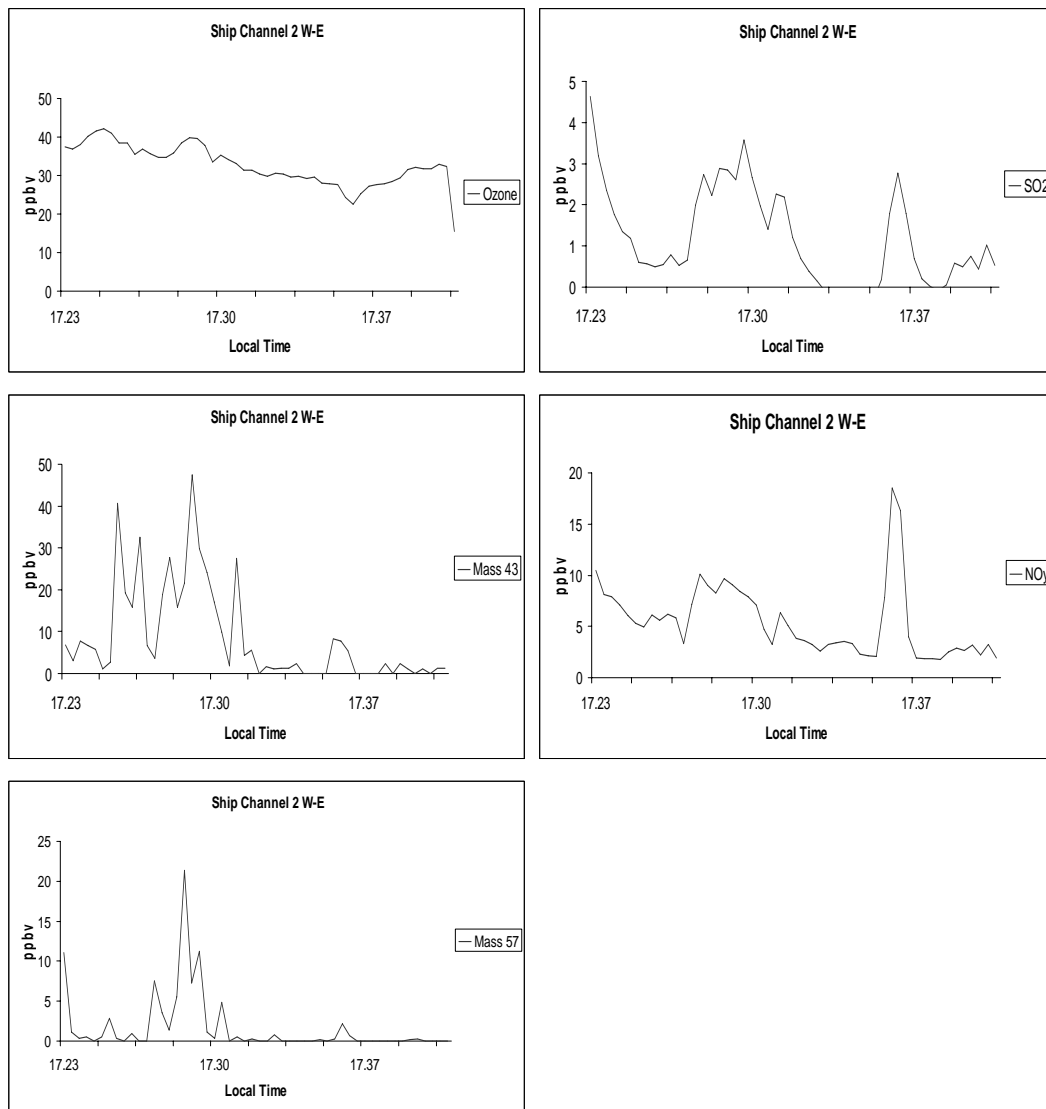


Figure 9. Mixing ratios determined along a ship channel transect flown along a west to east axis approximately 3 miles north of the Houston Ship Channel. This route was flown at 2000' MSL on 07/26.

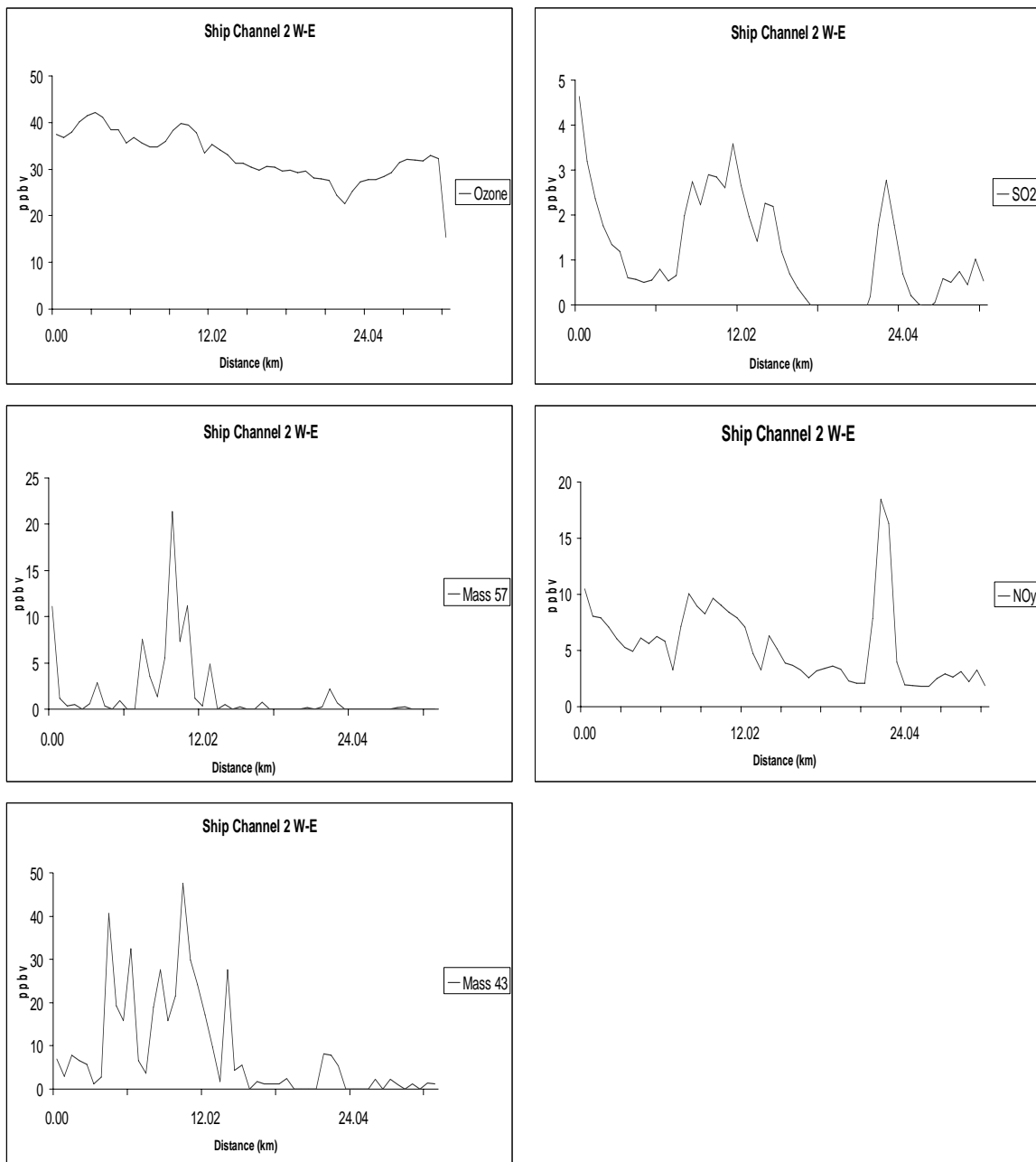


Figure 10. Mixing ratios determined along a ship channel transect flown along a west to east axis approximately 3 miles north of the Houston Ship Channel, relative to distance. This route was flown at 2000' MSL on 07/26.

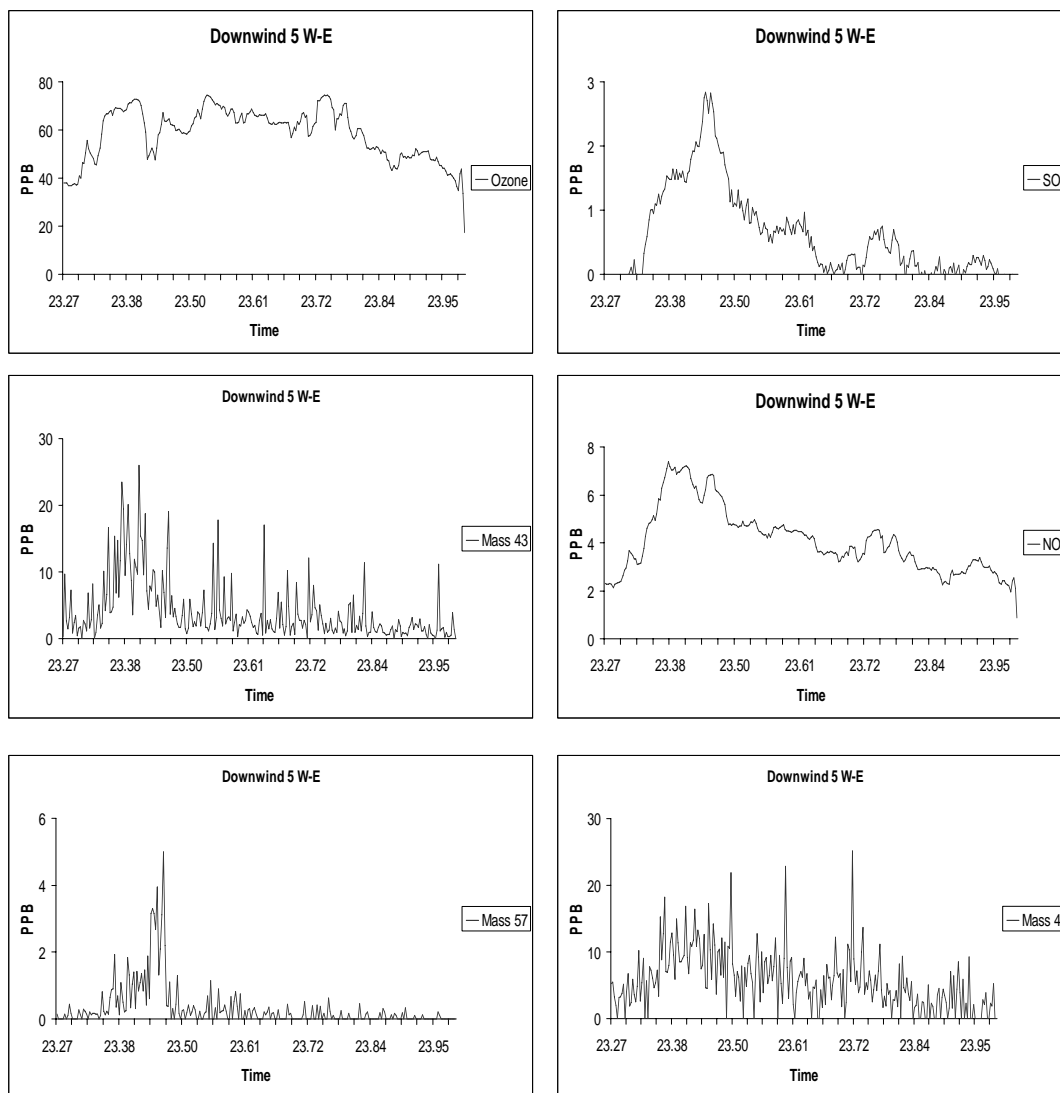


Figure 11. This transect was the fifth downwind transect taken on 07/26-07/27 mission approximately 120 miles from the ship channel after the plume had been tracked for 5 ½ hours. Flight altitude was 2000' MSL.

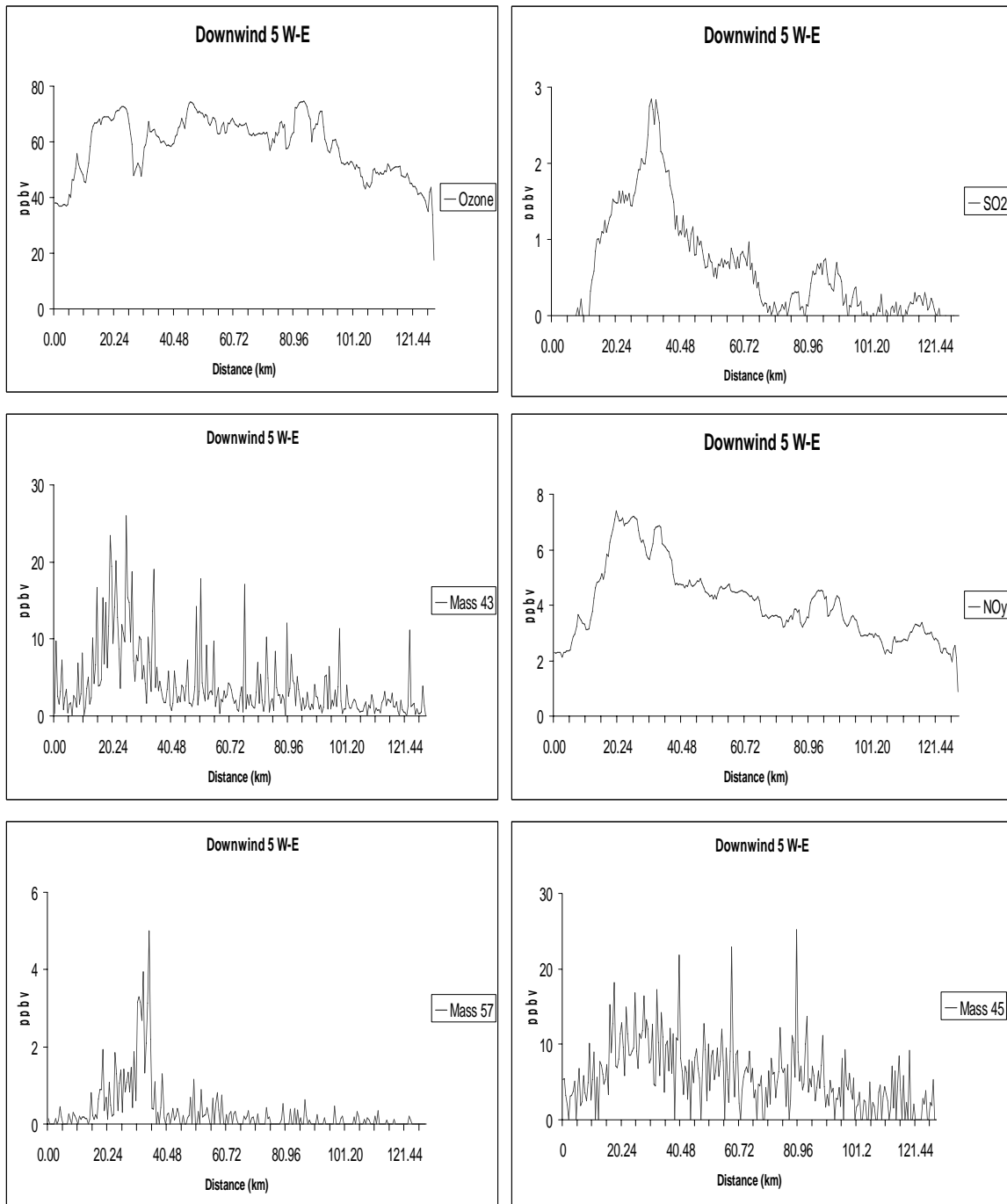


Figure 12. The fifth downwind transect taken on the 07/26-07/27 mission depicted with respect to distance along this linear transect.

