

Project H48-2005

**Aircraft Measurements of Highly Reactive Volatile Organic
Compounds Using Proton Transfer Reaction Mass Spectrometry (PTR-
MS) During TexAQS II**

Final Report

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EXECUTIVE SUMMARY

This project had two primary objectives. The first was to demonstrate that the Ionicon compact proton transfer reaction mass spectrometer (PTR-MS) could be used to gain valuable information regarding the presence and amount of volatile organic compounds (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.

The PTR-MS instrumentation was used during the Southeast Texas Tetroon Study (SETTS) from 17 July - 31 July and the Northeast Texas Plume Study (NETPS) from 1 August - 31 August. The instrument conducted airborne measurements of VOCs during both of these projects flying 5 missions totaling approximately 40 flight hours during SETTS and 11 missions totaling approximately 60 hours during NETPS.

The primary purpose of SETTS was to track the movement of tetroons (balloons) after they had been launched and conduct trace gas measurements of the air mass the tetroon 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 (acetaldehyde) 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 (Fig 10-14). The chemical evolution of this plume was minimal due to the lack of sunlight.

A total of four transects were conducted that sampled polluted Houston ship channel air due to the fact that the primary goal of SETTS was to track tetroons not sample ship channel air. On the flight conducted on the evening of July 21 a pronounced peak of mass 57 which is primarily associated with butenes, octane and MTBE was encountered while conducting a ship channel transect at around 7:30 PM CDT (Fig 4). This peak had a magnitude of 28 ppbv against a background of approximately 500 pptv and the peak lasted for five measurement cycles of the instrument which is a time duration of approximately 50 seconds. On the three subsequent transects of the ship channel conducted on July 26 a smaller mass 57 peak was located in the same general area of the ship channel (Fig 9).

Another VOC finding of interest during SETTS occurred during the evening of July 23 when an overflight of the forested Trinity River Valley at night produced mass 69 (isoprene) and mass 71 (methyl vinyl ketone and methacrolein) peaks of 800 pptv and 8 ppbv respectively. Isoprene is a biogenic VOC and methyl vinyl ketone and methacrolein are its oxidation products. This flight was done at 11:30 PM CDT at 1500' above the valley suggesting the possibility of higher VOC concentrations at a lower altitude and an earlier time during the evening (Fig 7, 8).

The NETPS campaign focused on the emissions from power plants in northeast Texas and attempted to study the evolution of these plumes as they passed through the Dallas metropolitan area. Unfortunately the vast majority of these plumes did not intercept the Dallas area but stayed in rural areas. Power plants do not emit VOCs in general so during these rural flights the primary VOCs of interest were again mass 69 and mass 71 biogenic VOCs found in river valley areas (Fig 19, 20).

Flights were conducted downwind of Dallas on 6 days and generally the only VOC masses which were found to be elevated on these mid to late afternoon flights were mass 43 and mass 45 (acetaldehyde). These masses were not always elevated but when they were they were found within the elevated urban plume of O₃ and CO or just to the side of it (Fig 17, 18).

In summary the compact PTR-MS was able to locate, quantify and track the movement of VOC plumes associated with industrial, urban and biogenic sources. Tracking chemical evolution of VOCs was limited by the lack of chemical evolution during evening flights and the lack of flights originating in a high VOC area such as the Houston ship channel area during the daytime which could then track evolution of VOC plumes. While these flights succeeded as a demonstration of the PTR-MS ability they did not produce a substantial statistical database for any of the findings mentioned above. A future study which focused more exclusively on one aspect of these findings will probably yield more statistically relevant results. This study could be focused on any one of the following; ship channel emissions of VOCs, tracking the chemical evolution of ship channel emissions of VOCs during the daytime, studying the contribution of VOCs to the downwind of Dallas urban plume (or any urban plume for that matter) during the daytime and finally a study of biogenic VOCs in forested river valley areas and any plumes associated with them.

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Introduction

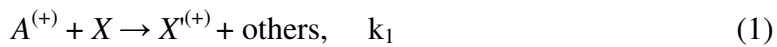
Results from the 2000 Texas Air Quality Study (TexAQS) have unambiguously established that highly reactive volatile organic compounds (HRVOCs) from petrochemical industrial sources are linked to rapid and efficient photochemical ozone production in the Houston Galveston area [e.g., Daum et al., 2003]. In particular, lower molecular weight alkenes such as ethylene, propylene, and butenes are identified to be most abundant inside petrochemical source plumes and dominate the reactivity of VOCs [Daum et al., 2003; Ryerson et al., 2003; Berkowitz et al., 2004]. Those field measurements also indicate that measurement-inferred emissions of the lighter alkenes are substantially higher than reported by current inventories [Karl et al., 2003; Ryerson et al., 2003; Wert et al., 2003]. Hence one of the most critical elements to quantify ozone formation in photochemical models and to implement SIP for cost-effective ozone control strategies lies in better assessments of the emission sources and inventories of HRVOCs from the industrial sources. In recognition of this need HARC Contract # H48.T3.2004 TAMU T2 was awarded to facilitate the purchase and use of the Ionicon Compact Proton Transfer Reaction Mass Spectrometer (PTR-MS) in airborne field studies conducted during the Summer of 2005.

The compact PTR-MS participated in the Southeast Texas Tetroon Study (SETTS) from 17-30 July and the Northeast Texas Plume Study (NETPS) from 1-31 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.

PTR-MS Methodology

Proton transfer-reaction mass spectrometry (PTR-MS) is a unique method for online quantification of VOCs in air developed by Lindinger et. al. and co-workers at the University of Innsbruck. Proton-transfer reactions of hydronium ions (H₃O⁺) are employed to ionize VOCs and the resulting product ion is then detected by mass spectrometry. VOCs directly emitted from natural and anthropogenic sources as well as their oxidation products may be quantified simultaneously by PTR-MS. Desirable features that PTR-MS offers which differentiate it from GC-MS systems and canister samples are a fast time response of seconds or less and the ability to continuously monitor VOCs and receive real time data that clearly shows the magnitude and spatial dimensions of VOC plumes.

The principle that PTR-MS 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

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

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

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

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

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

where P and T are the pressure and temperature within the drift tube and u_0 is the reduced ionic mobility taken from the literature.

For VOC detection, H_3O^+ is generally 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 ($165.5 \text{ kcal mol}^{-1}$). The method of employing PTR-MS to quantify atmospheric VOCs has been thoroughly discussed by Lindinger et al. and de Gouw et al..

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

Installation of the PTR-MS

The PTR-MS instrument was installed in the Twin Otter aircraft (Fig. 1) at the Twin Otter Research Aircraft facility located in Grand Junction CO from July 11-17. The PTR-MS instrument is composed of a square metal casing which contains the spectrometer, turbo pumps, inlet pump, drift tube, ion source, power supplies and an Ethernet control box. A 1/16" ID silcosteel coated inlet tube protrudes outwards from the front of the metal casing 4' and is surrounded by a heated sleeve (40°C). An additional 18" of Teflon

tubing (1/8" ID) lead from the inlet plate (Fig. 2) to the silcosteel coated tubing. A laptop computer connected to the PTR-MS instrument was used for in-flight control of the PTR-



Figure 1; The Twin Otter Research Aircraft



Figure 2; The inlet plate including PTR-MS inlet

MS. The PTR-MS instrument was controlled in flight by an instrument operator so that changes could be made in-flight to the species being measured.

Instrument QA/QC; Calibration and Background Checks

Calibrations of the PTR-MS system were conducted 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 run through the inlet plate of the aircraft while the aircraft was on the ground 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 get a feel for the effects of relative humidity as well as possible interferences not detected using zero air. Two calibrations were also conducted prior to the field program in an attempt to determine any dependence of the PTR-MS signal on the relative humidity of the sampled air and results of these calibrations are shown in fig x.. The PTR-MS system was found to be stable over the course of the field program. A calibration curve was created based on the sum of over 20 calibrations completed over the course 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. Calibration curves are shown in Fig. 3. 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.

The Texas Commission on Environmental Quality (TCEQ) also conducted calibrations, or audits, on two different occasions. The first audit was completed on July 19 at the beginning of the SETTS campaign while the second audit was conducted on August 15 midway through the NETPS campaign. The details of these audits are shown in spreadsheet format in the QA/QC report and only the highlights will be mentioned here. In both audits it was found that the PTR-MS underreported all calibrated VOCs by approximately a factor of 2 when the calibrated species was over approximately 3 ppb. Below 3 ppb certain species were underreported by larger amounts and the amount was more variable. The background for masses 43 and 45 was higher than optimum during the first audit due to not letting the instrument run for a long enough period before testing. During the second audit the background was in accordance with an average background while measuring therefore the second audit should be considered to be more representative of the measuring conditions encountered during the bulk of the flights. The second audit also compared well with the calibrations done daily by the Texas A & M research team and the calibrations curves developed based on those calibrations with the exception of propene which was overreported in the second audit but not overreported in our daily calibrations suggesting that something in the audits calibration gas mixture was fragmenting to mass 43.

