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MILAGRO**

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Measurements of volatile organic compounds using proton transfer reaction – mass spectrometry during the MILAGRO 2006 Campaign

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Abstract

5 Volatile organic compounds (VOCs) were measured by proton transfer reaction – mass spectrometry (PTR-MS) on a rooftop in the urban mixed residential and industrial area North Northeast of downtown Mexico City as part of the Megacity Initiative – Local and
10 Global Research Observations (MILAGRO) 2006 field campaign. Thirty eight individual masses were monitored during the campaign and many species were quantified including methanol, acetaldehyde, toluene, the sum of C₂ benzenes, the sum of C₃ benzenes, acetone, isoprene, benzene, and ethyl acetate. The VOC measurements were analyzed to gain a better understanding of the type of VOCs present in this re-
15 gion of the MCMA, their diurnal patterns and their origins. Diurnal profiles of weekday and weekend/holiday aromatic VOC concentrations show the influence of vehicular traffic during the morning rush hours and during the afternoon hours. Plumes including of elevated toluene as high as 216 parts per billion (ppb) and ethyl acetate as high as 183 ppb were frequently observed during the late night and early morning hours,
20 indicating the probability of significant industrial sources of the two compounds in the region. Wind fields during those peak episodes revealed no specific direction for the majority of the toluene plumes but the ethyl acetate plumes arrived at the site when winds were from the Southwest or West. The PTR-MS measurements combined with other VOC measuring techniques at the field site as well as VOC measurements con-
25 ducted in other areas of the Mexico City Metropolitan Area (MCMA) will help to develop a better understanding of the spatial pattern of VOCs and its variability in the MCMA.

1 Introduction

25 Mexico City Metropolitan Area (MCMA) 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 elevation, further enhancing photochemical activity and ozone

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production. Another factor contributing to the air pollution problem in this area is that the city lies in a valley surrounded by mountains and thermal inversions are common during the morning hours. Daily activities in the city lead to the emission of volatile organic compounds (VOCs) which react with nitrogen oxides ($\text{NO} + \text{NO}_2 = \text{NO}_x$) emitted primarily through combustion sources. This interaction leads to production of O_3 , secondary organic aerosols, and other toxic chemicals through photochemical processes (Lei et al., 2004, 2007; Zhang et al., 2004a). The Mexican one-hour air quality standard of 110 parts per billion (ppb) of O_3 has been violated in approximately 80% of the days annually and the maximum O_3 values of over 300 ppb have been recorded (INE, 2000).

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 and secondary organic aerosol formation (Molina et al., 2002; Zhang et al., 2004b; Lei et al., 2007). A study by Arriaga-Colina et al. (2004) comparing morning measurements of VOC/NO_x and CO/NO_x ratios with ratios in the 1998 emissions inventory suggested that the VOC/NO_x and CO/NO_x ratios in the emissions inventory may be underestimated by a factor of 2 to 3 in MCMA. Modeling work by West et al. (2004) compared measured non-methane hydrocarbons (NMHCs) to modeled NMHCs and achieved the best fit by increasing the VOC emissions by a factor of three. While Arriaga-Colina et al. (2004) and West et al. (2004) both suggested underestimated VOCs in the emissions inventory, flux measurements conducted during MCMA 2003 campaign utilizing a PTR-MS instrument by Velasco et al. (2005) showed a fairly good agreement between emissions inventory and measurements. 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. In this paper, we report VOC measurements using a PTR-MS instrument deployed and operated during the MILAGRO field campaign to better elucidate the VOC emissions and chemistry in the Mexico City area.

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2 Experimental methods

In March 2006, a PTR-MS instrument (Ionicon) was utilized to conduct measurements of VOCs in Mexico City during the MILAGRO 2006 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 the downtown Mexico City. This site (named T0) represented one of three supersites involved in the MILAGRO 2006 project. 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 MCMA. A PTR-MS instrument was also utilized both at the flux tower and the mobile van. The T1 and T2 supersites used canister samples analyzed by gas chromatography – flame ionization detection (GC-FID), differential optical absorption spectroscopy (DOAS), and proton transfer – ion trap – mass spectrometry (PT-IT-MS) to measure VOCs. The T0-IMP site also measured certain VOCs using DOAS, canisters, and GC methods, in addition to the PTR-MS measurements.