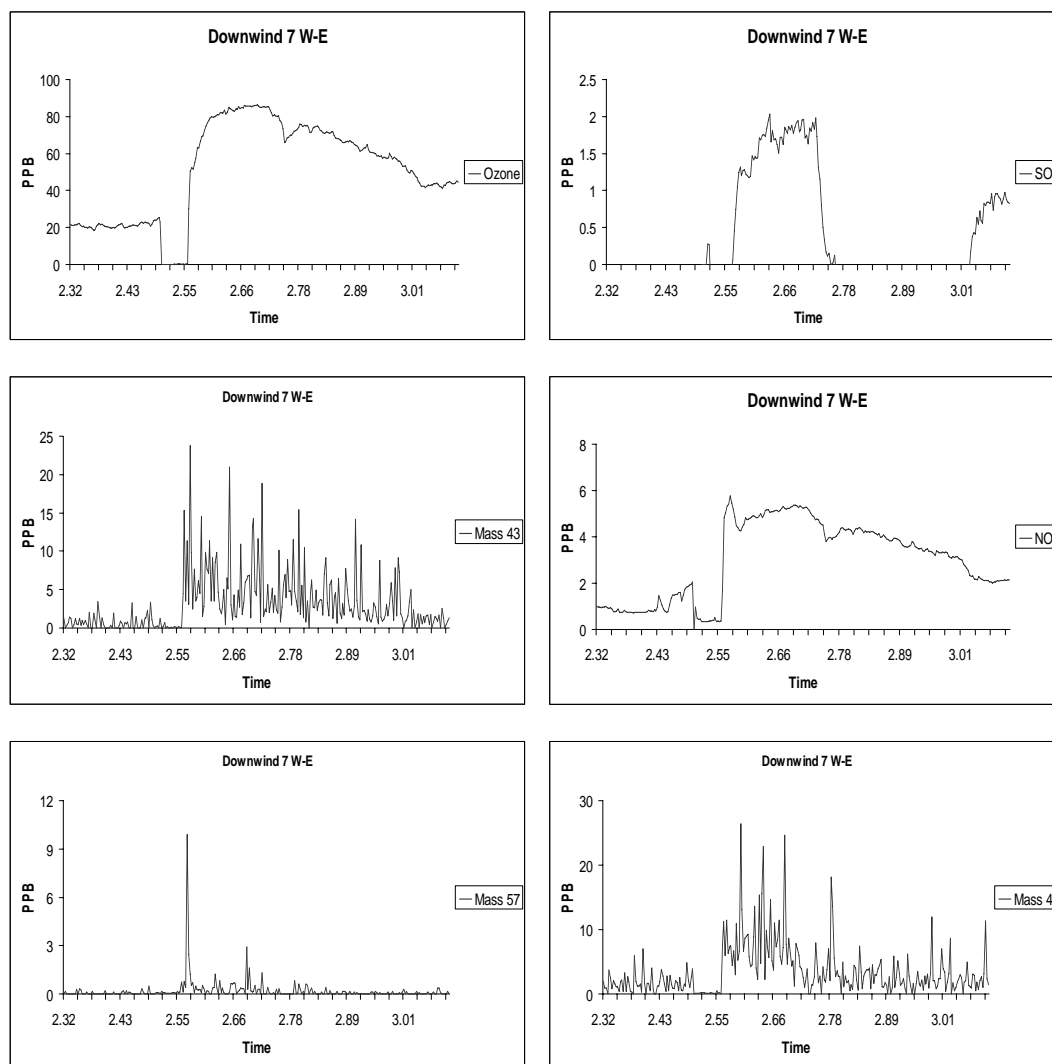


Figure 13. Concentrations from the seventh downwind transect on the 07/26-07/27 mission. This transect was conducted 200 miles downwind of Houston approximately nine hours after the ship channel transects. Flight altitude was 2000' MSL.

3.4 Overview of PTR-MS Usage in NETPS

For the NETPS campaign the Twin Otter aircraft base of operations was located at Midway Regional Airport located between Waxahatchie and Midlothian Texas. The NETPS campaign occurred from 1-31 August and its primary purpose was to track the evolution of power plant plumes as they approached the Dallas area as well as the interaction of the power plant plume with the urban plume downwind of Dallas. Flights occurred on ten days in support of these missions. Due to uncooperative weather conditions power plant plumes were generally not tracked into Dallas. In total four flights were done downwind of cement plants located in Ellis County, three flights were done tracking power plant plumes into the northeast Texas area and six flights were done downwind of the Dallas metropolitan area tracking the urban plume.

With regards to the cement plant source flights no VOC plumes were found that could be attributed to the cement plants themselves with the exception of one downwind pass conducted on August 31 which did indicate a mass 43 peak of 27 ppbv against a background of 5 ppbv shown in Figure 14. The mixing ratio of ozone was lowered while that of NO_y and SO₂ was elevated in this plume. While this one peak was substantial it should be noted that four Ellis County point source flights were conducted using approximately 40 transects downwind of the Ellis sources and no substantial VOC plumes were found in these flights. The flight that encountered the elevated mass 43 was conducted at approximately 19:30 while all others flew around midday. The lowest

altitude flown downwind of these plants was 1000' above ground level (AGL) which was low enough to encounter the stack plumes from these plants.

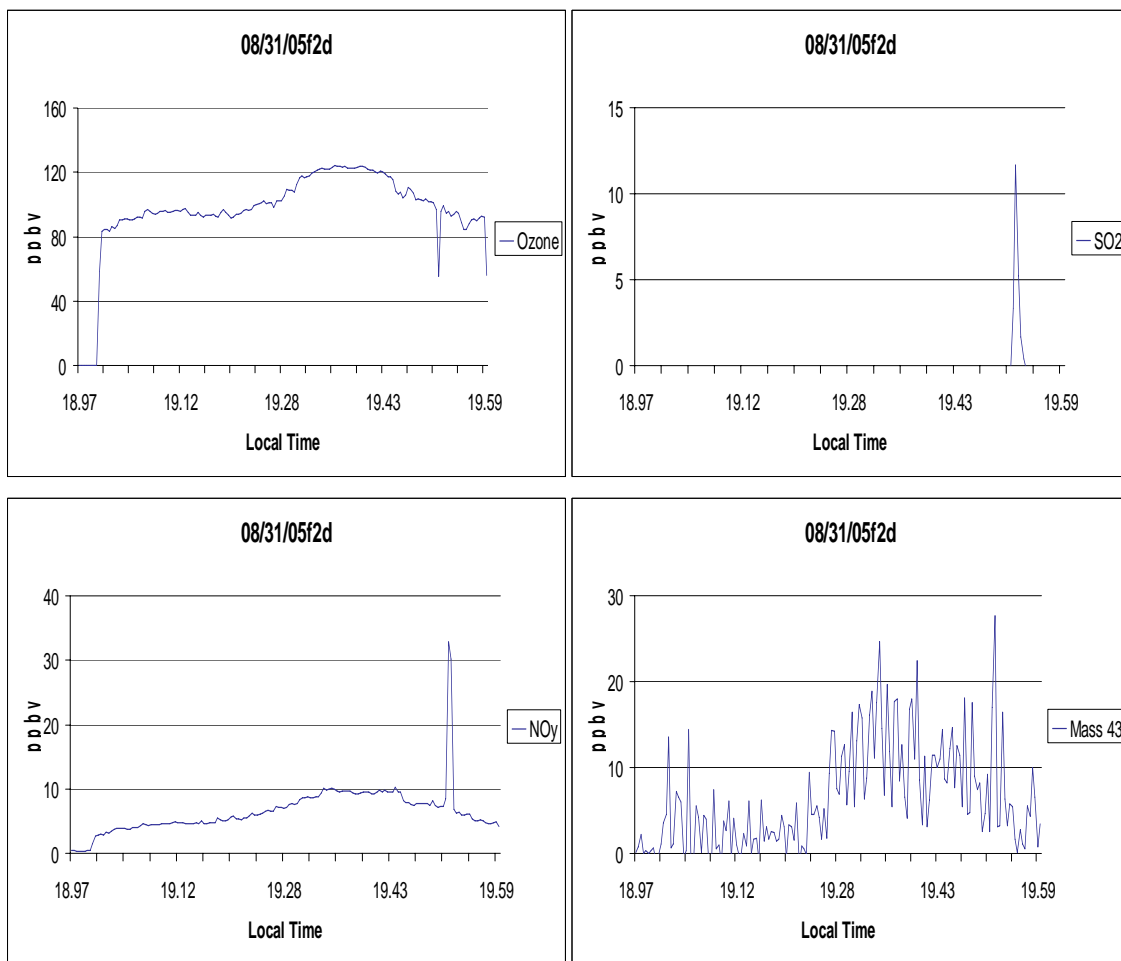


Figure 14. A tightly concentrated plume was crossed on 08/31 about 3 miles downwind of an Ellis County cement plant source. The broad urban pollution plume is encountered between 17.29 and 17.48 while the compact plume is encountered at 19.53. Mass 43 was the only VOC found elevated in the compact plume. Altitude was 2000' MSL.

The flights conducted downwind of Dallas all occurred in the afternoon hours and flew on the 24-26, 28, and 30-31 August. All flights encountered elevated mixing ratios of O₃ and CO within the urban plume downwind of Dallas. In the Dallas urban area the majority of the time only mass 43 and mass 45 were found to be elevated. During some flights the VOC plumes matched the O₃, CO and NO_x plumes (Figure 15) while in other cases these VOCs were offset to the side (Figure 16). It can be seen that in areas far away from the urban plume mass 43 and 45 dropped significantly. Generally speaking propene and acetaldehyde have previously been considered to be minor factors in the Dallas metropolitan area and future cross-comparisons are welcomed.

Missions were conducted that sampled the plumes of major NO_x and SO₂ emitting power plants including the Limestone, Big Brown and Sandow facilities on 18, 19 and 25 August. Winds were out of the southwest on these days which resulted in the power plant plumes being advected east of the Dallas area. Due to the lack of VOCs emitted by these power plants and the rural nature of the plumes track the primary VOCs the PTR-MS measured in these flights were mass 71 attributed to methyl vinyl ketone and methacrolein and mass 69 attributed to isoprene. Figure 17 displays elevated mass 71 and mass 69 observed while flying at an altitude of 1500' AGL over the Neches and Sabine river valleys during the afternoon hours. Mass 71 peaks of 5-7 ppbv and mass 69 peaks of 3-4 ppbv are seen in these areas. Masses associated with anthropogenic VOCs such as mass 43 and mass 57 as well as other anthropogenically derived trace gases measured by TVA including CO, O₃, NO_x and SO₂ were all at background levels in this area.

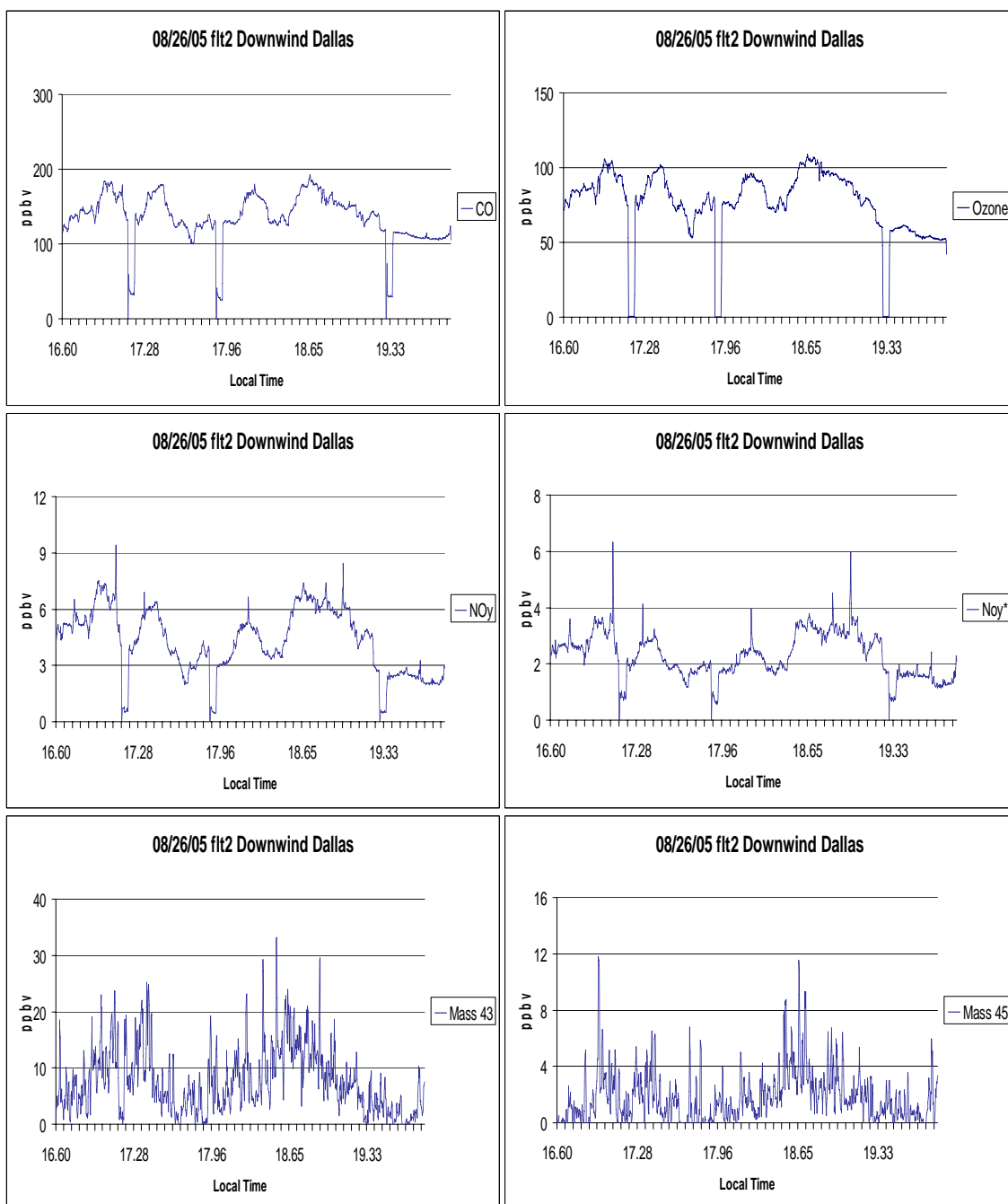


Figure 15. During this flight traversing the Dallas urban area plume VOC peaks were observed to be roughly co-located with O₃, CO, NO_y and NO_y*. Altitude was 2000' MSL.

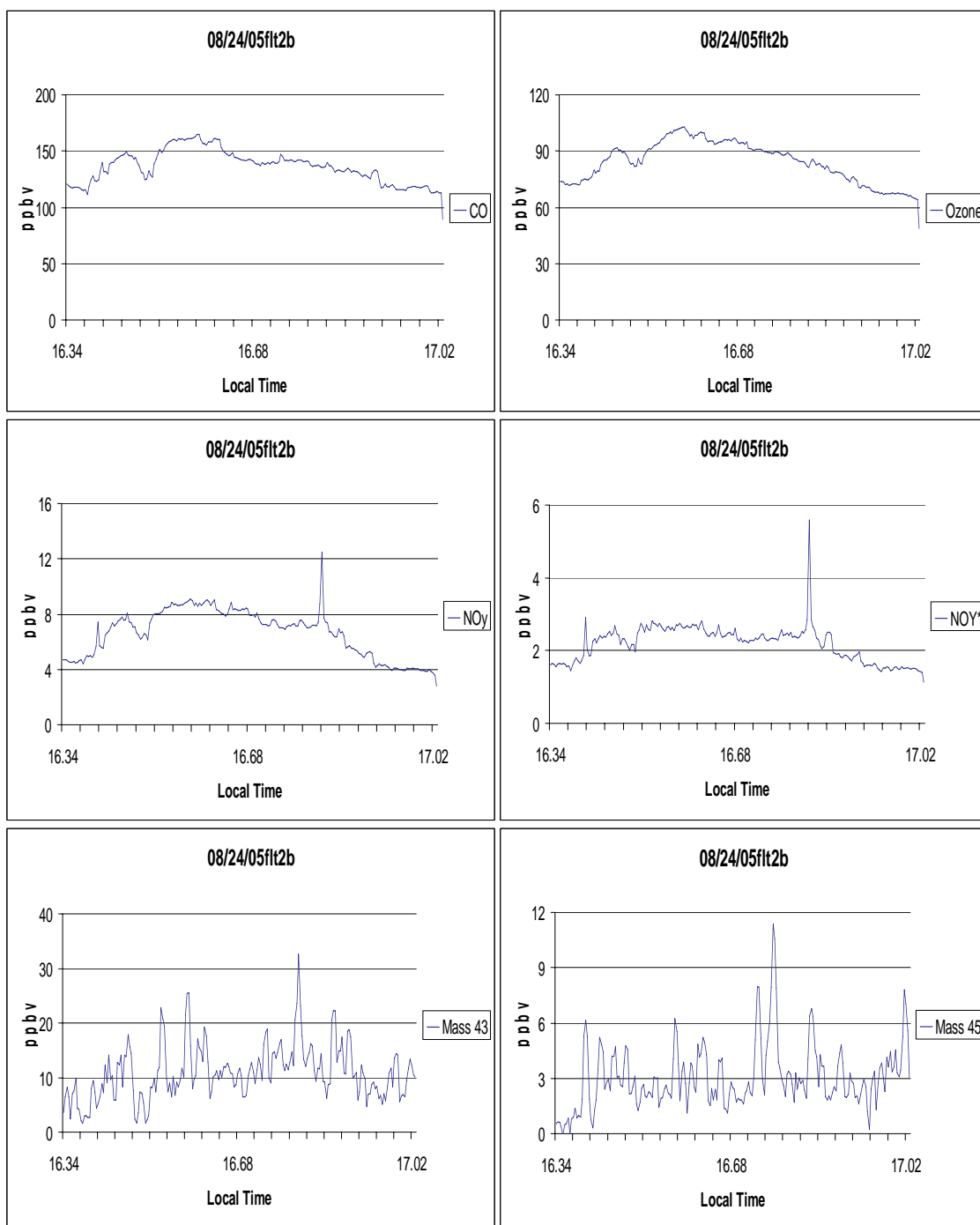


Figure 16. On this downwind of Dallas transect, mass 43 and mass 45 peaks appeared to be offset from the urban O₃, CO, NO_y and NO_y* plumes. Altitude was 2000' MSL.