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 PFA tee which was connected 2" inside of the inlet plate. Any excess flow vented out of the inlet plate keeping the drift tube pressure constant. During data analysis the background was determined to be the average of the cycles accumulated during the specific background check plus 2*SD of those cycles. A typical background check lasted 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 operations the PTR-MS was run 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 and the water cluster signal at mass 37 was limited to 5-7 % of the primary reagent ion using this E/n ratio. It is desirable to keep the E/n ratio as low as possible in order to limit the fragmentation of product ions. The instrument was run exclusively in single ion mode (SIM) while measuring although brief checks of the overall mass spectrum were made occasionally to look for any mass peaks of interest. While in SIM mode the instrument would cycle through between 5-8 masses at 2 seconds per mass so that any given mass which was part of the measurement cycle was sampled every 10-16 seconds.

Overview of PTR-MS Usage in SETTS

The SETTS campaign occurred from 17-31 July and the base of operations for the Twin Otter aircraft was the Lone Star Executive Airport located near Conroe Texas approximately 30 miles north of downtown Houston Texas. The PTR-MS was used in a total of 5 missions during this campaign. These missions consisted of one practice tetron mission, three actual tetron missions and one flight conducted during the day downwind of the Houston Ship channel and the Houston urban plume. The tetron missions involved launching an altitude controlled balloon which carried sensors giving information regarding GPS location, temperature, pressure and moisture as well as a modem transmitting this data to the Twin Otter research aircraft and a control team on the ground. This tetron would then travel along with the parcel of air into which it was launched thereby tagging that air parcel. Twin Otter flights would then conduct transects in the area of the tagged air parcel and the urban plume.

The first mission was a "dry run" practice for the tetron team. On this mission no tetron was actually launched and the Twin Otter did not attempt to intersect the urban plume. The purpose of the mission was to ensure communications worked well between the Twin Otter, the operations base at the airport and a tetron which was driven around the airfield simulating a tetron in flight.

For the real tetron flights the decision to conduct these flights at night was made by the tetron team. The desire to avoid convective activity which could damage the tetron as well as thoroughly dilute the urban plume was the basis for choosing night flights. The

three tetraon flights all produced a clear and unambiguous track of the movement of pollutants downwind of Houston.

The first tetraon 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 tetraon. This transect is shown in Fig 4-5. 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 and a rise in O₃ of 20 parts per billion (ppb) above the background O₃ is also seen within the same plume [Tennessee Valley Authority (TVA)]. A brief but substantial mass 43 peak can also be seen at 07:26:07 PM local daylight savings time and this peak corresponds with sudden NO_y, NO_y^{*}, NO₂ and NO peaks.

As the flight began to do transects downwind of Houston the PTRMS signal for the most part was dominated by mass 45 (acetaldehyde). One brief mass 45 (acetaldehyde) peak of approximately 40 ppb was sighted in an elevated O₃ air mass at 2000' just east of the Waco region at around 4:00 AM local time.

On the second tetraon flight which occurred the evening of July 23-24 as the first flight of the evening prepared to take off a communication problem caused by a short power interruption forced the shutdown and restart of the PTRMS. This delayed the use of the PTRMS until approximately 45 minutes into the first flight and 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 was not overflown on this flight.

Two particular transects are noteworthy on this flight. Figure 6 shows a transect which initially is located in a region rich in isoprene oxidation products, methyl vinyl ketone and methacrolein (MVK + MACR) that are detected at mass 71. The transect transitions from the rural VOC plume into the urban "Houston" VOC plume as can be seen by the rise in mass 57 and mass 45 (acetaldehyde). During the second flight of the evening at around 11:20 PM local time Fig. 7 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 MVK + MACR, however, in this area there are no other elevated anthropogenic VOC's and the mass 71 signal can be attributed to isoprene oxidation products with confidence. The flight path for this transect is shown in Fig. 8.

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 (Fig. 9). 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 (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.

The clearest evidence in this campaign of the downwind transport of the Houston urban plume occurred during the third tetraon flight. Several arcs were flown during the course of the evening progressing along with the urban plume downwind of Houston eventually reaching the area between Shreveport LA and Texarkana TX. 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 show elevated mass 43 and mass 45 (acetaldehyde) within the plume through all arcs, while mass 57 is elevated within plumes in all but the final arc. Two transects are shown in Fig. 10-13. Each transect is shown both with PTR-MS data only as well as PTR-MS data in combination with TVA data to give a clearer picture of the complete urban plume. Figure 14 shows the route flown on this evening. Backgrounds were low and stable on this evening.

The final mission of the SETTS campaign involved overflight of the Houston ship channel followed by arcs downwind of both the ship channel and the urban area. There were no tetraons associated with this flight which was done during the daytime and intended to be primarily for the benefit of the PTR-MS. The urban plume was encountered downwind of Houston to the south of the city with elevated mass 57 and acetaldehyde as shown in Fig. 15. Unfortunately, there was also a power interruption at the beginning of this flight which led to a higher and more variable than optimum background for masses 43 and 45. The overflight of the Houston ship channel on this flight did not encounter elevated VOCs due to a combination of flight track restrictions and wind directions. This flight was also terminated early due to the emergence of widespread convective activity.

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 midway 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 while on one day the Twin Otter aircraft along with its instrumentation including PTR-MS was used to conduct a flight across a stationary front in the Dallas area. The details of every flight will not be discussed here, rather the highlights of certain flights where VOCs were substantial will be discussed. Due to uncooperative weather conditions power plant plumes were generally not tracked into Dallas. In total four flights were done downwind of the Ellis County cement plant sources, 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 made on August 31 which did show a mass 43 peak of 27 ppb against a background of 5 ppb shown in Fig. 16. While this one peak is 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 propene + fragments was conducted at approximately 7:30 PM while all others were flown around midday. The lowest we flew downwind of these plants was 1000' AGL which was low enough to encounter the stack plumes from these plants.

The flights conducted downwind of Dallas all occurred in the afternoon hours and were flown on 24, 25, 26, 28, 30 and 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 (acetaldehyde) were found to be elevated. During some flights the VOC plumes matched the O₃, CO and NO_x plumes (Fig. 17) while in other cases these VOCs were offset to the side (Fig.18). It can be seen that in areas far away from the urban plume mass 43 and 45 do drop significantly. Generally speaking propene and acetaldehyde have previously been considered to be minor factors in the Dallas metropolitan area and we welcome future cross-comparisons.

Flights were conducted that sampled the plumes of major NO_x and SO₂ emitting power plants such as Limestone, Big Brown and Sandow 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 (MVK + MACR) and mass 69 (isoprene). Figure 19 shows elevated mass 71 (MVK + MACR) and mass 69 (isoprene) observed while flying at 1500' over the Neches and Sabine river valleys during the afternoon hours. Mass 71 (MVK + MACR) peaks of 5-7 ppb and mass 69 (isoprene) peaks of 3-4 ppb are seen in these areas. Masses associated with anthropogenic VOCs such as mass 43 (propene + pentenes + propanol) and mass 57 (butenes + octane + MTBE) 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. The flight track of these transects is shown in Fig. 20.

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. A detailed can by can intercomparison is shown in spreadsheet format in the QA/QC report and only general comments regarding the findings will be made here. The fragmentation table found in Warneke et al was used to assign species to the masses measured. 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 although 3 were taken in minor plumes and in these minor plumes (<10 ppb) 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. Mass 45 and mass 71 data acquired by the PTR-MS should not be expected to equal the canister totals for these masses as the canisters did not quantify acetaldehyde, methyl vinyl ketone or methacrolein. The canister data for isoprene did correlate somewhat with the PTR-MS data at mass 69.

Limitations to the Applicability of Data

When considering possible inaccuracies of the PTR-MS data collected during SETTS and NETPS three primary concerns warrant discussion. The first concern is that of a higher than normal background present in the PTR-MS measurements when measurements are conducted too soon after the startup of the instrument. As noted earlier measurements on July 23 and July 29 suffered initially from a higher than optimum background which decreased as the flights on these days progressed. The first audit conducted by TCEQ was also conducted too soon after instrument start up although we did not realize this fact at the time. This problem was corrected during the NETPS project by installing a universal power supply and during future campaigns the instrument will be kept on at all times once the campaign has started. Secondly as mentioned earlier PTR-MS measures the signal at a mass and there are only a few masses which can be indisputably attributed to only one hydrocarbon species without interference. The fragmentation patterns of 56 separate hydrocarbons are analyzed by Warneke et. al. and illustrate the complexity in assigning a given species to a mass. Finally we were unable to use a catalytic converter when determining the background while airborne due to safety and power considerations. A catalytic converter would have maintained the relative humidity of the sample air while removing hydrocarbons and this would have removed any concerns regarding possible changes to the background as the humidity of the sample air was changed. We intend to utilize a catalytic converter in future campaigns.