Online measurements of VOCs were conducted using the PTR-MS at T0-IMP from 5–23 March and 26–31 March. The system was inoperable from 23–26 March due to a condensation problem. The PTR-MS sampled continuously between day and night. Throughout the campaign, a drift tube pressure was maintained at 2.1 millibars and an E/N ratio of 115 Townsend ($1 \text{ Td} = 10^{17} \text{ V cm}^2 \text{ molecule}^{-1}$) was utilized, where E is the electronic field strength in V cm^{-1} and N is the number concentration of the buffer gas in molecule cm^{-3} . There were a suite of 38 masses sampled sequentially by the PTR-MS during the majority of the field campaign. Each mass was monitored 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 to survey mass peaks that might have been missed while in the single ion scan mode. Background checks were performed for approximately 15 min once every three hours. Calibrations were conducted daily during the first half of the field campaign and

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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 need to increase the total measurement time.

The inlet was constructed of 0.25 inch outer diameter (OD) perfluoroalkoxy (PFA) tubing with a length of 14 ft and was pumped by a diaphragm pump at 30 standard liters per minute (slpm), maintaining a residence time of 2–3 s in the inlet. A small amount of the inlet flow (50–200 standard cubic centimeters per minute, 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 the background sample was taken at the time.

The instrument 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 a given time the background was the average of the backgrounds determined before and after the measurements. The use of a catalytic converter enabled background determinations while maintaining the ambient relative humidity the same as in the measurement mode.

Calibrations of the PTR-MS instrument during MILAGRO 2006 were conducted using a custom mix calibration gas cylinder (Spectra Gas) containing propene, 1-butene, acetone, isoprene, methyl ethyl ketone, benzene, toluene, m-xylene, 1,3,5-trimethylbenzene, and α -pinene. The mixing ratio of the calibrated gases varied between 2 and 20 ppb. The carrier gas for the calibration was ambient air which passed through the catalytic converter. The calibration flow connected with the inlet through a PFA fitting. Alternatively, VOC concentrations were calculated from the known ion-molecular reaction time and rate constants with the hydronium ions (H_3O^+) (Zhao et al., 2004a; 2004b). The performance of the PTR-MS was found to be slightly variable during the MILAGRO field campaign and for this reason the calibration curves from the preceding and following calibrations at a given time were employed rather than using an average of all calibration curves developed throughout the field campaign.

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3 Results and discussion

3.1 Local meteorological details

Surface winds at the IMP site obtained by Argonne National Laboratory were characterized by a strong diurnal cycle with wind speeds between 0.5 and 3.0 m s⁻¹ during the early morning hours (00:00–08:00 local time, LT). 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 LT). During the campaign, wind direction was variable and a trend was difficult to identify, although there appeared to be a slight preference for a wind from either the East or West during the early morning hours. Preliminary analysis of profiler data gathered by the University of Alabama-Huntsville at the IMP site indicated early morning boundary layer heights of 300–500 m and late afternoon boundary layer heights of 3000–4000 m. These measurements were in agreement with those reported previously by De Foy et al. (2005), who found surface temperature inversions below 500 m for most nights and daytime boundary layer growth to 4000 m during the MCMA 2003 campaign. Low temperatures in the morning were typically 50–55°F and the high temperatures were typically between 75 and 80°F. Relative humidity ranged from 50–80% in the early morning hours and 10–40% during the afternoon. No precipitation occurred during the first two and half weeks of the field campaign, but during the last one and half weeks of the campaign there were several occurrences of scattered thunderstorms in the late afternoon.

3.2 Interpretation of mass spectral assignments

3.2.1 Mass 33

The ion signal at mass 33 is attributed to methanol. There are no known hydrocarbons which interfere with the measurement of methanol at mass 33 (de Gouw and Warneke,

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2007; Rogers et al., 2006). Methanol was not calibrated during the field campaign and a rate constant of $2 \times 10^{-9} \text{ cm}^3/\text{s}$ was used to determine its concentration.

3.2.2 Mass 42

Mass 42 is assigned to acetonitrile. Some small alkanes might contribute to the signal at mass 42 by reacting with O_2^+ . However, this interference usually is found trivial (de Gouw and Warneke, 2007).

3.2.3 Mass 45

The signal at mass 45 is attributed to acetaldehyde. Carbon dioxide (CO_2) was found weakly contributing to ion signals at mass 45 with 1 ppmv CO_2 equivalent to 1 pptv acetaldehyde (Rogers et al., 2006). In addition, because CO_2 was not removed by the catalytic converter, the CO_2 interference should be accounted for by background checks. The CO_2 interference could play a more significant role in a clean air mass when attempting to measure low mixing ratios of acetaldehyde but this was never the case at the urban T0 site. Calibrations were conducted with this compound throughout the field campaign.