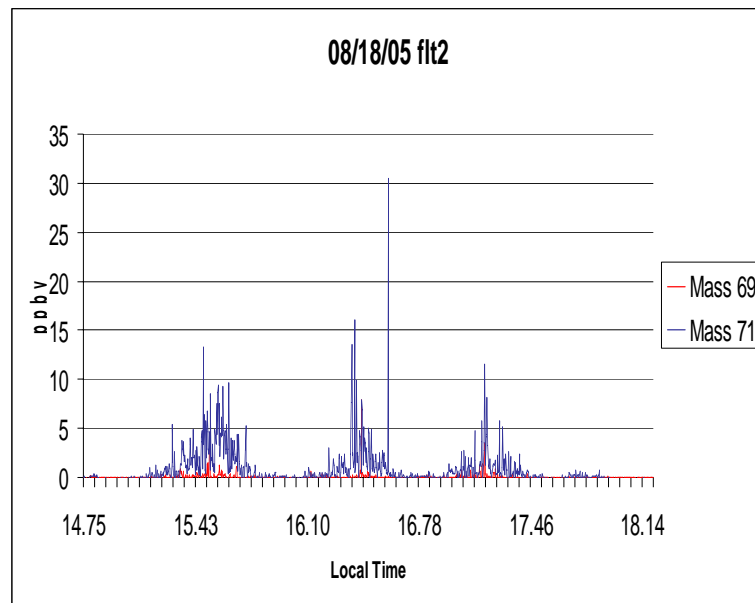


Figure 17. Elevated mass 71 and mass 69 observed while flying at an altitude of 1500' AGL over the Neches and Sabine river valleys during the afternoon hours of 08/18.

3.5 Speciation of Masses

It would be very useful to the discussion of VOC plumes emanating from the Houston Ship Channel and urban areas if we were able to speciate with a high degree of confidence the masses which we see elevated in these plumes. This is possible for mass 45 which has been determined to be acetaldehyde as mentioned earlier in the Methodology section. Mass 43 and mass 57 unfortunately are considerably more difficult to speciate. Propene is detected at mass 43 and due to propenes reactivity with OH and its implication as one of the most efficient VOCs for O₃ production there is a strong motivation to measure this species. PTR-MS measurements and intercomparisons with GC-FID conducted during TexAQS 2000 indicate that concentrations above approximately 5-10 ppbv in the ship channel area at mass 43 may be attributed to propene [Karl *et al.*, 2003; Kuster *et al.*, 2004]. Unfortunately there are a large number of species which fragment to mass 43 such as pentenes, acetic acid and heavier acetates. There are even a few species such as cyclopropane and 2-propanol which while they are considered to be present in the atmosphere at much lower levels than propene are also predominantly found at mass 43 [Warneke *et al.*, 2003]. Considering previous findings it should then be considered more likely that the mass 43 readings found over the ship channel are in fact propene due to their high mixing ratios and location. There is considerably more doubt as to the speciation of mass 43 readings as the distance from the ship channel is increased although there is still some evidence supporting the theory that this is in fact propene. The fact that the mass 43 plume is co-located with an

acetaldehyde plume supports mass 43 being propene in this instance because propene oxidizes to form acetaldehyde. It should also be considered that if a plume of air is tracked from the ship channel during the evening hours when reactions will be minimized the chemical makeup of that plume should not change substantially as it moves through space. The difficulty then, is to ensure that the ship channel plumes that were measured in earlier transects are what the tetraon is tracking. Obviously it would have been advantageous to launch the tetraon from the ship channel area itself, however this was not logistically possible due to flight regulations and airports in the vicinity. Regarding mass 57, it is generally considered to be the sum of butenes, MTBE, butanal and methylcyclohexane. Octane also fractionalizes to mass 57, however its primary ion, mass 71, was not elevated in the majority of mass 57 plumes identified indicating octane was probably not present in large amounts.

3.6 Intercomparison of PTR-MS Data with Canister Data

The TVA research team gathered canister samples in flight during both the SETTS and NETPS projects for later analysis to determine hydrocarbon species present in the samples. The fragmentation table found in *Warneke et al.*, (2003) was used to assign species to the masses measured for the purpose of intercomparison with PTR-MS. There were a total of 104 cans sampled while the PTR-MS was operating. The vast majority of cans showed benzene, toluene and xylenes to be below the level of detection for the PTR-MS and they were. Propene and pentene readings detected by the canister were generally much lower than the PTR-MS readings for mass 43 although there were

exceptions. With regards to mass 57, unfortunately no canister samples were taken while in major mass 57 plumes. Three canisters were taken in minor mass 57 plumes and in these minor plumes (<10 ppbv) the PTR-MS had higher readings than the combined canister readings for the various butenes, octane and MTBE which can all be found to some extent at mass 57. The canisters did not quantify oxygenated VOCs such as acetaldehyde, methyl vinyl ketone and methacrolein so intercomparison of these species was not possible. The canister data for isoprene did correlate somewhat with the PTR-MS data at mass 69. In the future, intercomparisons utilizing canisters may yield better results if the canister is allowed to fill over a longer time period which will then encompass a greater number of PTR-MS cycles. Canisters on these missions had a 30 second fill time which typically encompassed 1-2 PTR-MS cycles.

3.7 Conclusion

The primary purpose of SETTS was to track the movement of tetroons after they had been launched and conduct trace gas measurements of the air mass the tetron tagged as that air mass moved dynamically through space. Due to convective instability during the daylight hours the decision was made to conduct these flights in the evening. The PTR-MS was able to track the movement of VOCs at night within the tagged air parcel. On the evening of July 26-27 a polluted air mass with elevated mass 43, mass 45 and mass 57 VOCs along with elevated O₃, CO, and NO_x was tracked from the Houston metropolitan area to an area northwest of Shreveport LA, a distance of over 200 miles.

The chemical evolution of this plume was minimal due to the lack of sunlight. Future airborne measurement campaigns which determined the frequency of these elevated VOC plumes would be useful. If VOC plumes similar to the plume event of July 26-27 are found to be a frequent occurrence then transport of VOCs out of the Houston metropolitan area may need to be considered by areas downwind of the Houston area when they are determining how to attain their air quality goals. During the SETTS campaign the PTR-MS also observed mass 57 plumes elevated by as much as a factor of 100 over background levels in a specific area of the Houston Ship Channel on multiple occasions and elevated mixing ratios of isoprene and isoprene oxidation products were measured at night over forested river valleys

The primary goal of the PTR-MS involvement with the NETPS study was to provide online VOC measurement support during a study which was intended to focus primarily on power plant plumes. While VOC plumes were not collocated with the power plant plumes that were studied, high biogenic VOC levels were encountered over East Texas river valleys. Elevated acetaldehyde and mass 43 readings were also encountered downwind of the Dallas-Fort Worth metropolitan area during some afternoon missions. This study suggests that future measurement campaigns that examined biogenic VOCs in East Texas, particularly in the vicinity of forested river valleys, might display higher biogenic VOCs than current models depict. Measurements of VOCs downwind of the Dallas-Fort Worth metropolitan area might also better elucidate the VOC emissions in the metropolitan area.

4. THE MILAGRO 2006 FIELD CAMPAIGN

4.1 Introduction

Mexico City is the location of some of the most severe air pollution in the world. The city has a population of 18 million people and is home to 3 million vehicles and 35,000 industries [Molina *et al*, 2002]. Mexico City is located in the tropics at a high altitude enhancing photochemical activity leading to ozone production. Another factor that contributes to the air pollution problem in this area is that the city lies in a valley surrounded by mountains leading to the frequent occurrence of thermal inversions in the morning hours. Daily activities in the city lead to the emission of VOCs which react with nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$) emitted primarily through combustion sources. This reaction then leads to the production of O_3 through photochemical processes. The Mexican 1 hour air quality standard of 110 ppbv of O_3 is violated during approximately 80% of the days during the course of a year and peak O_3 values of over 300 ppbv have been recorded [INE, 2000].

The Megacity Initiative – Local and Global Research Observations (MILAGRO) 2006 campaign represented an unprecedented international effort to observe and quantify the fate of anthropogenic pollutants emitting from the world's second largest city. The PTR-MS instrument we deployed and operated during the MILAGRO field campaign was one of many critical components necessary to a better elucidation of the

VOC emissions and chemistry in the Mexico City area. While measurements of ozone and NO_x are common in Mexico City measurements of VOCs have been much less common and are important for understanding ozone formation [*Molina et al.*, 2002]. A study by *Arriaga-Colina et al.*, (2004) comparing morning measurements of VOC/NO_x and CO/NO_x ratios with ratios in the official 1998 emissions inventory suggest that the VOC/NO_x and CO/NO_x ratios in the official emissions inventory may be underestimated by a factor of 2 to 3. Modeling work by *West et al.*, (2004) comparing measured non-methane hydrocarbons (NMHCs) to modeled NMHCs achieves the best fit by using a factor of 3 increase in VOC emissions. While *Arriaga-Colina et al.*, (2004) and *West et al.*, (2004) both suggest underestimated VOCs in the emissions inventory, flux measurements conducted during MILAGRO 2003 utilizing PTR-MS by *Velasco et al.*, (2005) show fairly good agreement between emissions inventory and measurements. The use of our PTR-MS based VOC measurements in combination with other VOC measurements conducted throughout the Mexico City Metropolitan area during MILAGRO 2006 should present a clearer determination of the accuracy of current emissions inventories.

4.2 Experimental Methods

In March 2006 the Ionicon Compact PTR-MS instrument was utilized to conduct elevated surface based measurements of VOCs in Mexico City during the MILAGRO campaign. The measurements were conducted on the rooftop of a five story building

located at the Instituto Mexicano del Petrolea (IMP) facility approximately 7 miles north-northeast of downtown Mexico City. This site was named T0 and was one of three supersites involved in the MILAGRO project. Figure 18 shows the surface sites involved in the MILAGRO 2006 field campaign. The other two supersites, named T1 and T2, were located farther from Mexico City to the northeast of the city. In addition to the supersites there was also a flux tower constructed in downtown Mexico City and a mobile research van which moved to various sites around the Mexico City Metropolitan Area (MCMA). PTR-MS instrumentation was utilized by other groups at the flux tower and the mobile van. The T1 and T2 supersites used canister samples, DOAS, and IT-GC-MS to measure VOCs. The T0-IMP site also measured certain VOCs using DOAS, canisters, and GC methods in addition to our PTR-MS measurements.

Continuous online measurements of VOCs were conducted using the PTR-MS at T0-IMP from March 5-23 and then again from March 26-31. The system was inoperable from March 23-26 due to a condensation problem. The PTR-MS sampled day and night regardless of whether an instrument operator was present. Throughout the campaign drift tube pressure was maintained at 2.05 millibars and an E/n ratio of 115 Townsend was utilized. There were a suite of 38 masses sampled sequentially by the PTR-MS during the bulk of the field campaign. Each mass was scanned for two seconds so that the time between samples was approximately 76 seconds. Spectral scans from mass 21-250 were also conducted for one half hour every two hours when personnel were present to look for any mass peaks that might have been missed while in single ion scan mode. Background checks were performed for roughly 15 minutes once every three hours when

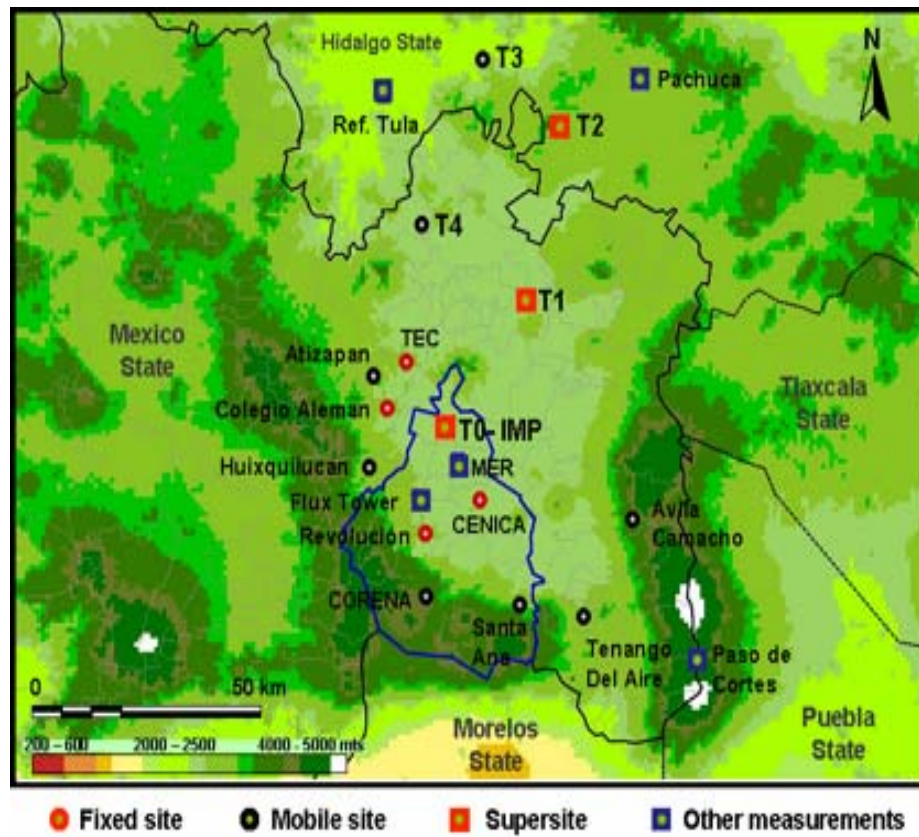


Figure 18. Surface sites located in and around the Mexico City Metropolitan Area during MILAGRO 2006. Figure courtesy of *Molina Center for Energy and the Environment*, Accessed June 2006.

personnel were present. Calibrations were conducted daily during the first half of the field campaign and once every other day toward the latter stages of the field campaign after it had been determined that the system was relatively stable and there was a strong desire to increase measuring time.

The inlet was constructed of ¼" outer diameter (OD), PFA tubing with a length of 14' and was pumped by a diaphragm pump at 30 liters per minute (LPM) maintaining a residence time of 2-3 seconds in the inlet. A small amount of the inlet flow (50-200 sccm) was diverted to the PTR-MS at a PFA tee upstream of the pump. This flow then passed directly into the PTR-MS or was diverted into a catalytic converter if background samples were being taken at the time.

The instrumental background was determined by passing the sample air through a catalytic converter en route to the PTR-MS. Background checks typically lasted 10 cycles and at any given time the background applied was the average of the backgrounds determined before and after that measurement. The use of a catalytic converter was determined to be preferable to using zero air when determining the instrumental background of the PTR-MS because any question of humidity dependence with regards to the background was eliminated.

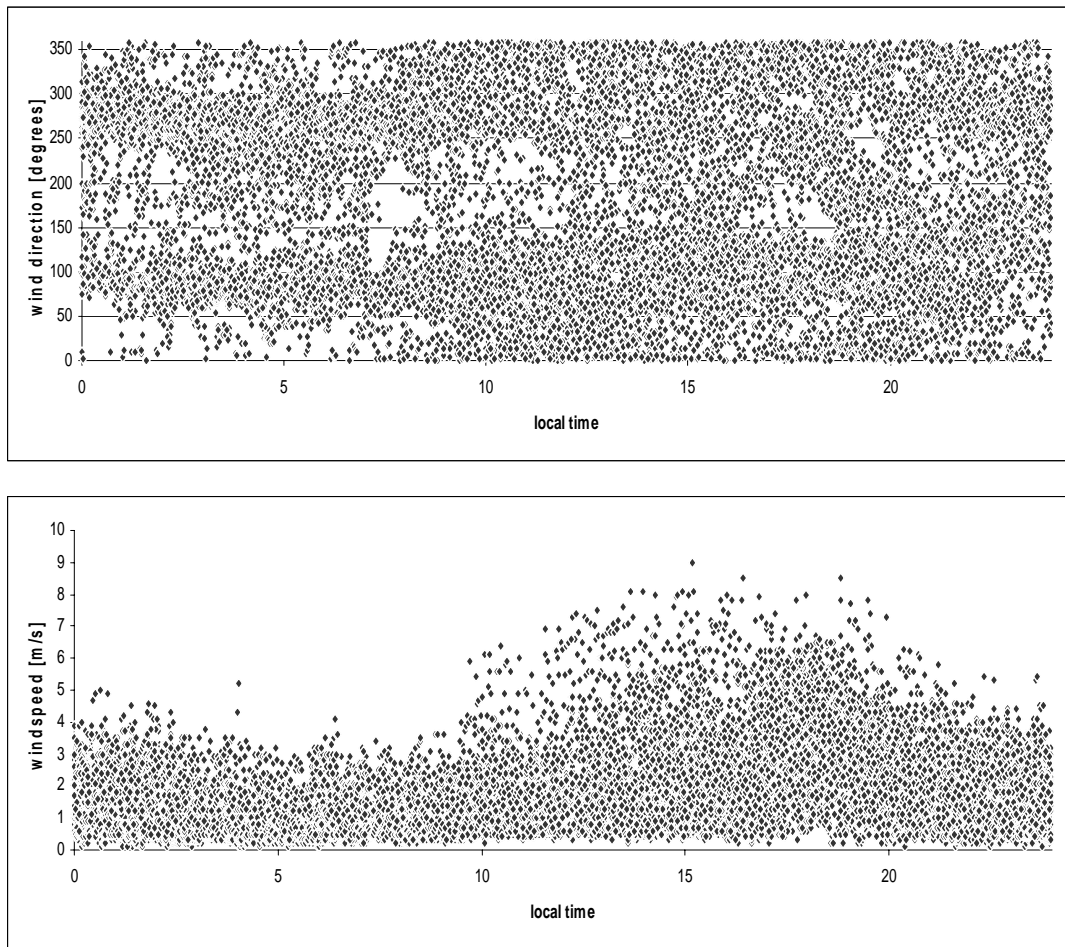


Figure 19. Scatter plots showing all wind direction measurements and wind speed measurements plotted against the time of day that they occurred.