Conclusions

The compact PTR-MS was able to locate, quantify and track the movement of VOC plumes associated with industrial, urban and biogenic sources. During the July 26-27 flight the Houston VOC plume was found to move a considerable distance (200 miles) at night, showing that 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 best to attain their air quality goals. Elevated levels of mass 69 (isoprene) and especially mass 71 (isoprene oxidation products) over forested river valley areas of rural Texas were in the 5-10 ppb range at flight altitude and could potentially affect urban air quality given the right wind patterns. Flights over the Houston Ship Channel showed a consistent mass 57 peak in a particular area of the ship channel on multiple transects associated with two different dates although actual source identification was not accomplished due to the high number of hydrocarbon emitting facilities in the central ship channel region. Flights

downwind of the Dallas area revealed occasionally higher than expected values of mass 45 (acetaldehyde) and mass 43.

While these flights succeeded as a demonstration of the PTR-MS ability they did not produce a substantial statistical database for any of the findings mentioned above. Tracking chemical evolution of VOCs was limited by the lack of chemical evolution during evening flights and the lack of flights originating in a high VOC area such as the Houston ship channel area during the daytime which could then track evolution of VOC plumes. With regards to the ship channel flights only 5 transects were made of the Houston ship channel during the SETTS campaign and they all occurred within the hours of 5:00 – 8:00 PM local time. There were only two canister samples taken during polluted ship channel transects. The scope of the PTR-MS was also to measure a broad suite of VOCs and a narrower focus in the future could better answer questions regarding specific VOCs. Future studies which focused more exclusively on any of the previously mentioned highlighted findings could potentially yield a high return on the investment. These studies could be focused on any one of the following; ship channel emissions of VOCs, tracking the chemical evolution of ship channel emissions of VOCs during the daytime, studying the contribution of VOCs to the downwind of Dallas urban plume (or any urban plume for that matter) during the daytime and finally a study of biogenic VOCs in forested river valley areas and any plumes associated with them.

Acknowledgements

The results shown in this report are made possible by the culmination of group efforts in both the SETTS and NETPS campaigns. Researchers from Battelle Northwest Laboratories and the University of Massachusetts conducted the mission planning for SETTS. Researchers from the University of Alabama at Huntsville conducted the mission planning for NETPS. Extensive aircraft instrumentation was installed by the Tennessee Valley Authority (TVA) to monitor CO, O₃, NO_y, NO_y*, NO₂, NO and SO₂ as well as various meteorological variables and the GPS location of the aircraft. The TVA research teams assistance in the initial installment of the PTR-MS as well as continued troubleshooting assistance in the field environment is appreciated. It should also be noted that TVA raw data is used in this report in comparison with PTR-MS data. Grateful acknowledgement is also given to the Twin Otter pilots who went out of their way to accommodate in-flight mission modifications requested by the onboard research team while keeping safety concerns paramount.

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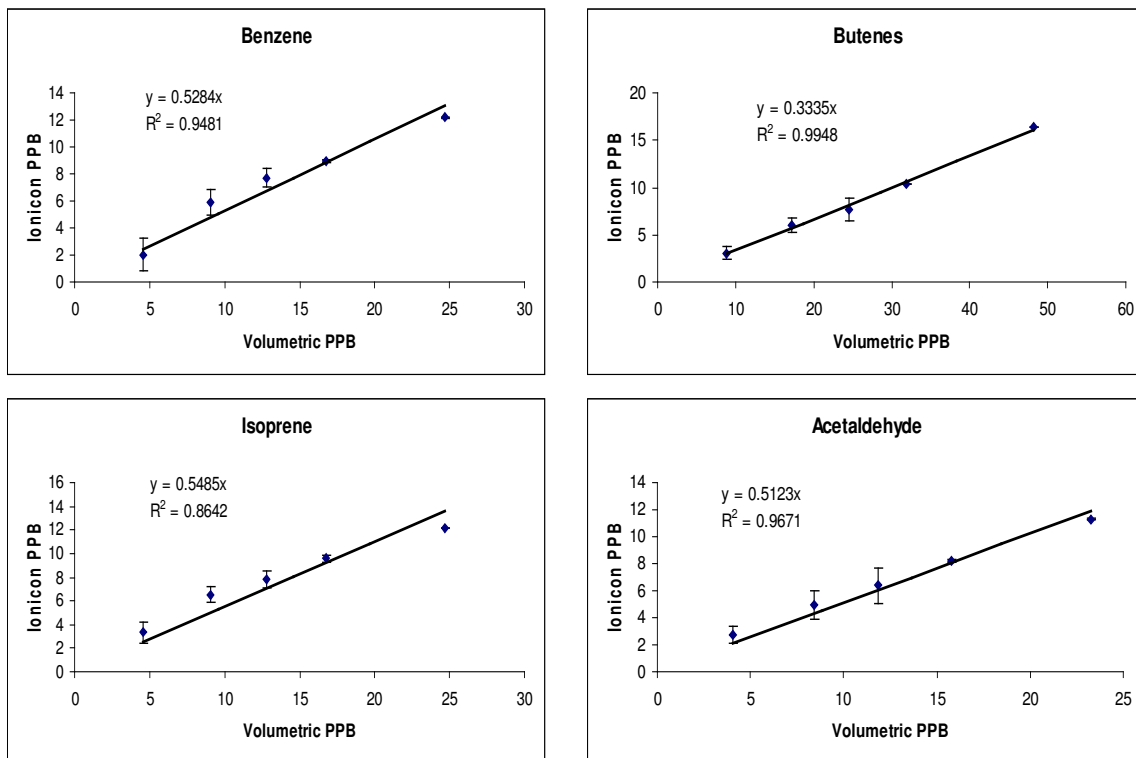


Fig. 3; Calibration curves developed from SETTS and NETPS calibrations. The curves are developed from an average of calibrations conducted throughout the study. The error bars are equal to 2*standard deviation.

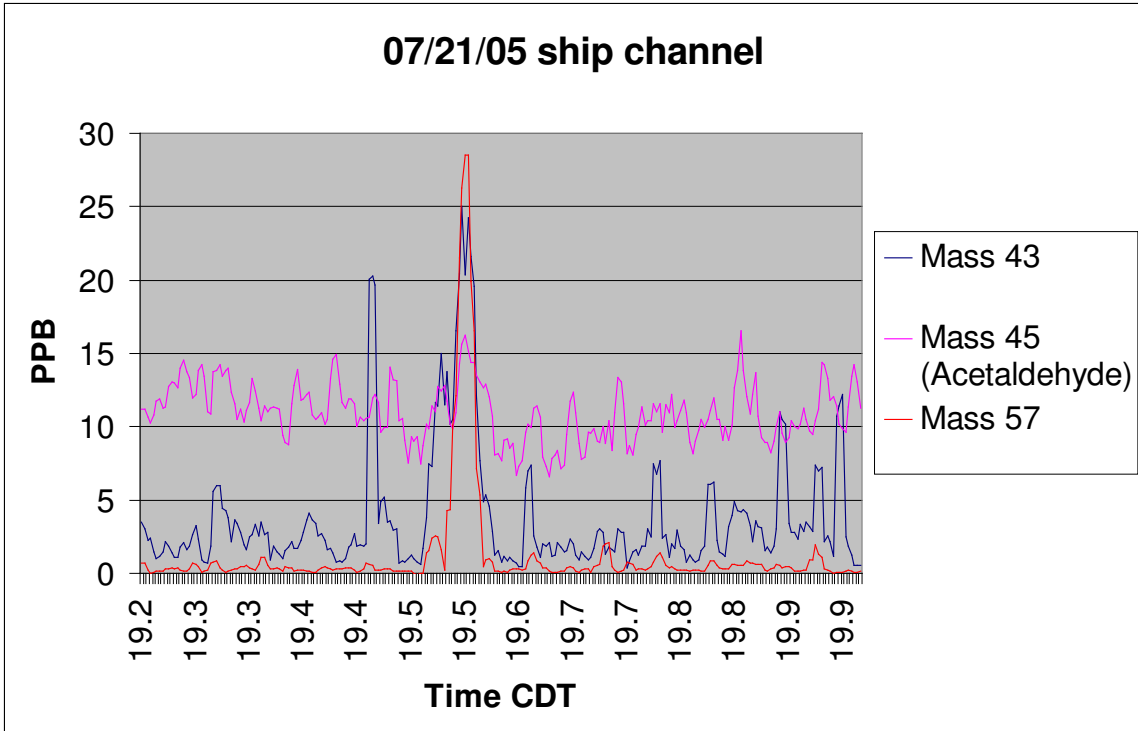


Fig. 4; Transect conducted 3 miles north of Houston ship channel while flying at 2000' MSL (mean sea level). Times are local daylight savings time.