3.2.4 Mass 59

Acetone, propanal, and glyoxal are all detected at mass 59 (Rogers et al., 2006). Calibrations of acetone were conducted throughout the field campaign and the signal at mass 59 was quantified based on the acetone calibrations. The signal at mass 59 may be considered to be the lower limit of the sum of these three species since glyoxal has a reaction rate constant considerably lower than that of propanal and acetone (Zhao and Zhang, 2004a).

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3.2.5 Mass 69

Isoprene is measured at mass 69. Several species also have been reported to be detected at mass 69 such as methyl butanal, ethyl vinyl alcohol and furan (Christian et al., 2004; Karl et al., 2001). However, isoprene was often found the dominant species at mass 69 within various kinds of air masses (de Gouw and Warneke, 2007). The PTR-MS was calibrated with isoprene standards throughout the campaign.

3.2.6 Mass 73

Methyl ethyl ketone (MEK) can be detected at mass 73 (de Gouw and Warneke, 2007). Substantial mass 73 signals were also assigned to methyl glyoxal, one of the major products from OH initiated oxidations of aromatic compounds (Zhao et al., 2005), which were observed with significant concentrations during the MILAGRO 2006 campaign. Water cluster, $\text{H}_3\text{O}+(\text{H}_2\text{O})_3$, can also be detected at mass 73, but under the experimental conditions no significant interference from water cluster was found during background checks throughout the field campaign. Mass 73 was calibrated with MEK standards during the field campaign and the same calibration factor was applied for both MEK and methyl glyoxal.

3.2.7 Mass 79

This mass is primarily attributed to benzene. Although there are possible contributions to mass 79 due to fragmentations of ethyl- and propyl- benzenes, the magnitude of the fragmentation is found to be trivial when the PTR-MS is operated at reduced E/N ratio (de Gouw and Warneke, 2007), which was maintained at 115 Td throughout the campaign. Benzene was calibrated throughout the field campaign.

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3.2.8 Mass 89

The ion observed at this mass is attributed to ethyl acetate. Mass 89 correlated well with masses 43 and 61 during the field campaign, which was also observed during laboratory tests with pure ethyl acetate samples. Rogers et al. (2006) also observed ethyl acetate during the MCMA 2003 campaign and the finding was further confirmed by gas chromatography measurements. Ethyl acetate was not calibrated during the campaign and a rate constant of $2 \times 10^{-9} \text{ cm}^3/\text{s}$ was used to quantify its concentration. The fragmentation was also accounted for in the data reported here. There are other species such as butyric acid measured at mass 89 and their presence cannot be ruled out.

3.2.9 Mass 93

The ion observed at this mass is attributed to toluene. Fragmentation of monoterpenes can present a minor interference (de Gouw and Warneke, 2007). Warneke et al. (2003) found about 7% of monoterpenes fragmented to mass 93. The monoterpene signal at mass 137 was consistently much lower than the mass 93 signal during the field campaign. Toluene was calibrated throughout the field campaign.

3.2.10 Mass 105

Both styrene and peroxy isobutyryl nitrate (PiBN) can be detected at mass 105. Styrene is mostly emitted from petrochemical industry sources and PiBN is usually found in aged plumes (de Gouw and Warneke, 2007). Given there were petrochemical facilities near the T0 observation site, we assigned the mass 105 as styrene.

3.3 VOC diurnal profiles

The diurnal profiles for four selected aromatic VOCs are shown in Fig. 1. The measurements for the selected aromatic VOCs that occurred within each hourly time are

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summed and averaged for weekdays and weekends/holidays separately. 20 and 21 March 2006 were national holidays and non-working days for many citizens of Mexico City so that these dates were considered to better match the weekend activity. Totally, the measurements were conducted on 16 weekdays and 6 weekends/Holidays. The aromatics are represented by toluene at mass 93, styrene at mass 105, the sum of C₂ benzenes including xylenes at mass 107, and the sum of C₃ benzenes at mass 121. On weekdays aromatics attained their highest concentration from 06:00–07:00 LT for masses 105 (about 1.3 ppb) and 107 and 07:00–08:00 LT for masses 93 and 121. On weekends/holidays the aromatics detected at masses 105, 107, and 121 peaked at the similar times as their weekday highs, while the mass 93 reached the maximum value during the 02:00–03:00 LT period. The weekday peaks for masses 93, 107, and 121 were about 26, 19, 11 ppb, respectively, and were slightly higher than those of the corresponding weekend/holiday values.