Calibrations during MILAGRO were conducted using a custom mix calibration gas cylinder (Spectra) containing propene, 1-butene, acetone, isoprene, methyl ethyl ketone, benzene, toluene, m-xylene, 1,3,5-trimethylbenzene and alpha-pinene. The mixing ratio of the calibrated gases was varied between 2 – 20 ppbv. The carrier gas for these calibrations was ambient air which had passed through the catalytic converter. The calibration flow connected with the inlet through a PFA fitting. The performance of the PTR-MS was found to be slightly variable during the MILAGRO field campaign and for this reason it was determined that it would be most fitting to apply calibration curves derived from the preceding and following calibrations at any given time rather than using an average of all calibration curves developed throughout the field campaign as had been done during the TEXAQS 2005 campaign.

4.3 Results and Discussion

4.3.1 Local Meteorological Details

Surface-based winds at the IMP site obtained by Argonne National Laboratory were characterized by a strong diurnal cycle with winds between 0.5 and 3.0 m s⁻¹ during the early morning hours (0:00-8:00) as shown in Figure 19. Winds gradually increased throughout the day corresponding with the developing boundary layer and attained their maximum value of 5-9 m s⁻¹ in the late afternoon and early evening time periods (15:00-19:00). Wind direction was extremely variable and a trend is difficult to detect although

there does seem to be a slight preference for a wind from either the east or west during the early morning hours. Preliminary analyses of profiler data gathered by the University of Alabama-Huntsville at the IMP site indicates early morning boundary layer heights between 300-500 meters and late afternoon boundary layer heights of 3000-4000 meters. These measurements are in agreement with *de Foy et al.*, (2005) who found surface temperature inversions below 500 meters for most nights and daytime boundary layer growth to 4000 meters during the MCMA 2003 campaign. Low temperatures in the morning were typically 50-55°F and high temperatures were typically 75-80°F. Relative humidity ranged from 50-80% in the early morning hours and 10-40% during the afternoon. Precipitation did not occur during the first 2 ½ weeks of this field campaign but during the last 1 ½ weeks of the campaign scattered late afternoon thunderstorms did occur.

4.3.2 Diurnal Profile of VOCs

The diurnal profiles for 8 selected masses are shown in Figure 20. Every measurement for these selected masses that occurred within each hourly block of time was added and averaged for weekdays and weekends/holidays separately. A national holiday is celebrated on March 21 and March 20 is also a non working day for many citizens of Mexico City so these dates were considered to better match a weekend activity profile. In total sampling was conducted on 16 weekdays and 6 weekend/Holidays. The aromatics were represented by toluene at mass 93, the sum of C₂

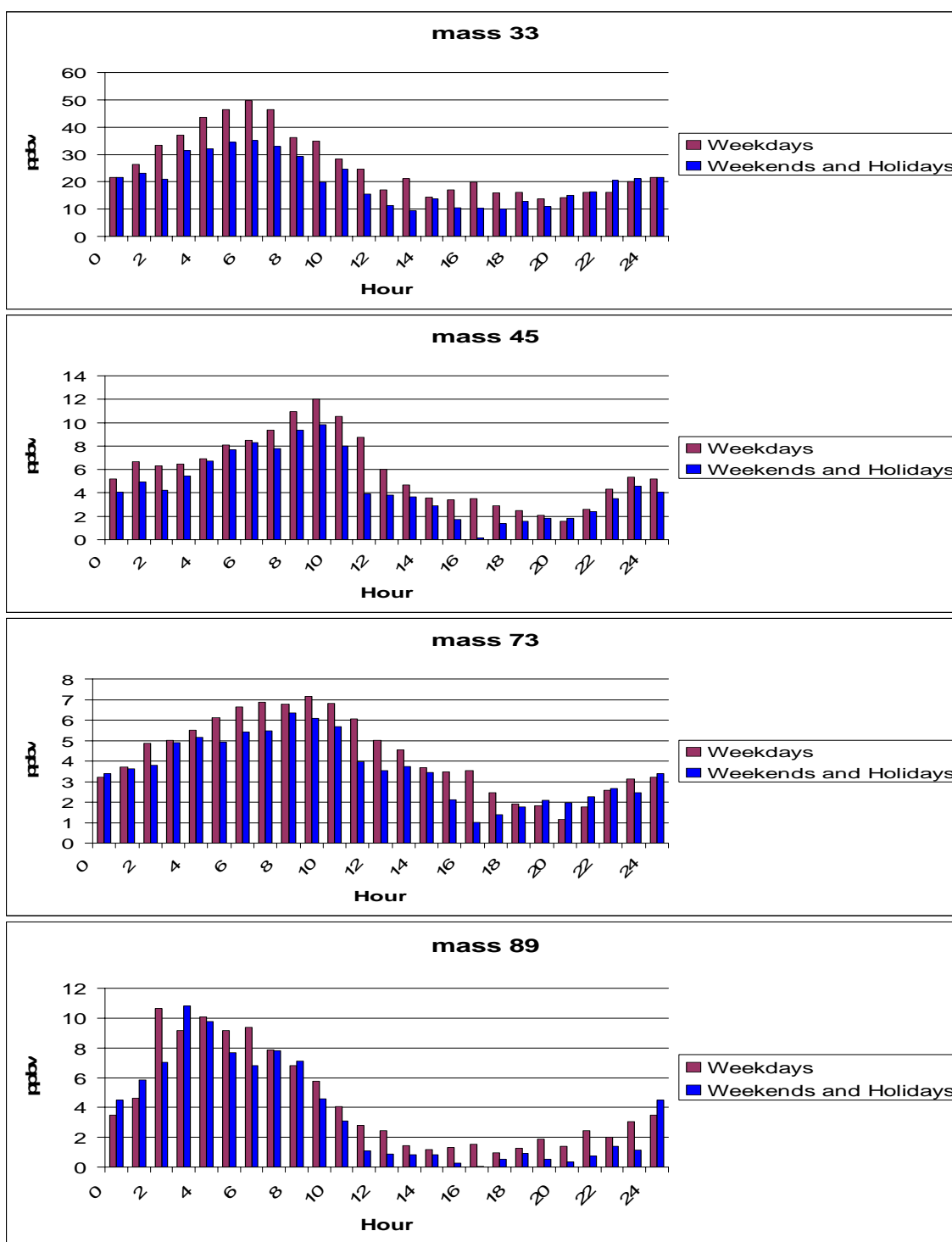


Figure 20. The diurnal profiles for masses, 33, 45, 73, 93, 101, 107 and 121 both during weekdays and weekends/holidays.

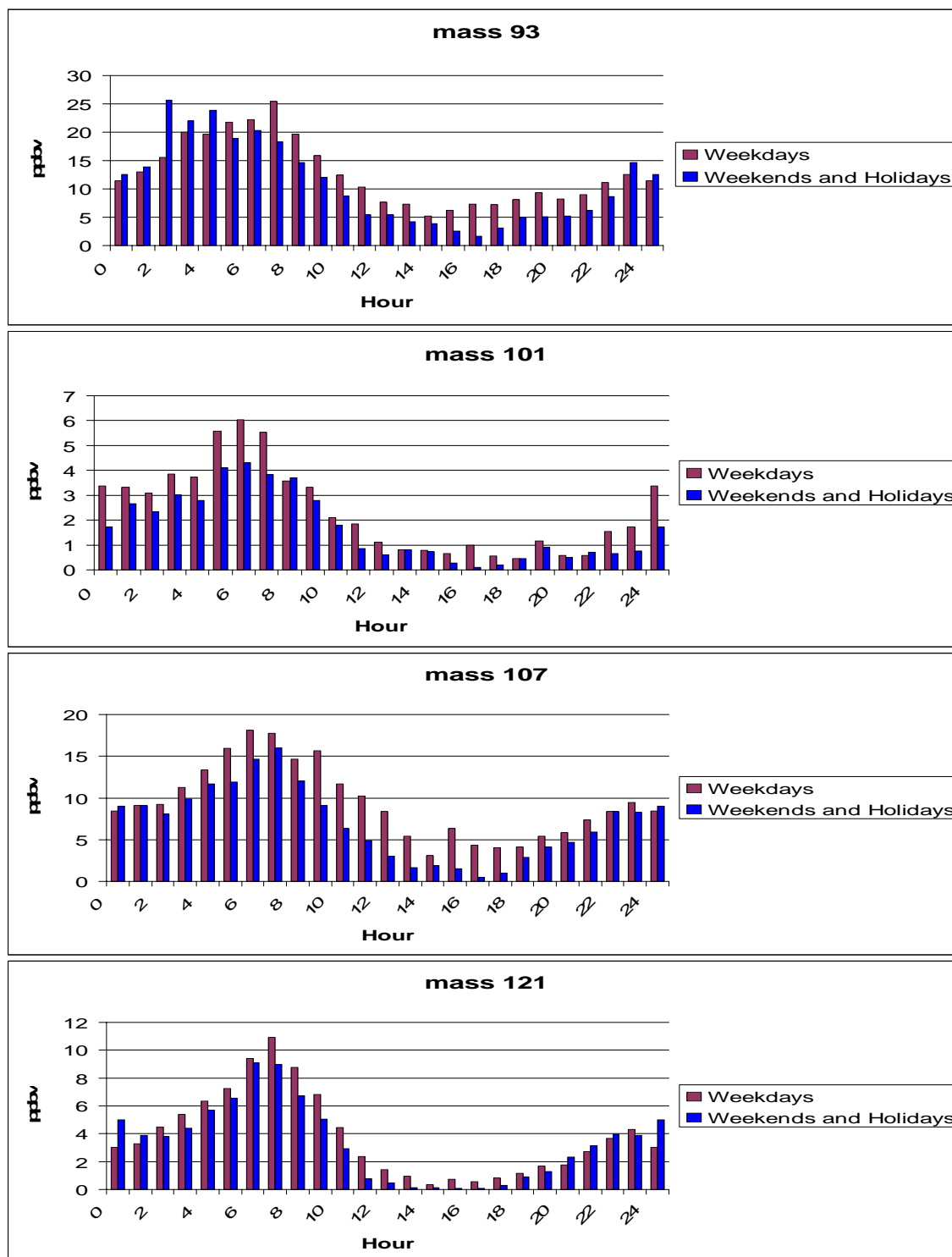


Figure 20. Continued

benzenes including xylenes at mass 107 and the sum of C₃ benzenes at mass 121. Oxygenated VOCs depicted include acetaldehyde at mass 45 and the sum of methyl ethyl ketone and methyl glyoxal at mass 73. Mass 33 is attributed to methanol, mass 89 is attributed to ethyl acetate and mass 101 is attributed to the sum of hexenal, hexanone and 2,3 pentane-dione.

On weekdays aromatics attained their highest concentration during the 6:00-7:00 time block for mass 107 and 7:00-8:00 time block for masses 93 and 121. The oxygenated VOCs peak later in the morning during the 9:00-10:00 time block for both masses 45 and 73. Mass 89 peaks during the evening hour time block of 2:00-3:00. On weekends/holidays the aromatics detected at masses 107 and 121 peak at similar times to their weekday highs peaking during the 7:00-8:00 and 6:00-7:00 time periods respectively while mass 93 peaks during the 2:00-3:00 time period. Regarding the oxygenated VOCs, mass 45 peaks during the same time period on weekends/holidays as it does on weekdays while mass 73 peaks one hour earlier. Mass 89 peaks from 3:00-4:00 during the weekend/holiday time periods, one hour later than its weekday peak.

The differences between weekday and weekend diurnal patterns were best characterized as subtle yet detectable for most masses. All species were seen to have a slightly lower average mixing ratio during the daylight hours on weekends as compared with the same times on weekdays. Figure 21 depicts how average aromatic mixing ratios for a one hour block of time changed throughout the course of the field campaign. The 08:00-09:00 hour time block is representative of a rush hour time period while the 12:00-13:00 hour time block is representative of midday traffic. Upon examination of

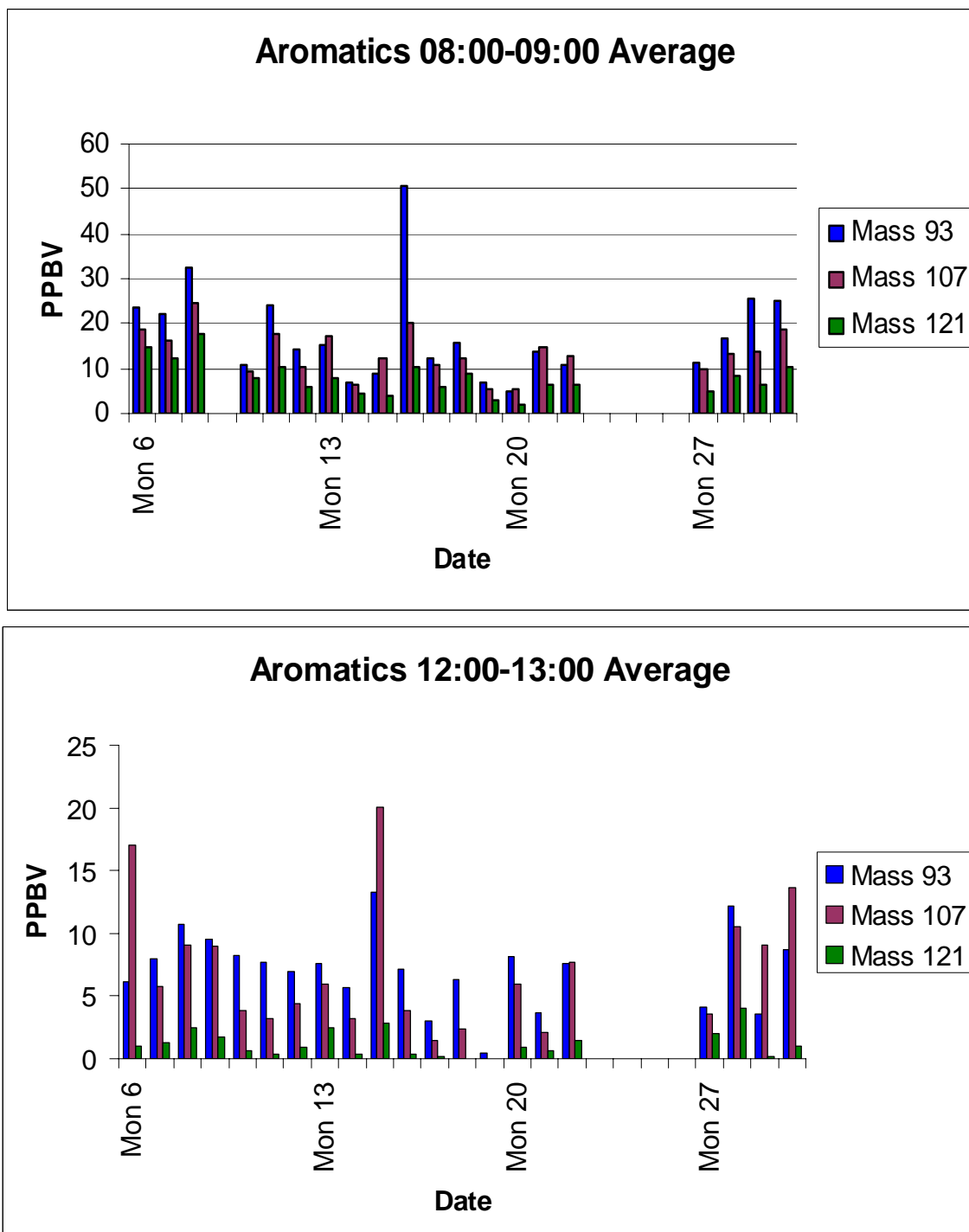


Figure 21. The average aromatic mixing ratios for the 08:00-09:00 and 12:00-13:00 time blocks throughout the course of the field campaign are depicted.

these graphs it is apparent that any difference in weekday versus weekend and holiday mixing ratios is indeed very subtle. One reason for the slightly higher average of the weekday data versus the weekend/holiday data may be that a few high event days occurring on weekdays skewed the weekday average. During the evening hours results were mixed with methanol and C₂ benzenes showing lower weekend mixing ratios while toluene and ethyl acetate show no difference or even slightly higher mixing ratios on the weekends. It should be recognized that the sample size in this comparison is small and other factors particularly meteorology may have played a role in influencing the overall averages. Only two weekends were sampled by our PTR-MS during MILAGRO. Consideration also needs to be given to how representative of the yearly average emissions and meteorology during the month of March are, if attempting to extrapolate these diurnal magnitudes and patterns beyond the month of March. Despite these limitations, certain preliminary conclusions may be arrived at when analyzing these diurnal patterns.