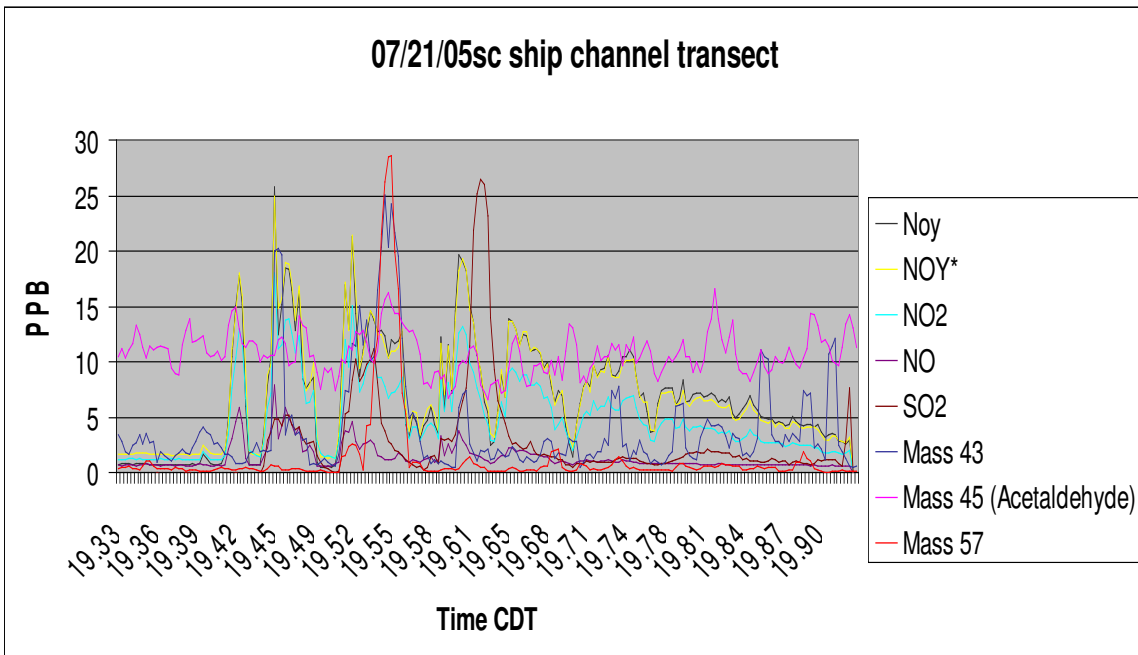


Fig. 5; The 07/21 ship channel transect including O₃, NO_x and SO₂ raw data provided by TVA.

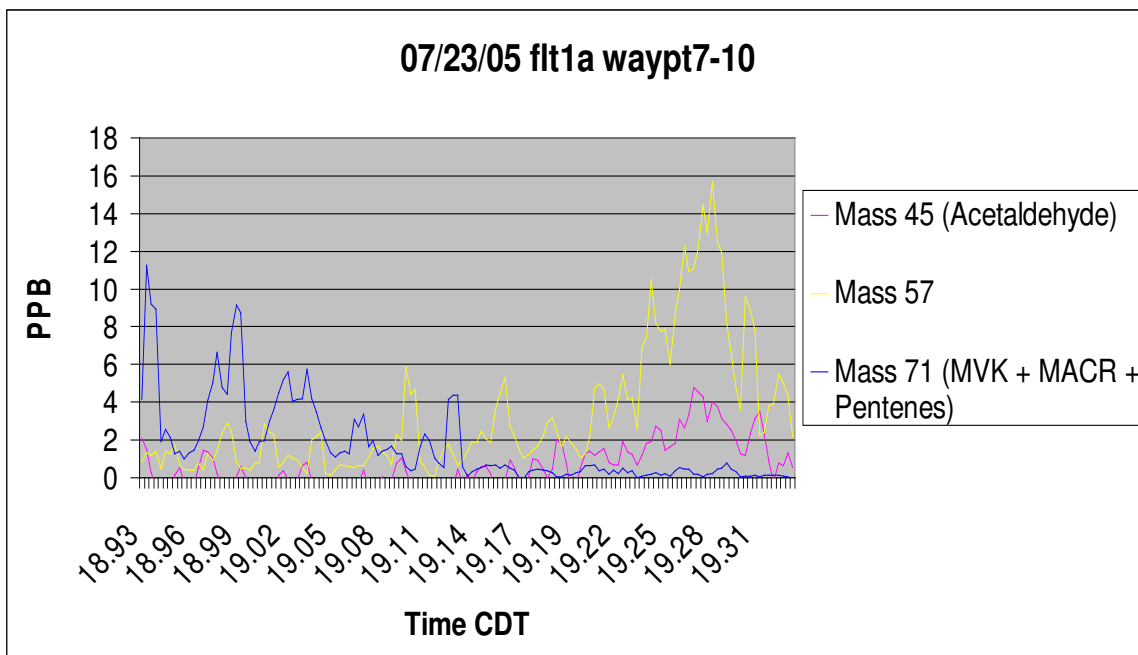


Fig. 6; Arc flown approximately 20 miles north of Houston moving East to West at 2000' MSL. Arc begins in rural heavily forested area and ends after crossing the Houston urban plume.

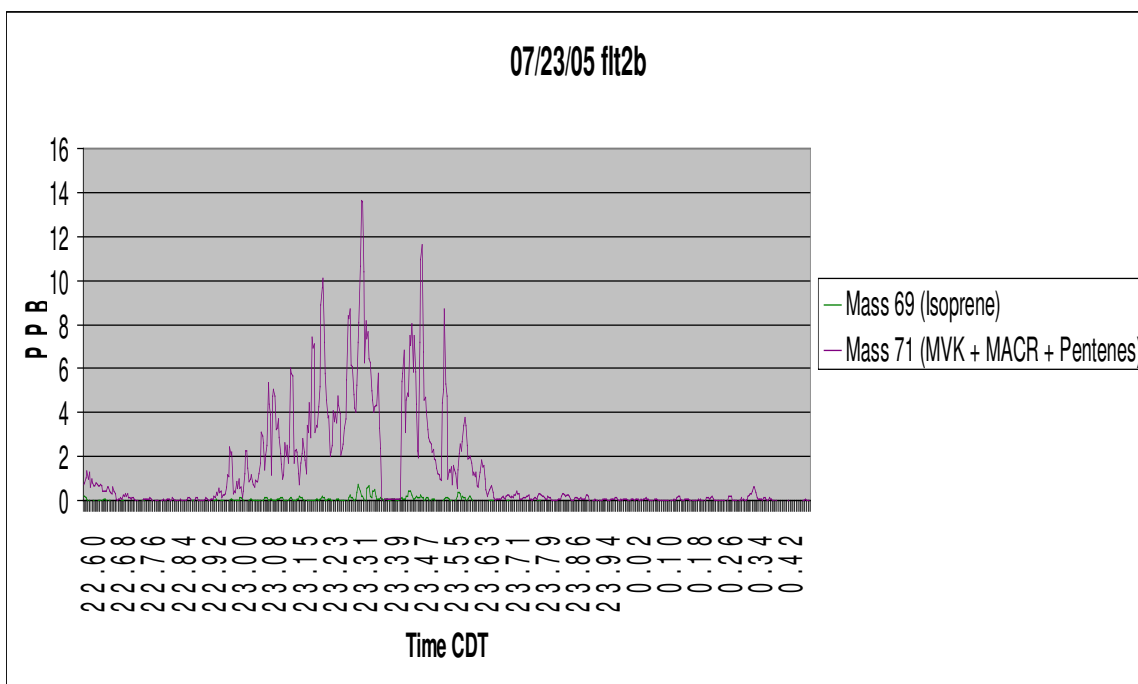


Fig. 7: Transect done over forested area showing the presence of mass 69 (isoprene) and mass 71 (isoprene oxidation products) at night. Altitude of transect is 2000' MSL.



Fig. 8; The flight path of the transect shown in Fig. 7.