Four selected oxygenated VOCs were depicted in Fig. 2, including methanol at mass 33, acetaldehyde at mass 45, the sum of methyl ethyl ketone (MEK) and methylglyoxal at mass 73, and ethyl acetate at mass 89. The weekday mass 89 reached the maximum of about 35 ppb during 07:00–08:00 LT. The masses 45 and 73 peaked later in the morning during the 9:00–10:00 LT for, with the maximum weekday values of about 12 and 7 ppb, respectively. The ethyl acetate mass 89 reached a peak (about 21 ppb for the weekday value) during the evening hour of 02:00–03:00 LT. The mass 45 peaked during the same time period on weekdays and weekends/holidays, while mass 73 during weekends/holidays attained the daily peak one hour earlier than weekdays. The mass 89 during the weekends/holidays time period reached the maximum from 03:00 to 04:00 LT, about one hour later than its weekday peak. Except for mass 89, the other three oxygenated VOCs showed a larger weekday peak than the weekend/holiday peak.

The differences between weekday and weekend diurnal patterns for the VOCs were best characterized as subtle yet detectable for most species. All species, particularly the aromatics, had lower mixing ratios during the daylight hours on weekends com-

pared with the same time periods on weekdays. During the evening hours, methanol and C₂ benzenes showed lower weekend mixing ratios, while toluene and ethyl acetate showed little difference or even slightly higher mixing ratios on the weekends.

Figure 3 shows the diurnal profiles of two biogenic VOCs, isoprene at mass 69 and monoterpenes at mass 137, and a biomass-burning marker, acetonitrile at mass 42. All three species peaked in the morning hour of 07:00–08:00 LT. The daily peak values for masses 69, 137, and 42, were about 1.7, 1.2, and 3.5 ppb, respectively. As expected, no difference between weekdays and weekend/holidays was found for these species. The isoprene emission depended on light and temperature, which could explain the smaller peak observed between 13:00 and 14:00 LT. Monoterpenes were continuously emitted during nighttime and mainly destroyed by reactions with the hydroxyl radicals OH (Fan et al., 2005). Thus, monoterpenes were built up during nighttime and depleted quickly after sunrise. The mass 42 was a biomass-burning marker and several biomass-burning events were visually identified during the MCMA 2006 campaign. The profile of mass 42 was likely controlled by the physical mixing processes, i.e. variations in the boundary layer height. Because of their high reactivity with OH, the biogenic VOCs (isoprene and pinenes) can contribute to O₃ and secondary organic aerosol formation in the urban areas (Li et al., 2007).

All of the species had elevated morning mixing ratios, which decreased with the boundary layer development during the course of the day, indicating that VOCs were produced in the Mexico City urban area. The C₂ and C₃ benzenes showed the 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 is likely industrial in nature, and further studies are needed to investigate VOC emissions by factories in this 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.

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3.4 VOC Plumes of interest

The PTR-MS instrument sequentially scanned 38 masses throughout the majority of the MILAGRO 2006 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 ppb. This might not be surprising, considering that the methanol average in the daytime was approximately 10 ppb and the boundary layer increased in height by a factor of ten during the day. There were two species in particular that displayed increases in their mixing ratios by a factor of ten or more during time periods ranging from 10–140 min during the nighttime and early morning hours. These species were toluene and ethyl acetate.

3.4.1 Toluene

Mixing ratios of toluene higher than 50 ppb were encountered for 14 of the 20 evenings that the PTR-MS sampled sequentially in single ion monitor mode. Table 1 summarizes the peak concentration, time of occurrence, duration, date and day of week pertaining to the toluene plumes with the ten highest magnitudes. It is evident that the elevated toluene plumes primarily occurred during the periods of light traffic activity in the region. Only one plume coincided with the typical morning high traffic times between 06:00–09:00 LT. The remaining 9 peaks happened between the hours of 23:00–06:00 LT and only one of these peaks happened during the transitional period from light to heavy traffic that occurred between 05:00–06:00 LT. Forty percent of these peaks happened during weekends and holidays.