All of the masses had elevated morning mixing ratios which decreased as the boundary layer rose during the course of the day indicating that all species were produced in the Mexico City urban area. The C₂ and C₃ benzenes showed diurnal profiles consistent with a traffic based emission source. The diurnal profile of toluene indicated both characteristics of a traffic based emission source as well as a periodically intense nighttime source which was unrelated to the volume of traffic. This source may have been industrial in nature and further studies should be done investigating VOC emissions by factories in the area to determine the location of this source and the

magnitude of its impact. Ethyl acetate displayed a diurnal profile showing that its emissions were clearly related to industrial activity during the evening hours. Suspected toluene and ethyl acetate plumes are both discussed in detail in the upcoming section regarding “VOC Plumes of Interest”.

4.3.3 VOC Plumes of Interest

As stated earlier the PTR-MS sequentially scanned 38 masses throughout the majority of the MILAGRO field campaign. During the evening hours most masses had increased mixing ratios and this could generally be attributed to the decrease in the mixed layer height overnight. Methanol showed the largest mixing ratio during the evening on average, typically rising above 50 ppbv which was not surprising considering that the methanol average in the daytime was approximately 10 ppbv and the boundary layer appears to have increased in height by a factor of ten during the day. There were two species in particular that displayed increases in their mixing ratio by a factor of ten or more during time periods ranging from 10-140 minutes during the nighttime and early morning hours. These species were toluene and ethyl acetate.

4.3.3a Mass 93: Toluene

Mixing ratios of toluene higher than 50 ppbv were encountered for 14 of the 20 evenings that the PTR-MS sampled sequentially in single ion mode. Table 2 details the

magnitudes, baselines, wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the toluene peaks with the ten highest magnitudes. This is not a complete list of all toluene peaks encountered during the campaign but is a large enough sample to draw some preliminary conclusions.

Upon examining the times and dates of these plumes it is evident that they primarily occurred during periods of light traffic activity in the region. Only one peak occurred during the typical morning high traffic times between 6:00-9:00. The remaining 9 peaks all happened between the hours of 23:00-6:00 and only one of these peaks happened during the transitional period from light to heavy traffic that occurred between 5:00-6:00. Forty percent of these peaks happened during weekends and holidays.

Figure 22 displays a series of graphs for each peak indicating wind directions and wind speeds obtained at the rooftop site along with a graph of the peak itself. Wind data were not available for three of the time periods covered by peaks. Of the seven episodes that occurred during periods with available wind data three appeared to have wind fields that were relatively consistent in their direction and magnitude. The episodes of the 9, 12 and 21 of March featured winds from 221° , 191° and 246° respectively and all had wind speeds very close to 1 m/s. Three other cases featured quite variable wind direction over the course of the evening making it difficult to attribute a direction of approach of the plume (March 8, 11 and 26). Finally the March 17 case involved a very low wind speed of 0.5 m/s and there is some doubt as to whether this plume was actually being transported or whether it had become stationary over the measurement site. In

conclusion the plumes did not appear to have a common origin based on the varying surface winds accompanying these plumes.

Table 2. The magnitudes, backgrounds (mixing ratio outside of plume), wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the toluene plumes with the ten highest magnitudes. * Denotes holidays.

Magnitude ppb	Baseline ppb	Date	Time (local)	Duration (minutes)	Day	Wind Dir. °	Wind Speed (m/s)
229	12.5	17	2:53-3:35 AM	42	Friday	109	0.6
215	13.8	11	12:49-1:17AM	28	Saturday	239	0.5
202	23	21	4:29-4:56 AM	27	Tuesday*	246	0.86
191	20	12	1:53-3:18 AM	85	Sunday	183	0.96
185	8	26	11:22-11:57 PM	35	Sunday	215	0.6
177	7	9	11:13-11:34 PM	21	Thursday	221	1.08
142	19.5	8	1:14-1:31 AM	17	Wednesday	148	1.27
124	30	7	7:06-7:38 AM	32	Tuesday	N/A	N/A
124	26	31	4:26-4:39 AM	13	Friday	N/A	N/A
123	11	6	3:36-5:20 AM	104	Monday	N/A	N/A

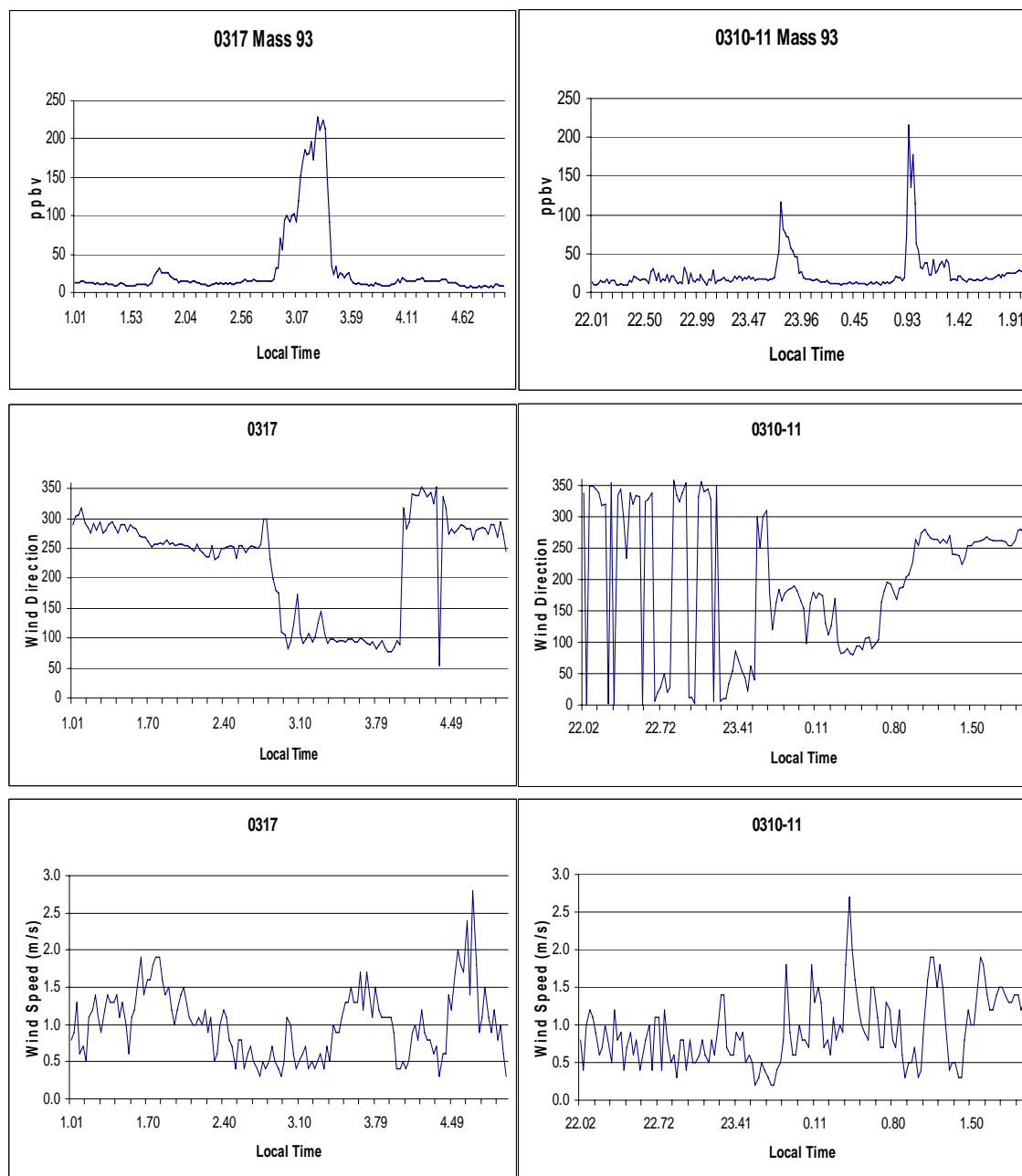


Figure 22. Mixing ratio, wind direction and wind speed plotted versus local time for the seven highest toluene plumes observed.

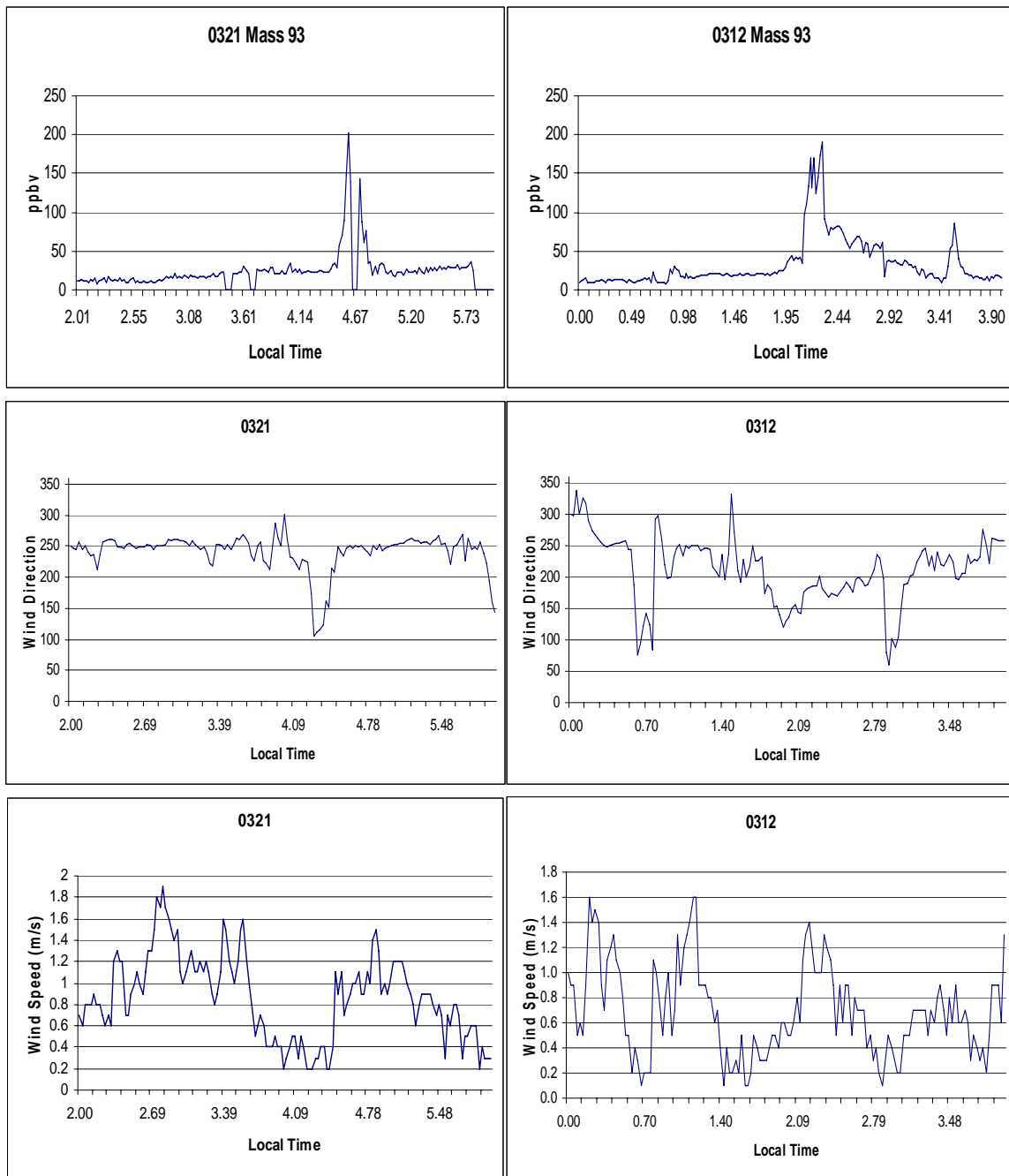


Figure 22. Continued

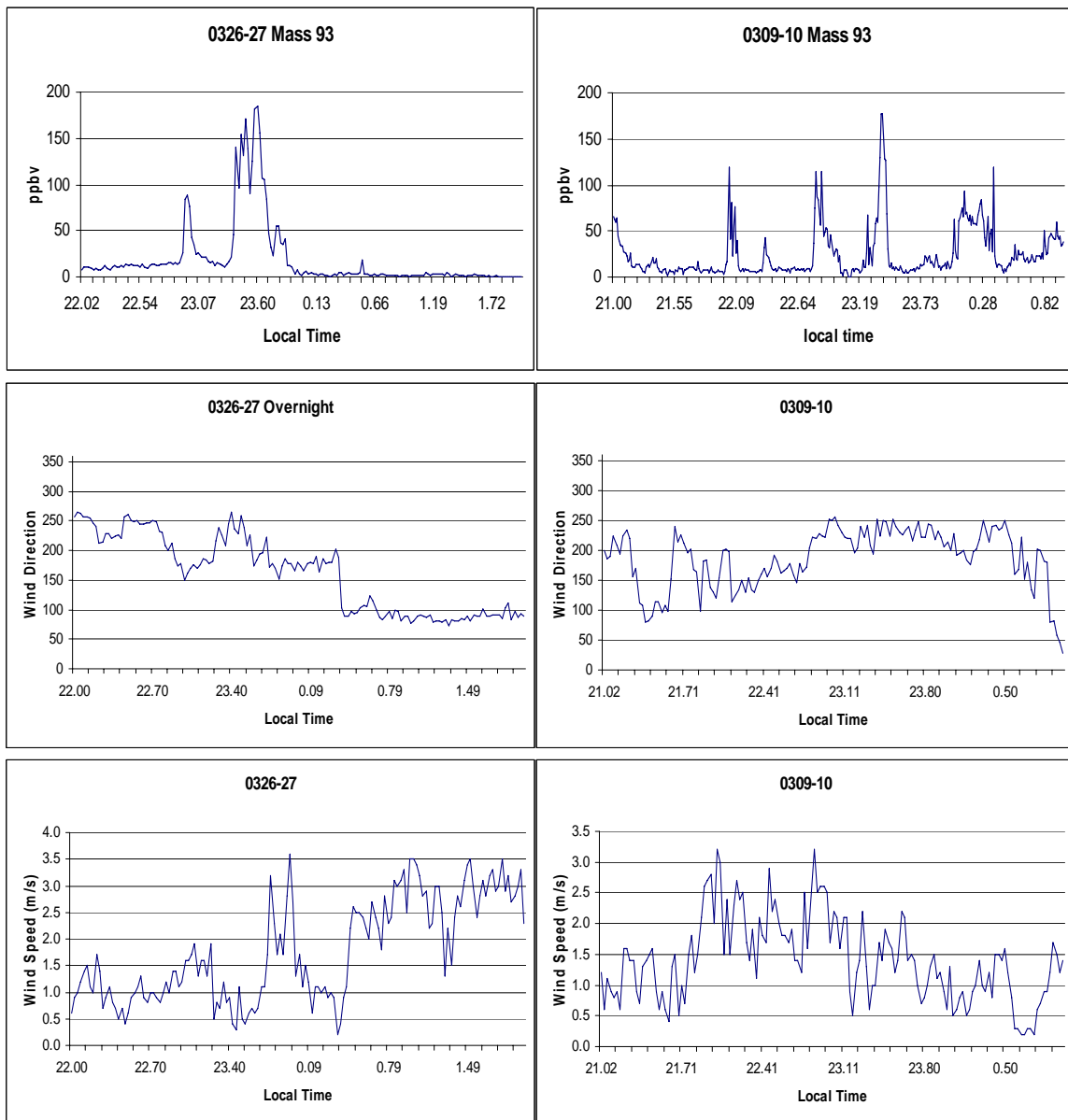


Figure 22. Continued

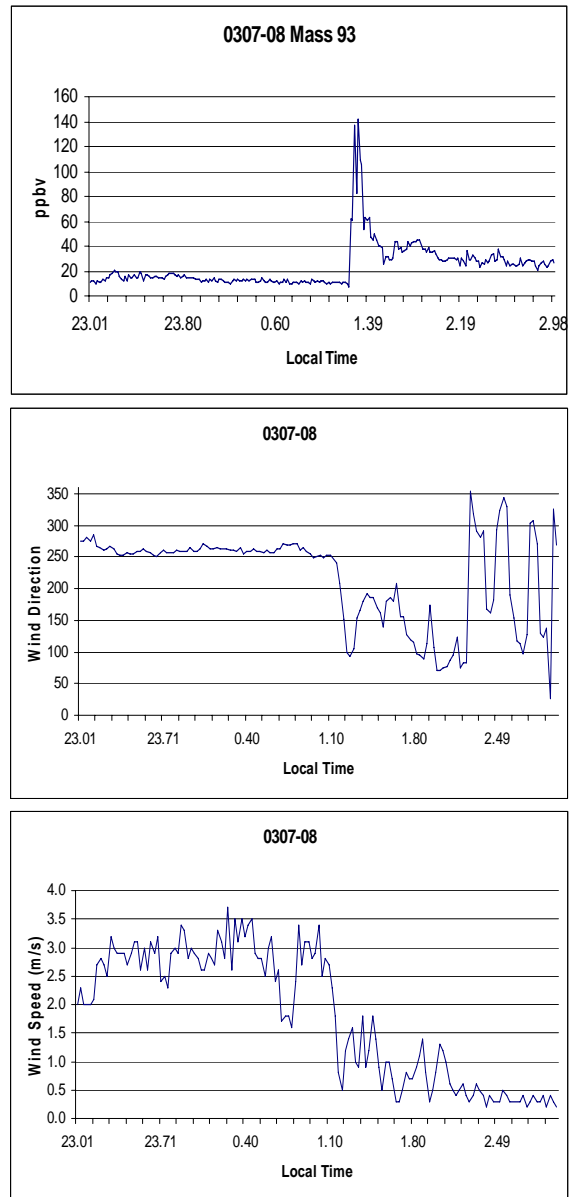


Figure 22. Continued

It is worth noting that while PTR-MS measures the signal at a given mass and there are many masses where different species contribute and complicate the task of assigning a specific measurement to an individual species mass 93 has been found in numerous previous laboratory and field studies to be attributable to toluene only [Warneke *et al.*, 2003, De Gouw *et al.*, 2003a, 2003b]. The limited number of species (chloroacetone, alpha pinene and beta pinene) that have been found to fragment to mass 93 by Warneke *et al.*, (2003) showed no indication of being present at the time of these plumes as their parent ions were monitored by the PTR-MS and found to be below 0.5 ppbv in all cases. No other masses were found to rise in correlation with these mass 93 plumes indicating that toluene appeared to be the only VOC in these plumes. is worth noting that while PTR-MS measures the signal at a given mass and there are many masses where different species contribute and complicate the task of assigning a specific measurement to an individual species mass 93 has been found in numerous previous laboratory and field studies to be attributable to toluene only [Warneke *et al.*, 2003, De Gouw *et al.*, 2003a, 2003b]. The limited number of species (chloroacetone, alpha pinene and beta pinene) that have been found to fragment to mass 93 by Warneke *et al.*, (2003) showed no indication of being present at the time of these plumes as their parent ions were monitored by the PTR-MS and found to be below 0.5 ppbv in all cases. No other masses were found to rise in correlation with these mass 93 plumes indicating that toluene appeared to be the only VOC in these plumes.