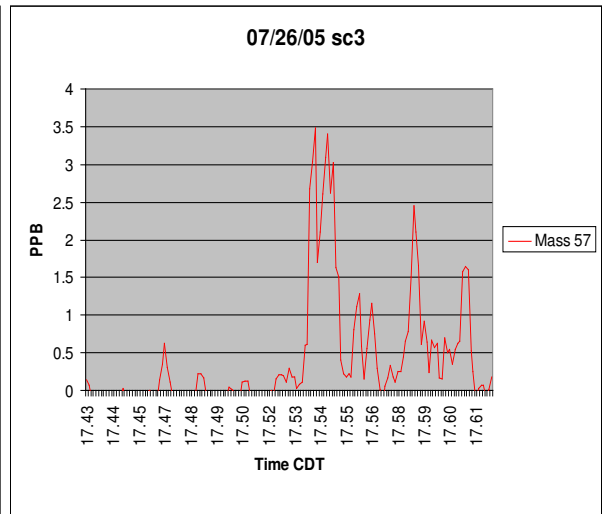
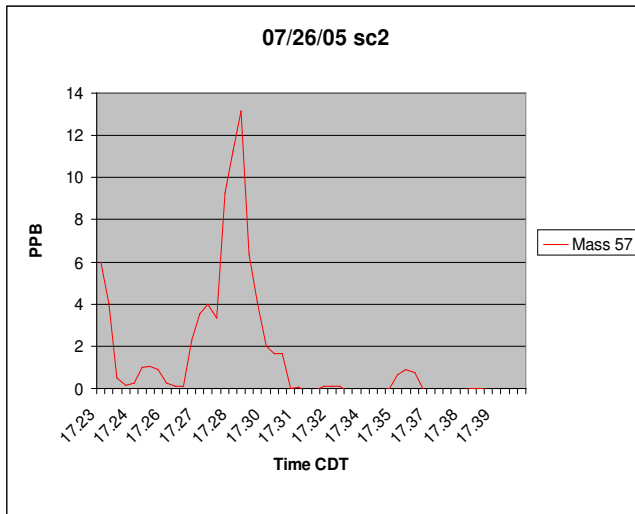
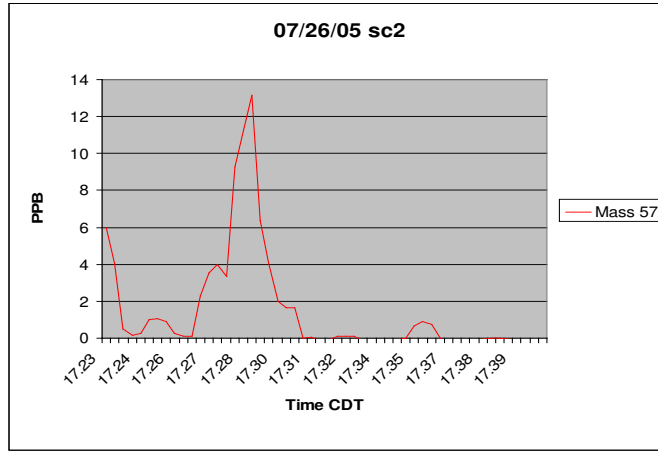


Fig. 9; Three consecutive transects flown 3 miles north of the Houston ship channel on 07/26 show a mass 57 peak in roughly the same location every time. This location is close to the location of the mass 57 peak found on 07/21. Altitude of all transects shown was 2000' MSL.

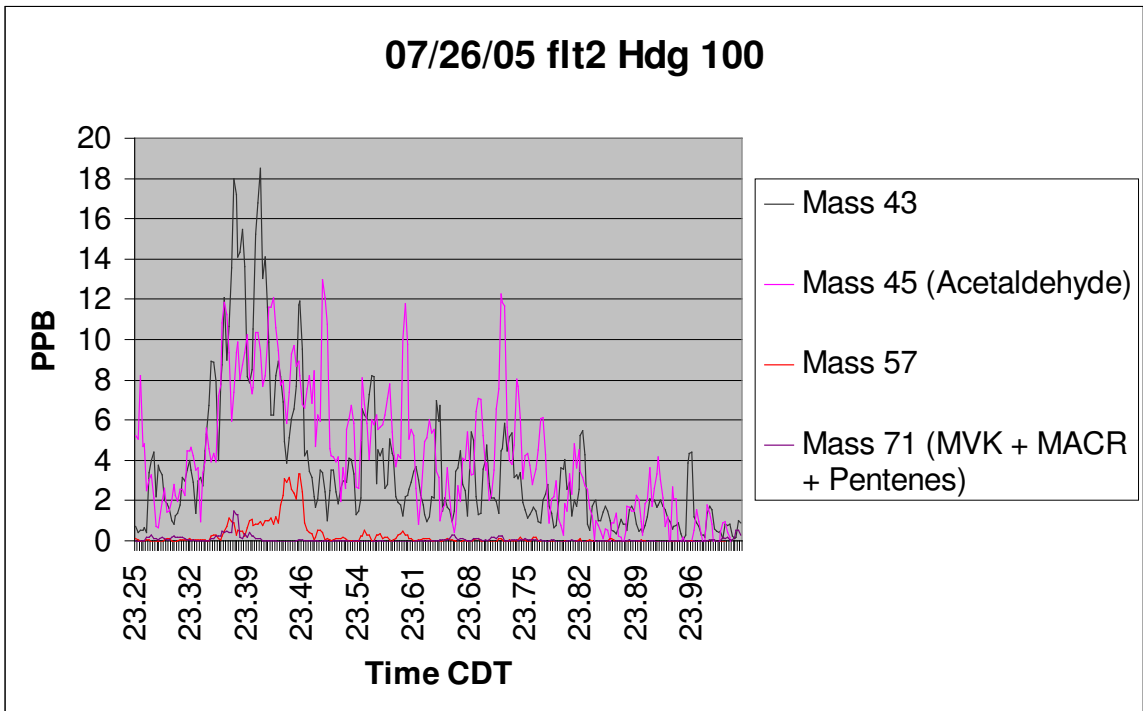


Fig. 10; This transect was executed approximately 90 miles NNE of Houston at 2000' MSL.

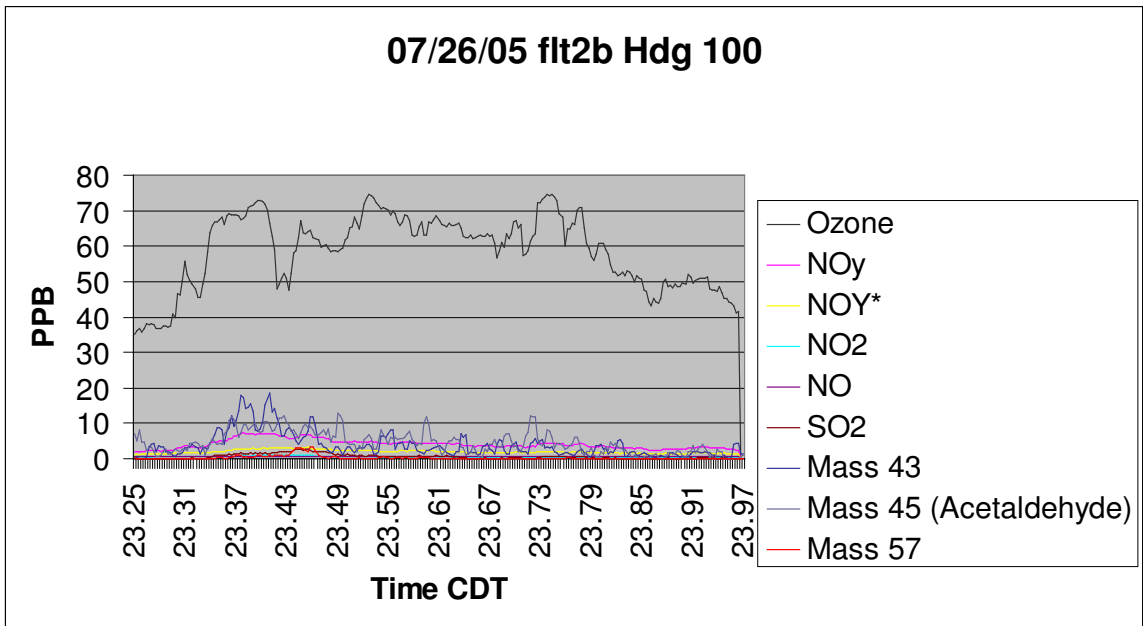


Fig 11; The same transect as shown in Fig 10 including TVA raw data.

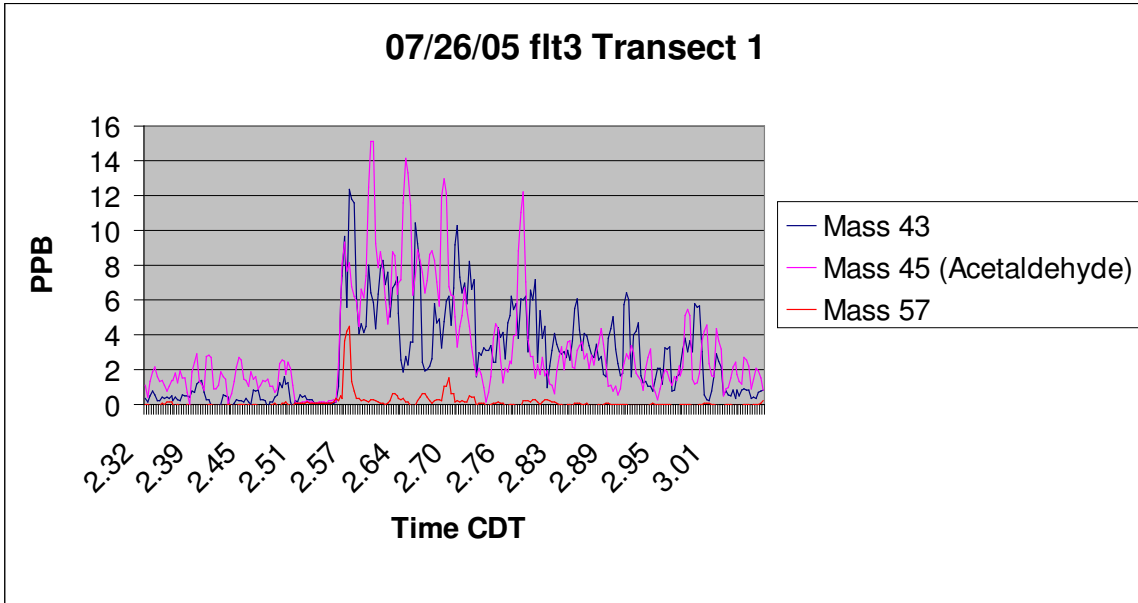


Fig. 12; This west-east transect was conducted approximately 200 miles NNE of Houston at 2000' MSL.

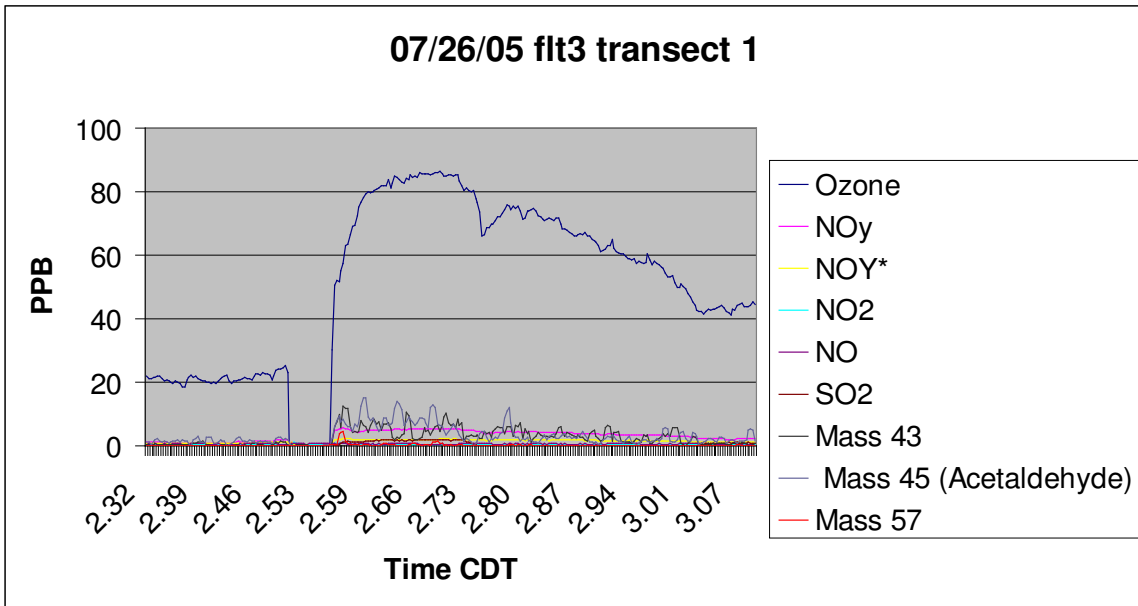


Fig13; The same transect as shown in Fig. 12 including TVA raw data.

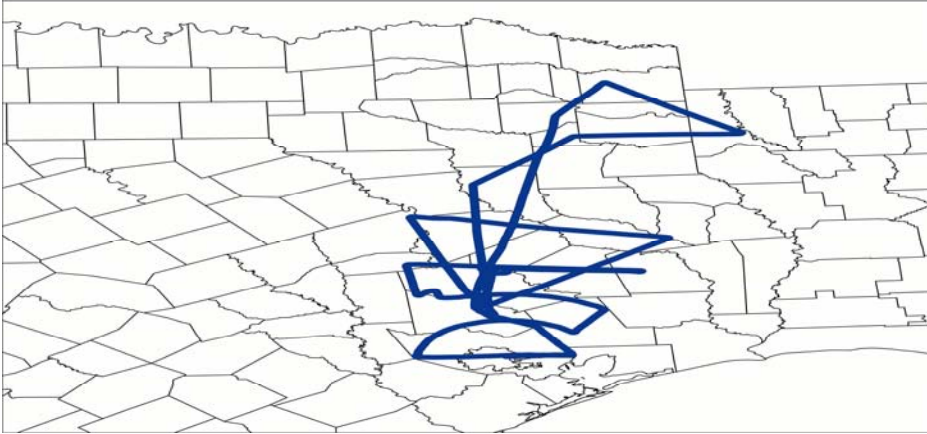


Fig 14; The flight track flown on the July 26-27 flight. The urban plume with enhanced VOCs was evident on all transects.

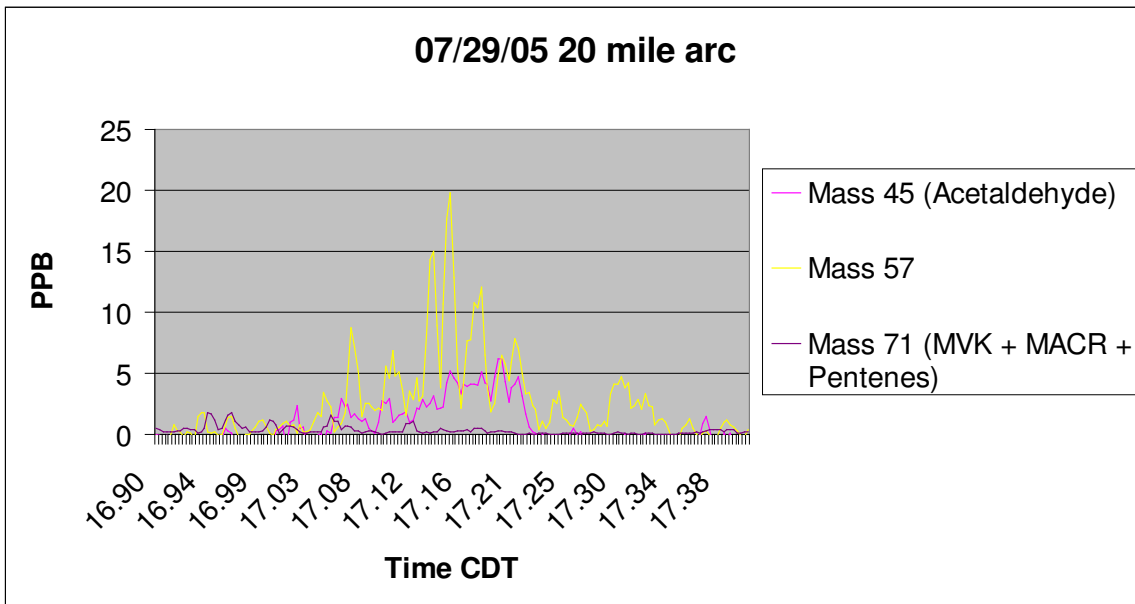


Fig. 15; This arc was flown to the south of Houston at 1700' MSL. This plume is most likely a mixture of ship channel and urban influence.