A second PTR-MS instrument was located at the IMP for a limited amount of time during the campaign when the Aerodyne mobile research laboratory parked there

and they have provided data for intercomparison purposes (courtesy B. Knighton, Montana State University). Unfortunately, there was only one major toluene plume that was measured during the time the van was located at the IMP (March 6 10:00- March 7 10:00, March 27 21:00 – March 30 9:00). The plume which occurred on the morning of March 7 was measured by both instruments and is shown in Figure 23. The Aerodyne van PTR-MS measured fewer masses enabling a faster measuring cycle of 10 seconds explaining the greater frequency of measuring points within the plume measured by Aerodyne. The brief peak at 244 ppbv had a duration of only one cycle and obviously was not picked up by our PTR-MS which had a measuring cycle of 76 seconds. With the exception of this one point the two instruments measurements were closely correlated. The Aerodyne mobile van was located on a surface street approximately one block to the West of the building where our PTR-MS conducted measurements. The difference in location of the two instruments indicated that the plume was not due to any sort of local source contamination at either one of the two measuring sites.

For the determination of whether the source of these toluene peaks were industrial in nature or instead related to vehicular emissions another analytical technique of use was the comparison of ratios of aromatic compounds associated with vehicular use. If vehicular use was the primary source of toluene the ratios between toluene and other aromatics associated with traffic should have been constant. Figures 24 and 25 depict the ratios of toluene with benzene, C₂ benzenes and C₃ benzenes during the early morning toluene peak of March 17 as well as the peak which occurred around 07:00 on March 7. Below each of these graphs are graphs showing the mixing ratios of the

respective masses at the same time. Examination of the March 17 graphs shows quite clearly that the toluene plume is not accompanied by increases in any other aromatics. For the plume on March 7 there is a corresponding rise in at least one of the C₂ benzenes present at mass 107 however there is no rise in either mass 79 or mass 121.

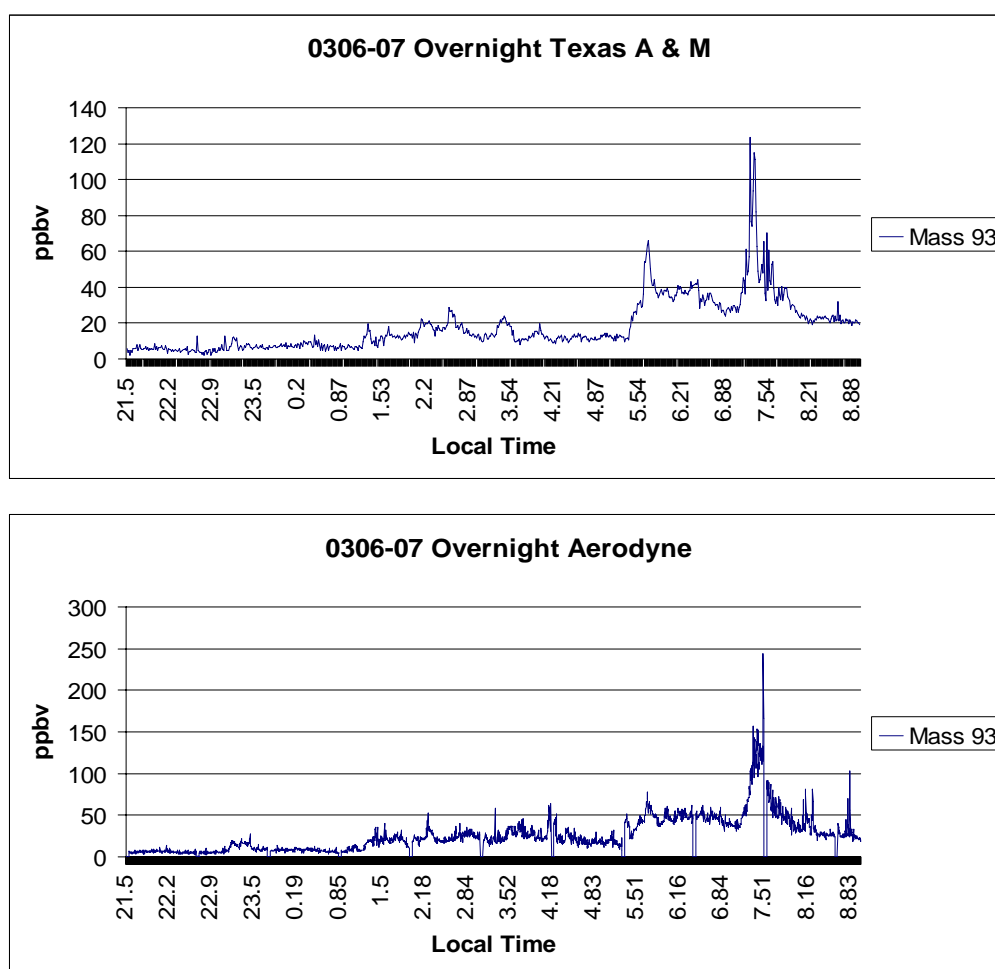


Figure 23. Intercomparison of mass 93 mixing ratio data obtained by Texas A&M and by Aerodyne on March 7.

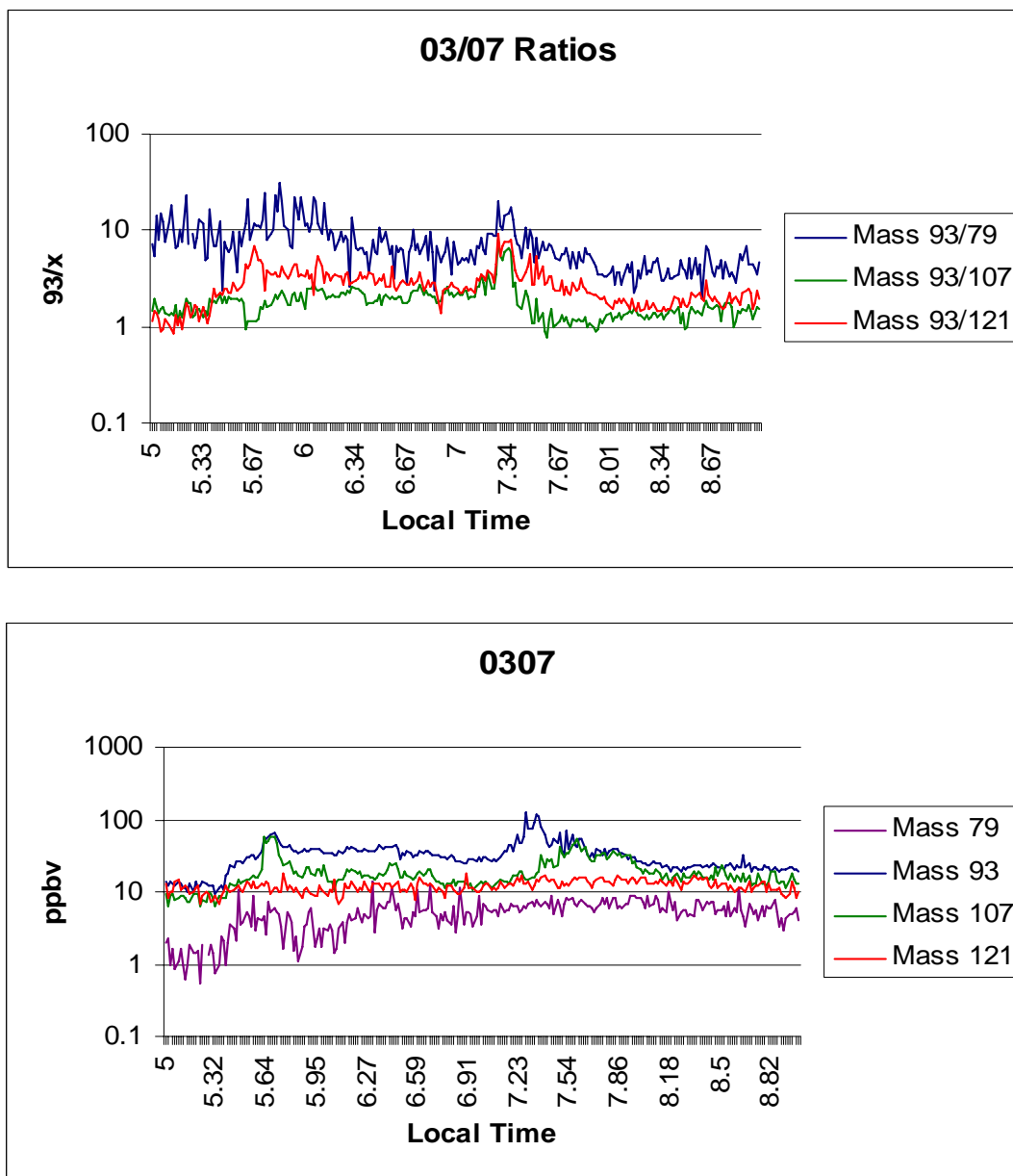


Figure 24. The top graph depicts the ratios of toluene with benzene, C₂ benzenes and C₃ benzenes during the toluene peak which occurred the morning of March 7. The bottom graph depicts the mixing ratio of these species on the morning of March 7.

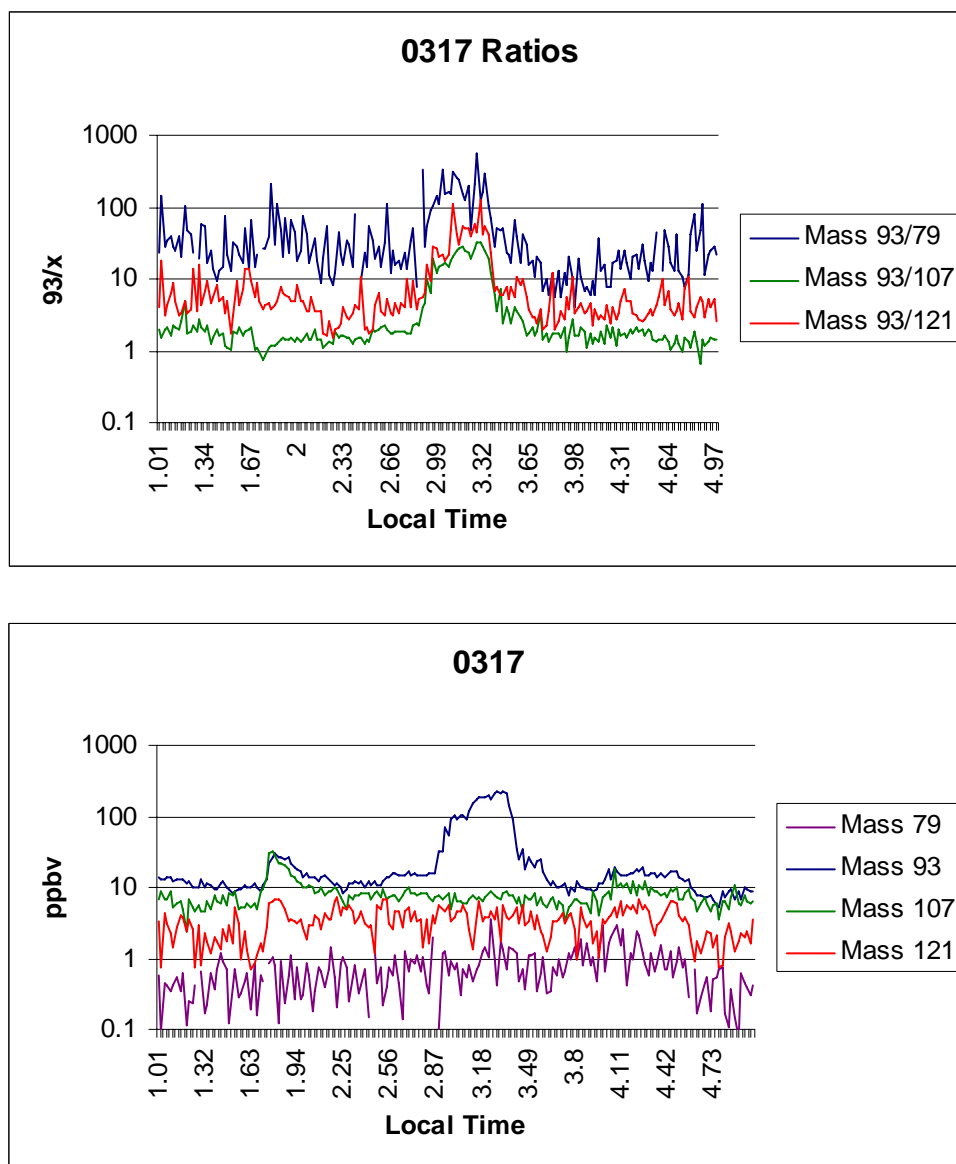


Figure 25. The top graph depicts the ratios of toluene with benzene, C_2 benzenes and C_3 benzenes during the toluene peak that occurred on March 17. The bottom graph depicts the mixing ratio of these species during the same time period.

For the determination of whether the source of these toluene peaks were industrial in nature or instead related to vehicular emissions another analytical technique of use was the comparison of ratios of aromatic compounds associated with vehicular use. If vehicular use was the primary source of toluene the ratios between toluene and other aromatics associated with traffic should have been constant. Figures 24 and 25 depict the ratios of toluene with benzene, C₂ benzenes and C₃ benzenes during the early morning toluene peak of March 17 as well as the peak which occurred around 07:00 on March 7. Below each of these graphs are graphs showing the mixing ratios of the respective masses at the same time. Examination of the March 17 graphs shows quite clearly that the toluene plume is not accompanied by increases in any other aromatics. For the plume on March 7 there is a corresponding rise in at least one of the C₂ benzenes present at mass 107 however there is no rise in either mass 79 or mass 121.

When considering the relevance of these plumes to the overall air pollution problem in Mexico City it should be recognized that while toluene is not the most reactive VOC with regards to OH at a high enough mixing ratio it will contribute substantially to ozone production. The March 7 plume was elevated 94 ppbv above the background level of toluene. Toluene has a calculated OH reaction rate coefficient of 5.96×10^{-12} (Atkinson, 1994, 1997) which is lower than the highly reactive alkenes usually associated most closely with rapid O₃ formation, propylene (26.3×10^{-12}) (Atkinson, 1994, 1997) and ethylene (8.52×10^{-12}) (Atkinson, 1994, 1997) but not too such a large extent as to allow the discounting of toluene as an ozone precursor. Most of these plumes were measured at night with the exception of the March 7 case which

was measured during early daylight hours before the boundary layer had risen significantly. The question of what happened to these high mixing ratio plumes of toluene that were observed in the middle of the evening is key to the actual relevance of these plumes. If they remained intact until daybreak and the subsequent rise in the boundary layer as appears to have occurred on March 7 then they were relevant ozone precursors.