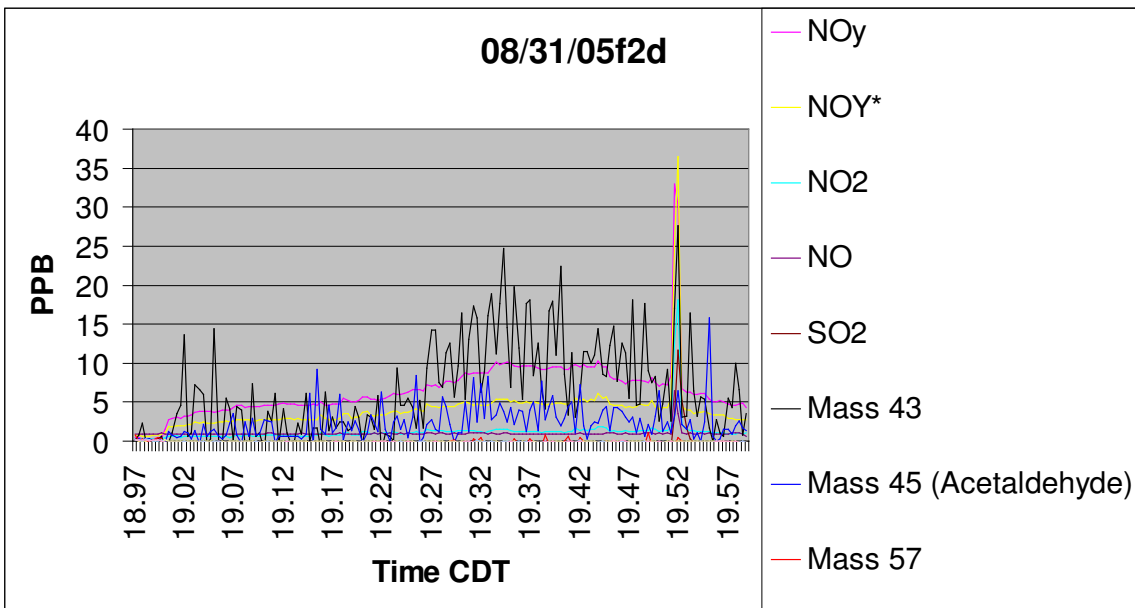
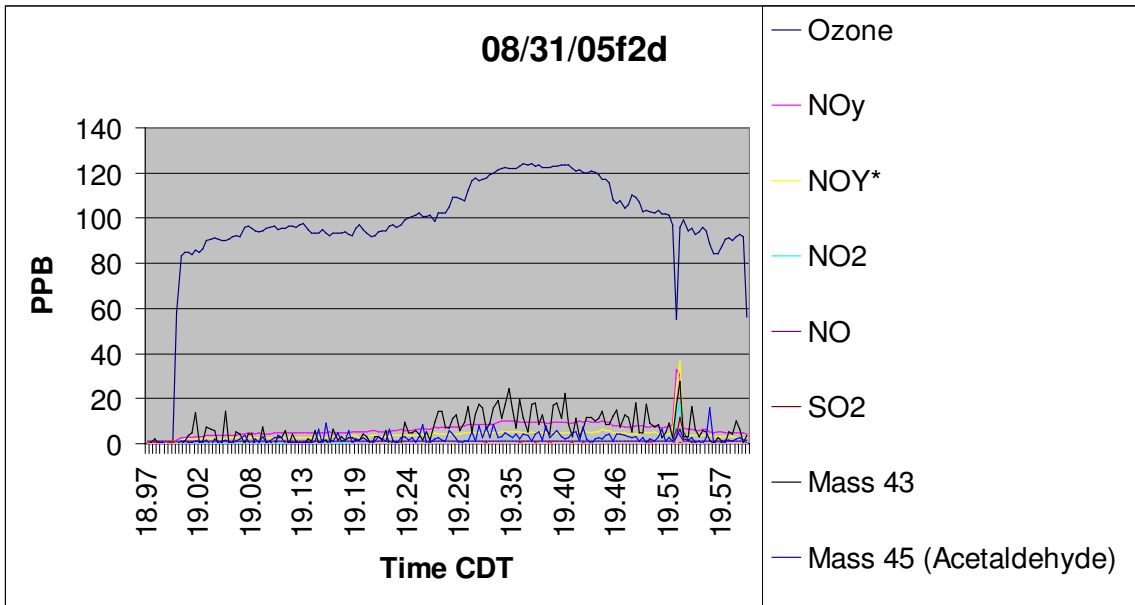


Fig. 16; A tightly concentrated plume was crossed on 08/31 about 3 miles downwind of an Ellis County cement plant source. The broad urban pollution plume is encountered between 17.29 and 17.48 while the compact plume is encountered at 19.53. Mass 43 were the only VOCs found elevated in the compact plume. Altitude was 2000' MSL.

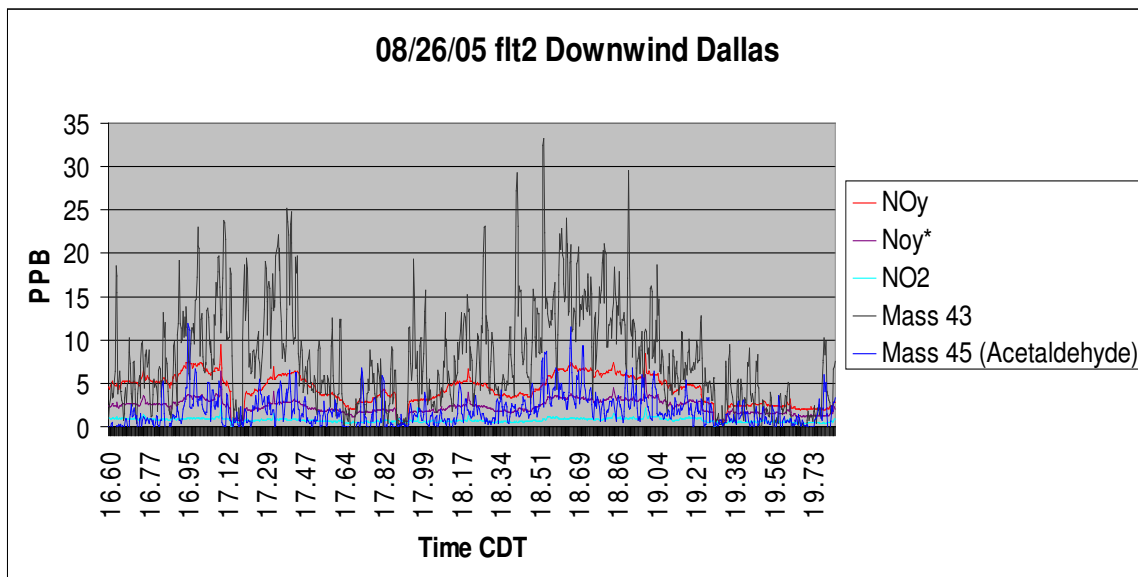
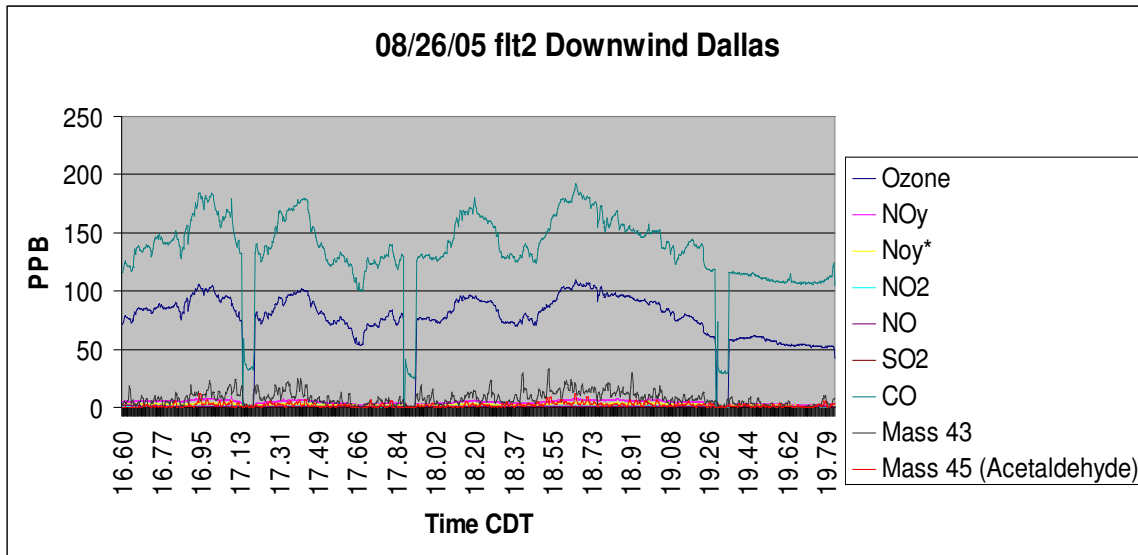


Fig. 17; During this flight traversing the Dallas urban plume VOC peaks can be seen to be roughly co-located with O₃ and CO in the top graph and with NO_y in the bottom graph. Altitude was 2000' MSL.