4.3.3b Mass 89: Ethyl Acetate

A set of three masses demonstrated highly correlated peaks during the evening and early morning hours where they all rose by at least a factor of 10 relative to their baseline values for time periods ranging from 10 minutes to as long as 2 hours periodically throughout the campaign. After some discussion and post-field experimentation it was determined that this signal which was seen at masses 43, 61 and 89 was attributable to ethyl acetate. Ethyl acetate's mass is 88 amu leading to the proton transfer signal at 89 and it was found to fragment to masses 61 and 43 in tests conducted with the PTR-MS in our laboratory following the MILAGRO field campaign. Using the same tunings and pressures as were used in MILAGRO a sample of ethyl acetate (Sigma Aldrich) was found to fragment to mass 61 at 30% and mass 43 at 18% while the remaining 52% did not fragment and was measured at mass 89. Previous studies which of course did not test all VOCs but rather a limited number [Warneke *et al.*, 2003] nonetheless did not show any compounds fragmenting to mass 89. It is also noteworthy

that none of the other 35 masses being measured showed any correlation with mass 89 which would have indicated possible fragmentation from higher masses.

Mixing ratios of ethyl acetate higher than 50 ppbv were encountered for 9 of the 17 evenings that the PTR-MS sampled mass 89. This mass was not sampled during the first few days of the campaign. Table 3 details the magnitudes, baselines, wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the mass 89 peaks with the ten highest magnitudes. An analysis of the times of occurrence of these plumes and the winds associated with them allows for some conclusions regarding the source of the ethyl acetate plumes.

The top ten ethyl acetate peaks all happened during the early morning hours between 01:00-07:00 and all occurred on weekday mornings although one of these mornings was a holiday. Despite the fact that the highest peaks did primarily occur on weekdays the diurnal averages discussed earlier show that ethyl acetate concentrations were still quite high on weekend/holiday early morning periods. Four of these peaks occurred at least partially during the transitional time period between 05:00-06:00 where traffic generally switches from light to heavy and one of these four extends into the heavy traffic time period after 06:00. That leaves 60% of the plumes occurring during periods of light traffic earlier than 05:00.

Table 3. The magnitudes, backgrounds (mixing ratio outside of plume), wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the ethyl acetate plumes with the ten highest magnitudes.

Magnitude ppb	Baseline ppb	Date	Time (local)	Duration (minutes)	Day	Wind Dir. °	Wind Speed (m/s)
198	15	29	5:51-6:14 AM	23	Wednesday	224	1
148	13	17	2:03-2:58 AM	55	Friday	236	0.74
140	11.5	16	3:32-5:44 AM	132	Thursday	232	0.65
140	18.9	29	3:41-4:19 AM	38	Wednesday	215	0.7
124	13.2	31	1:27-2:05 AM	38	Friday	N/A	N/A
123	25.5	31	4:21-4:47 AM	26	Friday	N/A	N/A
119	9.43	23	5:25-5:36 AM	11	Thursday	194	0.45
116	12.3	23	3:25-3:57 AM	32	Thursday	246	1.19
115	20.8	29	2:15-2:45 AM	30	Wednesday	241	1.06
99	25.5	21	5:04 -5:20 AM	16	Tuesday*	258	0.94

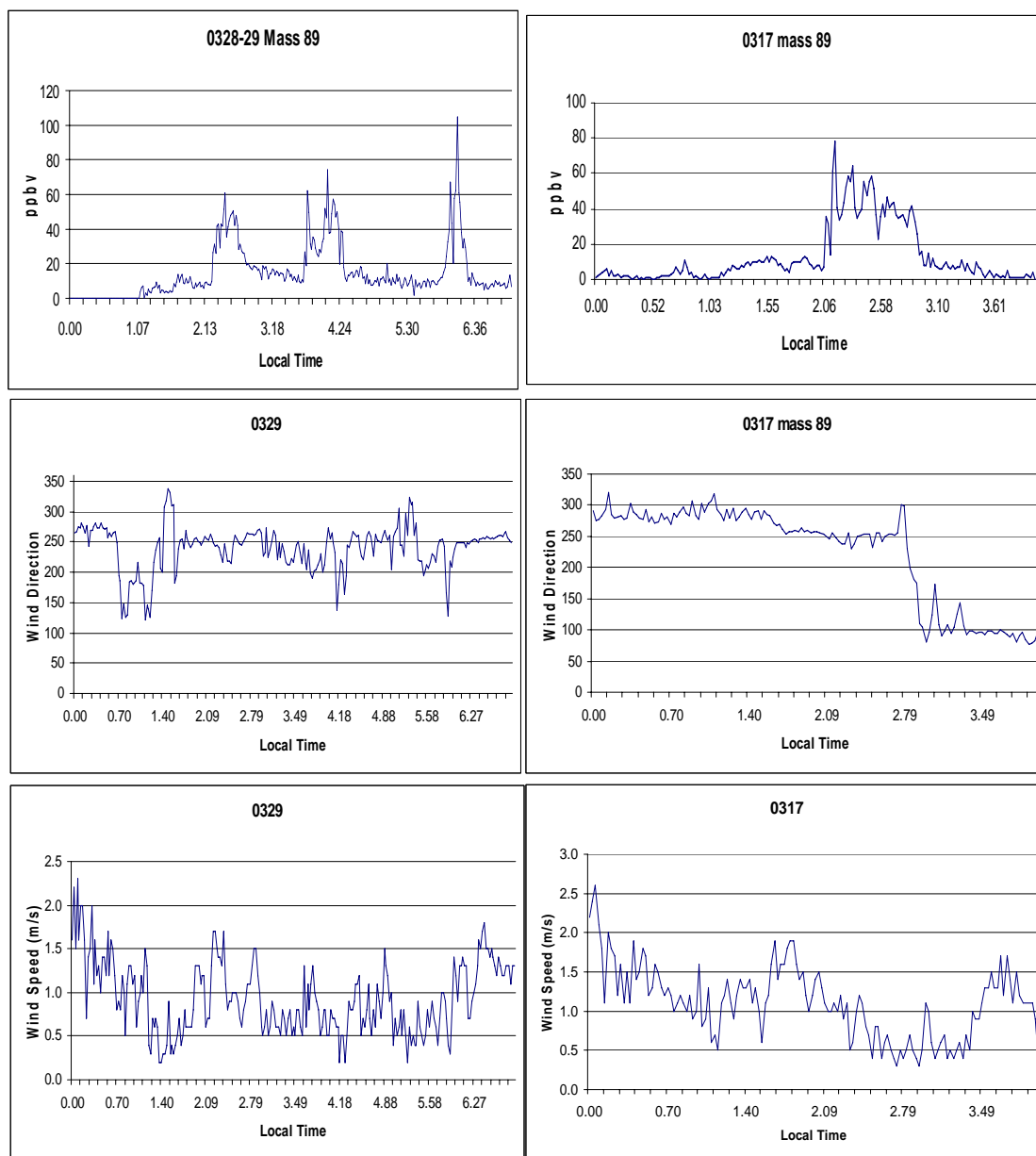


Figure 26. Mixing ratio, wind direction and wind speed plotted versus local time for the five evenings containing the highest ethyl acetate plumes observed.

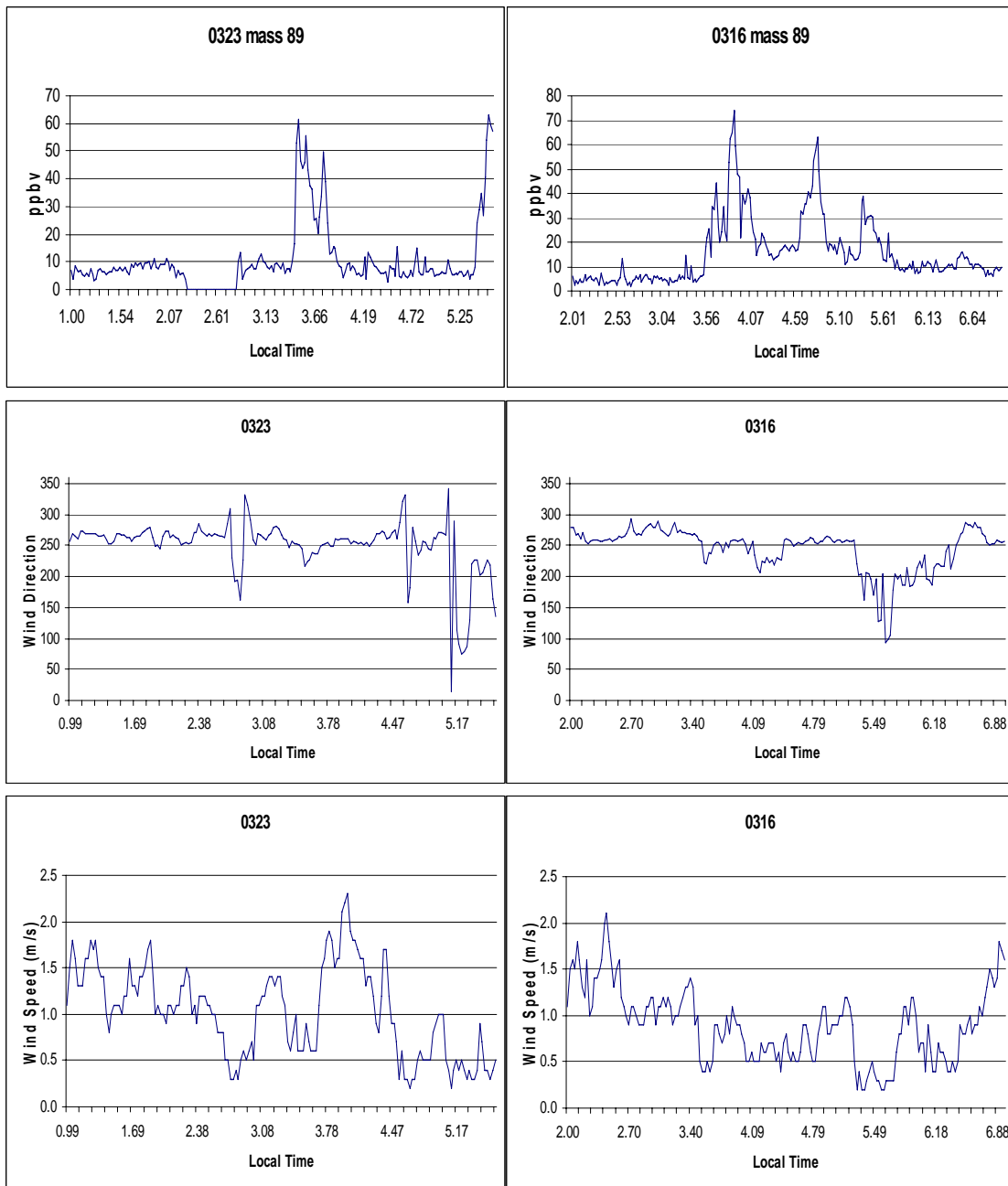


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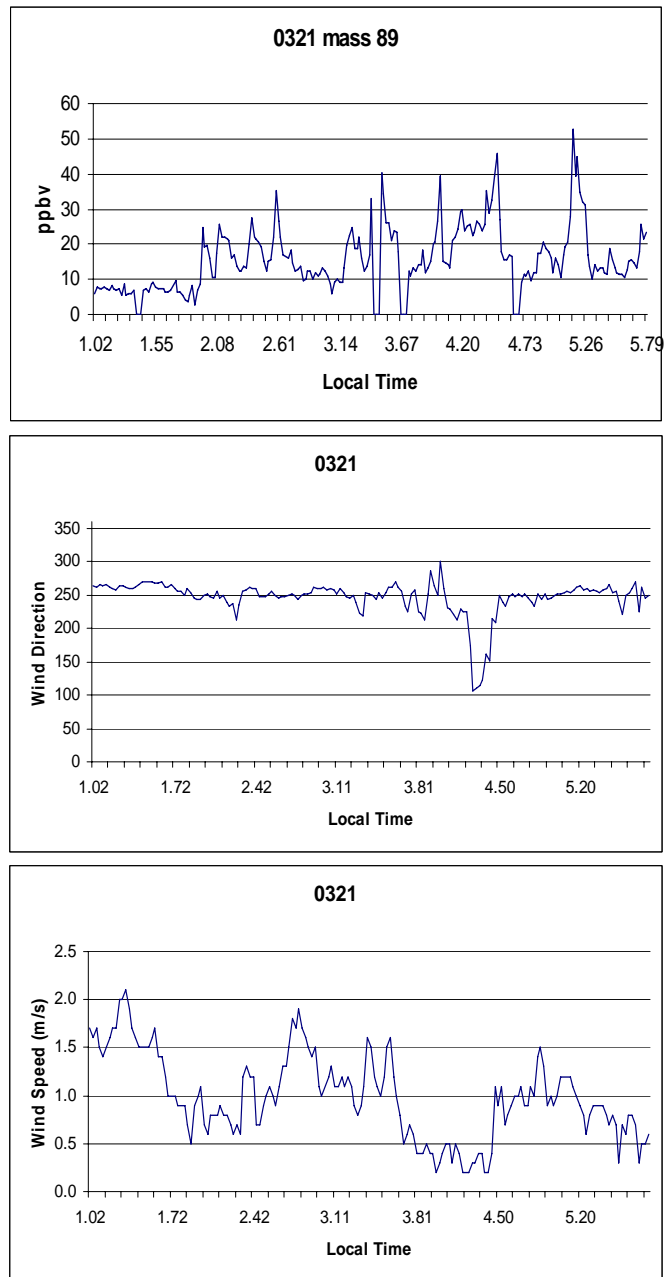


Figure 26. Continued

A series of graphs depicting the temporal changes in mass 89 signal, wind direction and wind speed is displayed in Figure 26 for the evenings during which these peaks took place. On these graphs the magnitude of mass 89 is not adjusted for the fragmentation pattern we verified in our laboratory explaining the difference between the magnitudes in the graph with the magnitudes reported on the table. On all five evenings there was a wind from approximately a 250° heading for a large portion of the evening including the bulk of the time periods when most peaks occur. Examination of Figure 26 also reveals that on many occasions when winds were very light (< 0.5 m/s) there is a tendency of the wind gauge to turn to approximately a 100° heading which is a somewhat debatable measurement due to the low wind speed but nonetheless slightly skews the average wind direction which is displayed in Table 3. Therefore it was concluded that these plumes did originate from a specific area which seems to have been located at around a 230-260° heading from the IMP facility. Of course it is quite possible that these plumes were turning as they evolved during the evening and the source may not actually have been within the degree range noted. Further studies which focused on the industrial areas to the southwest and west of the facility might be able to isolate the source of these plumes.

The Aerodyne mobile van was located at the IMP during the time period of the ethyl acetate peaks which were encountered on March 29. Figure 27 shows the mass 89 measurement results of both instruments during the early morning hours of March 29. The Aerodyne van did not continuously monitor mass 89 preferring instead to measure mass 89 once every few minutes as part of a spectral scan explaining the gaps in the data

on the Aerodyne graph. The two instruments both detect the three separate peaks on that evening and the magnitudes of the three peaks are reasonably similar. The data gaps in the Aerodyne data leave out some plume detail which should be considered when comparing the relative magnitudes of the peaks with each system.

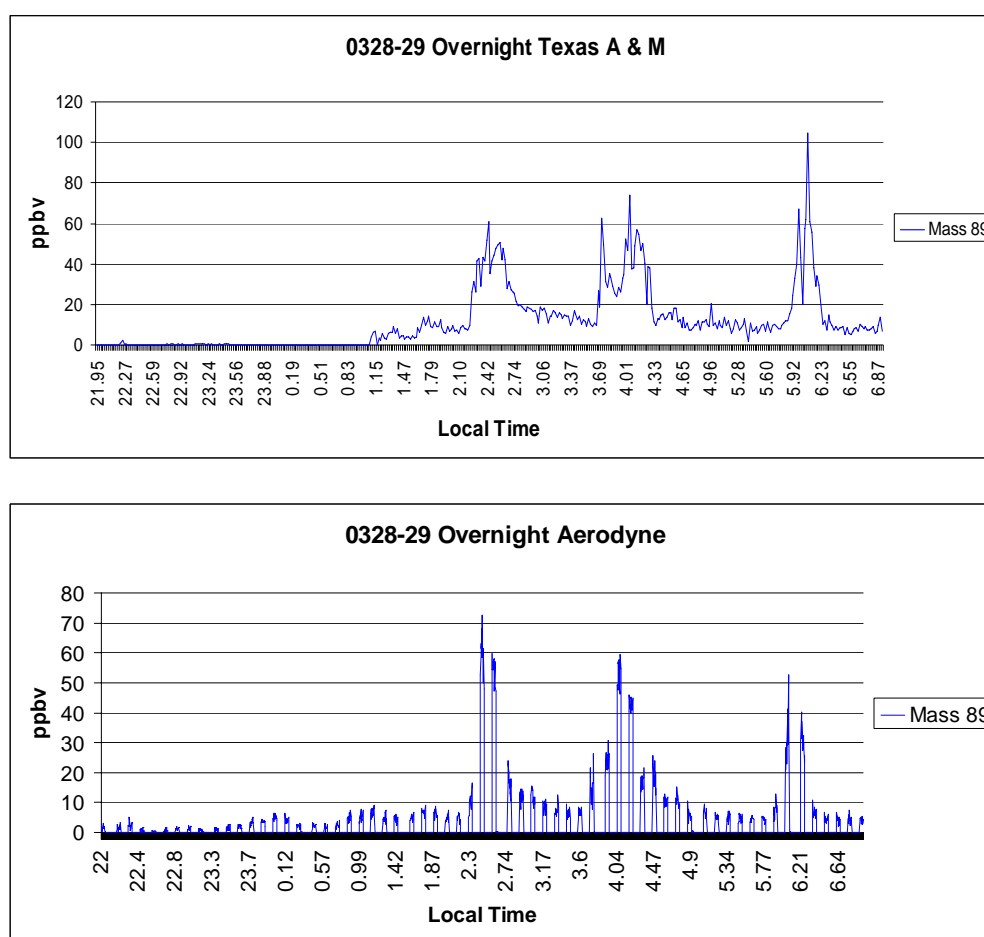


Figure 27. Intercomparison of mass 89 mixing ratio data obtained by Texas A&M and by Aerodyne on March 29.

Finally when considering the relevance of these ethyl acetate peaks to the urban air pollution problem in Mexico City consideration should be given to the fact that ethyl acetate has an OH reaction rate coefficient of (1.73×10^{-12}) (Picquet, 1998) which is approximately a factor of four lower than the well known ozone precursor ethylene (8.52×10^{-12}) (Atkinson, 1994, 1997). The peak that occurs at 6:00 on March 29 was observed within an hour of sunrise and was 183 ppbv above the background level. If this plume maintained its magnitude and integrity during the next hour as it proceeded downwind of the IMP it would have been a significant source of ozone precursor VOCs.

4.3.4 Intercomparison of O₃ and NO_x Data with PTR-MS VOC Data

Preliminary Ozone and NO_x measurement results from two evenings have been provided courtesy of Dr. Phil Stevens of Indiana University. The evening of March 29-30 produced VOC measurements which were typical of a relatively polluted weekday morning. Not surprisingly, NO_x is positively correlated with VOCs while O₃ is negatively correlated as is seen in Figure 28. While boundary layer heights are not available for evening hours it appears that an inversion may have become established and the mixing of surface level air with air aloft may have ceased at approximately 22:00 on this evening. Ozone rapidly declines at this time while NO_x and VOCs begin to slowly rise. Plumes of ethyl acetate and toluene during the early morning are also evident on this evening. Wind data was not available for this evening.

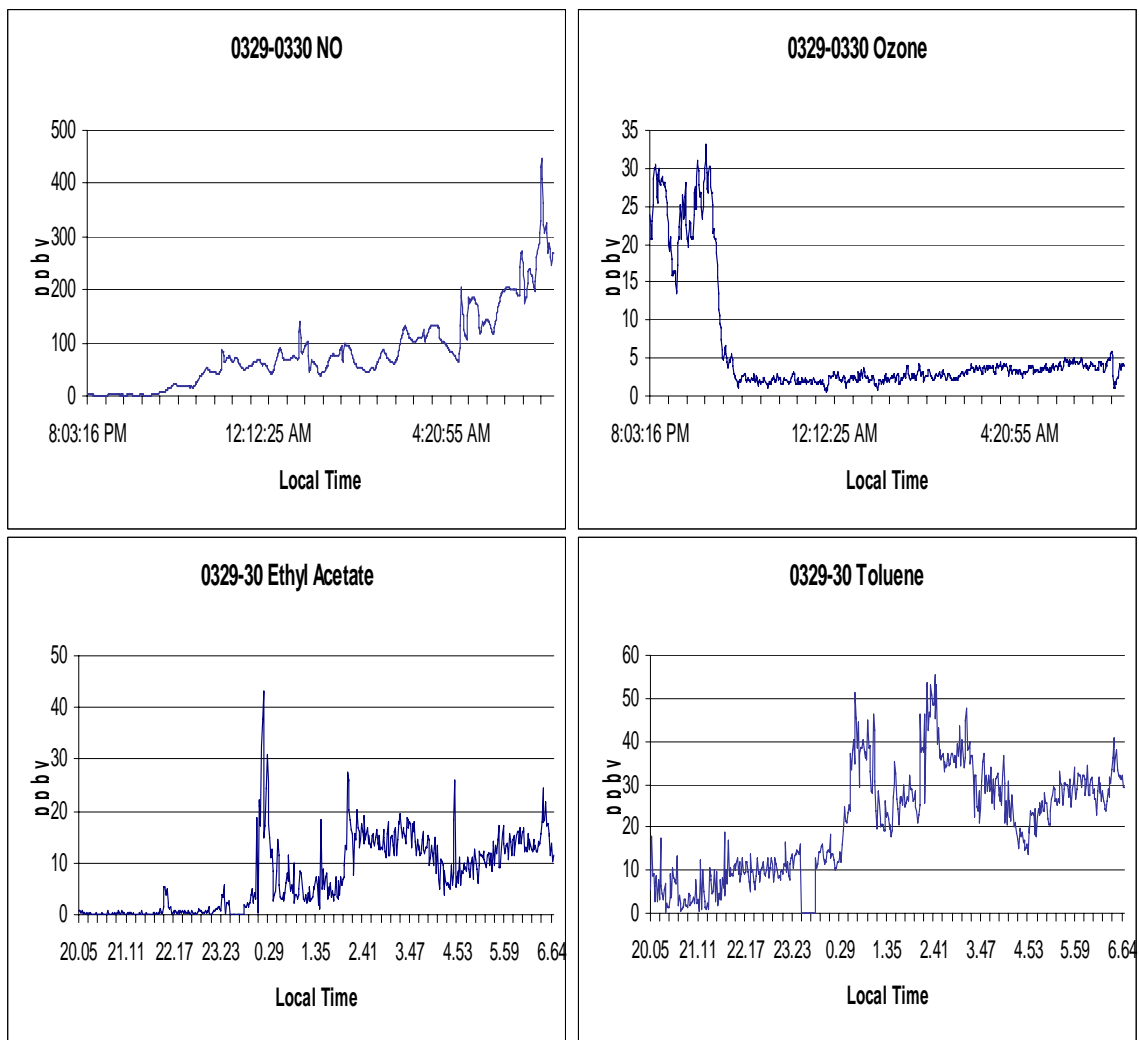


Figure 28. Ozone, NO, toluene and ethyl acetate measurements on the evening of March 29-30.

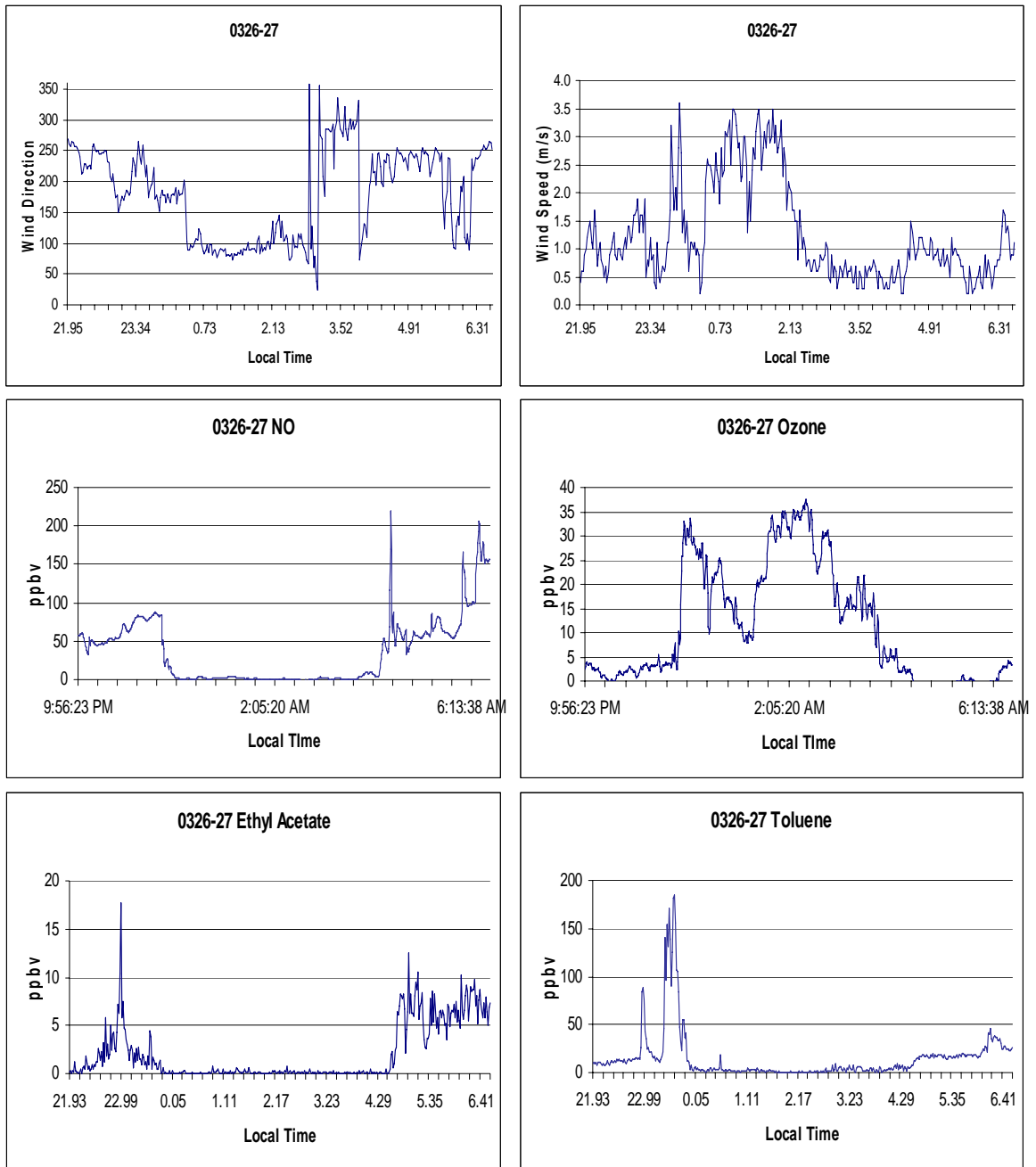


Figure 29. Ozone, NO, toluene and ethyl acetate measurements as well as wind data from the evening of March 26-27.

Ozone, NO, toluene and ethyl acetate measurements along with wind data from the evening of March 26-27 are shown in Figure 29. Again on this evening NO is positively correlated with VOCs while ozone is negatively correlated. The pattern of VOC mixing ratios is unusual on this evening in that mixing ratios become elevated around 22:00 then drop off rapidly and remain low between 00:00-03:30 before gradually becoming elevated once more. NO_x follows the same pattern as VOCs on this evening while ozone becomes higher during the middle portion of the evening when ethyl acetate, toluene and NO mixing ratios are suppressed. This measurement period occurred from Sunday night through Monday morning and traffic is not suspected to be the cause of the VOC plumes in the late evening hours. Observing the wind data it is apparent that winds became stronger and were generally from the East during the time period of low VOCs and NO_x as well as higher ozone.

4.4 Conclusion

A large number of ambient VOC concentrations were measured utilizing our PTR-MS instrument conducting rooftop based measurements in the urban mixed residential and industrial area north-northeast of downtown Mexico City as part of the MILAGRO 2006 campaign. The purpose behind our measurements of VOC concentrations was to gain a better understanding of the type of VOC species present in the particular area of the MCMA where we were located, their diurnal patterns and their origin.

The highest average VOC concentrations that PTR-MS was able to measure were from methanol (PTR-MS does not measure alkanes). Methanol peaks averaged approximately 50 ppbv during the morning rush hour time period. Aromatics were the second most abundant class of species measured by PTR-MS with toluene, C₂ benzenes and C₃ benzenes averaging 26, 18 and 11 ppbv respectively during the morning rush hour. The oxygenated VOC acetaldehyde was also found to peak at approximately 12 ppbv on average during the late morning hours. Biogenic VOCs were found to be quite minimal.

The diurnal patterns indicate that the highest mixing ratios of most VOCs were found between 06:00-09:00 and VOC concentrations decreased as the boundary layer rose during the mid-morning timeframe. No afternoon VOC peak was observed. Aromatic VOC mixing ratios maintained a slightly higher level on weekdays compared to weekend/holidays throughout the day indicating a possible traffic influence. The diurnal patterns of toluene and ethyl acetate indicated that industrial nighttime emissions of these species were significant in the area around the IMP facility.

Plumes of highly elevated VOC concentrations of toluene and ethyl acetate were observed during the late night and early morning hours. These plumes were elevated as much as 216 and 183 ppbv above their respective backgrounds and had time durations varying from 10 minutes to 2 hours. These plumes were also measured by a separate PTR-MS instrument in the Aerodyne mobile research van when it was parked at the IMP facility approximately 1 block west of our location at the surface street level. An analysis of surface winds coinciding with the time of the toluene plumes found no preferred wind

direction matching these peaks and therefore the toluene plumes were not attributed to a single source or even a single area. A comparison with other aromatics at the time of the toluene peaks indicated primarily no correlation although one of the C₂ benzenes did show a rough correlation at times. An analysis of the surface winds present during the time of the ethyl acetate plumes indicated that the winds were limited to a range of 230-260° leading to the preliminary conclusion that the ethyl acetate source was from a particular area to the southwest or west of the IMP facility. The toluene and ethyl acetate plumes were toxic and were relevant ozone precursors if they maintained their magnitude and integrity into the daylight hours. We display one toluene plume which was measured during the early daylight hours and one ethyl acetate plume which was measured only one hour prior to daylight.

The VOC concentration measurements we conducted may or may not be representative of the MCMA as a whole. We plan to integrate our measurements with other VOC measurements conducted during the MILAGRO 2006 campaign to develop a better understanding of both the overall spatial pattern of VOCs in the MCMA as well as its variability.

5. CONCLUSION

The TEXAQS 2005 and MILAGRO 2006 field campaigns were both valuable learning experiences regarding the identification of what VOCs were present in both locations as well as how to best measure them utilizing PTR-MS. In Texas it appeared that light alkenes emitted in the Houston Ship Channel area and their oxygenated products may have traveled during the nighttime hours to regions as far as 200 miles downstream. Isoprene levels over East Texas river valleys were found to be elevated even during the nighttime hours. A sizable mass 57 peak attributable to butenes, butanal or MTBE was encountered in the central region of the Houston Ship Channel on all overflights. The region downwind of Dallas occasionally showed elevated levels of light alkenes and their oxygenated products in the late afternoon.

Future projects which focused in a more concentrated manner on solving one of these problems would be beneficial. Some of these studies would be relatively straightforward such as the isoprene study in river valleys. An attempt to speciate the mass 57 plumes observed in the Houston Ship Channel and subsequently identify the source would involve extensive work with laboratory standards in advance and perhaps a partnership with a gas chromatography (GC) system which has superior speciation abilities, but would be highly beneficial. While a GC system offers superior speciation the PTR-MS system does a better job of displaying the dimensions of the plumes due to its online capability. The compact PTR-MS is also quite portable enabling it to be used on small moving platforms. For future studies involving mass 43 and the possibility of

the HRVOC propene being present at elevated levels extensive work with laboratory standards would need to be executed in advance of the field problem. If studies were done where mass 43 or mass 57 plumes were being studied it should be realized that the PTR-MS might need to be tuned in such a manner that other masses would not be able to be sampled. This mass selective tuning would have to be applied in order to measure 1-3 butadiene which is detected at mass 55. 1-3 butadiene is toxic and there has been concern about its levels in the Houston area. The E/n ratio would have to be increased to a high level in order to eliminate the water cluster which is found at mass 55 and tests with a 1-3 butadiene standard would need to be done in advance of field measurements to determine fragmentation patterns.

In the MILAGRO study the diurnal patterns of VOCs at the IMP location measured by PTR-MS showed evidence of the effect of vehicular traffic, the dramatic rise of the boundary layer and afternoon winds. Due to a combination of a high boundary layer at approximately 4000 meters and higher afternoon winds no peak of aromatics was seen in the late afternoon hours. A morning VOC peak was observed due to high morning traffic as well as a low boundary layer. Evidence of non-traffic related sources of VOCs is apparent in the diurnal profiles as well as specific plumes during the late night and early morning hours. Plumes of toluene and ethyl acetate of over 100 ppbv were encountered on multiple occasions during the late night and early morning hours and lasted from 10-200 minutes. While no specific direction of source could be attributed to the toluene plumes the ethyl acetate plumes were found to originate from the west-southwest. These plumes were relevant ozone precursors if the plumes

maintained their magnitude and integrity until daybreak. One toluene plume was encountered during daylight hours at 07:00 and one ethyl acetate plume was encountered at 06:00 shortly before daybreak suggesting that these plumes do frequently encounter daylight conditions early in the morning before the boundary layer rises.

Future studies that focus on determining the sources of these plumes would be beneficial. The PTR-MS mobility may be taken advantage of in this instance by deploying the PTR-MS on a mobile platform. Some work should be done with ethyl acetate standards prior to measurements and standards of species detected at masses 61 and 43 which ethyl acetate fragments into. The PTR-MS data obtained during MILAGRO 2006 will also be integrated with other VOC data obtained at the IMP and other sites as well as airborne measurements. This integration of VOC data covering the widest possible range of species and locations within the MCMA will present a clearer picture of the spatial and temporal variability of VOC concentrations throughout the MCMA.

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