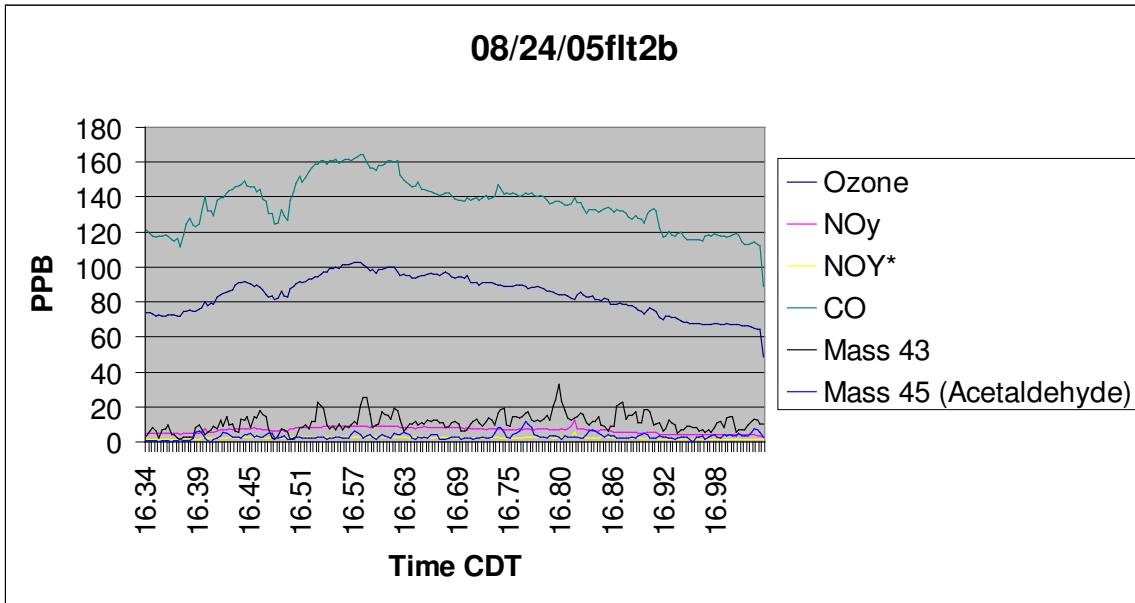


Fig. 18; On this downwind of Dallas traverse mass 43 and mass 45 (acetaldehyde) peaks appear to be offset from the urban O₃ and CO plumes. Altitude was 2000' MSL.

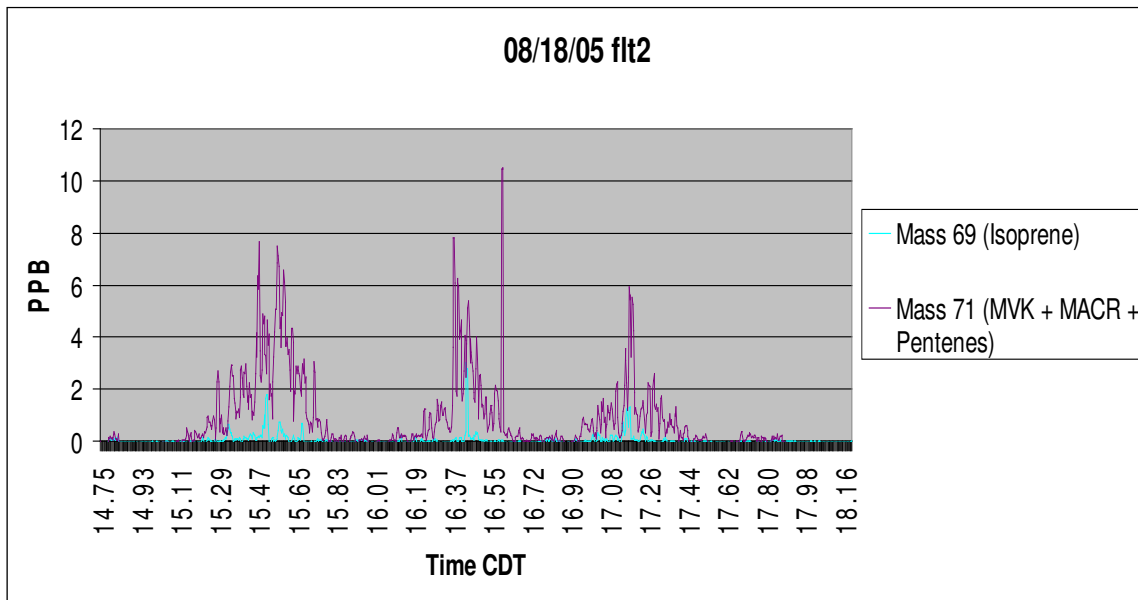


Fig. 19; This daytime flight was conducted in rural NE Texas at 1500-2000 MSL and shows elevated mass 69 (isoprene) and mass 71 (isoprene oxidation products).



Fig. 20; The transects which crossed elevated mass 69 (isoprene) and mass 71 (isoprene oxidation products) on the 08/18 flight. The elevated VOCs were encountered at the eastern edge of these transects.

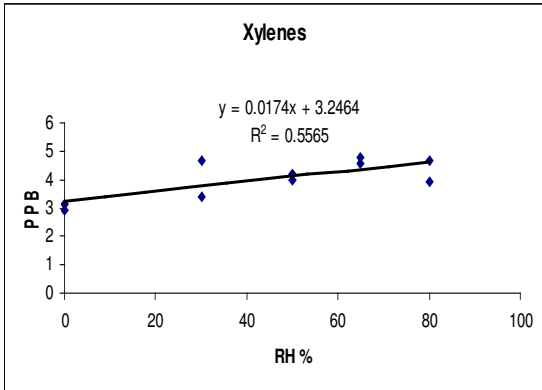
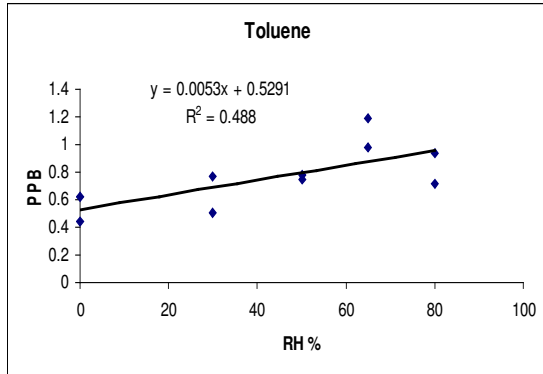
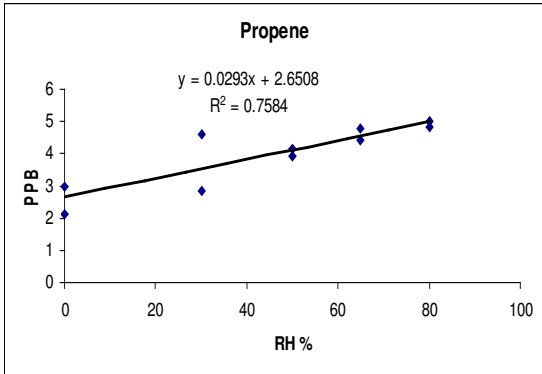
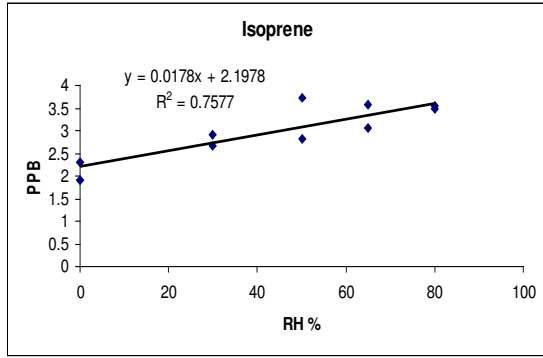
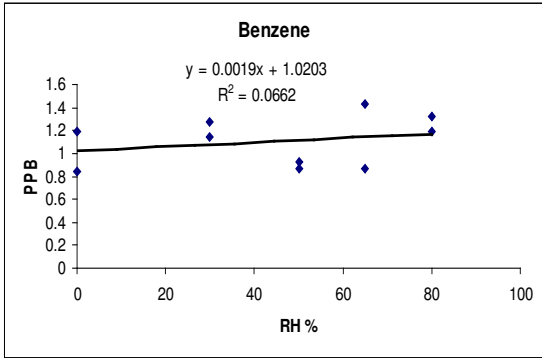
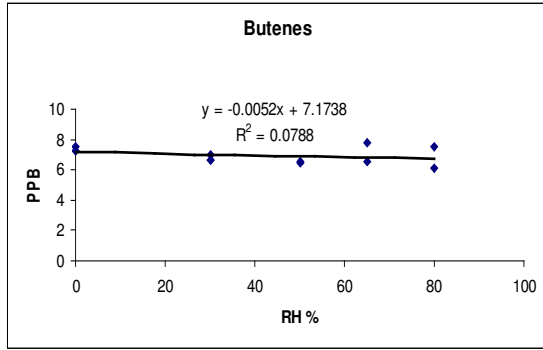
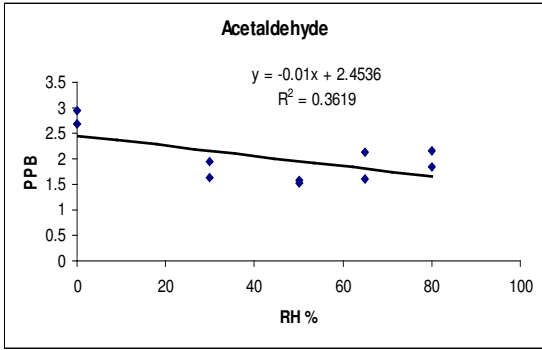


Fig. 21; The results of two calibrations conducted to determine dependence of PTR-MS signal on relative humidity are shown. Actual mixing ratios were 20 ppb for Xylenes, 13 ppb for Butenes and 6 ppb for the rest.