Figure 4 displays a series of toluene plumes. The gaps in the measurements were attributed to the periods for collection of the instrument background. As an example, on 17 March 2006, a toluene plume occurred between 02:50 and 03:25 a.m., with a peak concentration approaching 230 ppb. It is worth noting that while PTR-MS measures the signal at a given mass and there are likely masses of different species contributing and

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complicating the assignment of the mass peak (Warneke et al., 2003; de Gouw et al., 2003a, 2003b; Fortner et al., 2004). Previous laboratory and field studies have evaluated the assignment of the mass 93 to toluene; a limited number of species (chloroacetone, α -pinene and β -pinene) have been found to fragment to mass 93 (Warneke et al., 2003; de Gouw et al., 2003a, 2003b). However, the Texas A&M measurements showed no indication of the presence of those species at the time of the plumes as their parent ions were monitored by the PTR-MS and found to be below 0.5 ppb in all cases. No other masses were found to rise in correlation with the mass 93 plumes, indicating that toluene appeared to be the only VOC within the plumes.

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^o of March featured winds from 221^o, 183^o and 246^o, respectively, and all had wind speeds close to 1 m/s. Three other cases featured variable wind direction over the course of the evening, making it difficult to attribute a direction of approach of the plume (8, 11 and 26 March). The 17 March case involved a low wind speed of 0.5 m/s, likely indicating a stationary plume over the measurement site. Hence, the plumes did not appear to have a common origin based on the varying surface winds during the plume events.

A second PTR-MS instrument was located at the IMP for a limited amount of times during the campaign, when the Aerodyne mobile research laboratory parked there and provided data for intercomparison purposes. There was only one major toluene plume that was measured during the time when the Aerodyne van was located at the IMP (6 March 10:00–7 March 10:00 LT, 27 March 21:00–30 March 09:00 LT). The plume which occurred in the morning of 7 March was measured by both instruments, as shown in Fig. 5. The Aerodyne van PTR-MS measured fewer masses enabling a faster measuring cycle of 10 s explaining the greater frequency of measuring points within the plume measured by Aerodyne. The brief peak at 244 ppb had a duration of only one cycle and obviously was not picked up by the Texas A&M PTR-MS with a measuring cycle of 76 s. With the exception of this single point the two instruments measurements

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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 the locations of the two instruments excluded the possibility of local source contamination at either one of the two measuring sites.

5 For the determination of whether the source of these toluene peaks were industrial in nature or related to vehicular emissions, one analytical technique of use was the comparison of ratios of aromatic compounds associated with vehicular use. The toluene/benzene ratio has been used to indicate the photochemical age of air masses with a major contribution from automobile emissions (Warneke et al., 2007), and this
10 ratio can change significantly within a industrial toluene solvent plume (Rogers et al., 2006). We analyzed the ratio of toluene to benzene in an attempt to identify the origin of the toluene plumes observed during the MILAGRO 2006 campaign as either vehicular emissions or industrial emissions. A vehicular emission plume was usually encountered during rush hour and characterized by a relative low toluene/benzene ratio but an industrial plume was normally observed during midnight and distinguished by a much higher toluene/benzene ratio. Figure 6 depicts the ratio of toluene with
15 benzene during the early morning toluene peak of 17 March as well as the peak which occurred around 07:00 LT on 7 March . Also shown in Fig. 6 are traces of toluene (red). Examination of the 17 March measurements shows clearly that the toluene plume is
20 accompanied by an increase in the toluene/benzene ratio, indicating a likely industrial toluene source. On the other hand, for the plume on 7 March, there was no significant increase in the toluene/benzene ratio and this peak was observed during morning rash hours, reflecting most likely a traffic plume.

25 When considering the relevance of these plumes to the overall air pollution problem in Mexico City, it should be recognized that toluene is sufficiently active considering its reactivity with regard to OH (Picquet, 1998; Molina et al., 1999; Suh et al., 2002; Suh et al., 2003) and at a high enough mixing ratio it will contribute substantially to ozone and secondary organic aerosol production (Zhang et al., 2004b; Suh et al., 2006). Most of these plumes were measured at night with the exception of the 7 March case,

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which was measured during early daylight hours before the boundary layer had risen significantly. Clearly, the sources and impacts of those nighttime toluene plumes as relevant to ozone secondary organic aerosol precursors need to be further evaluated in MCMA.

5 3.4.2 Ethyl acetate

A set of three masses (43, 61, and 89) 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 min to as long as 2 h periodically throughout the campaign. After post-field experimentation, it was determined that this signal, which was observed at masses 43, 61, and 89, was attributable to ethyl acetate. Ethyl acetate has the atomic mass unit (amu) of 88, leading to the proton transfer signal at 89. As revealed from calibration conducted with the PTR-MS in our laboratory following the MILAGRO field campaign, ethyl acetate was found to fragment to masses 61 and 43. Using similar tunings and pressures as 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. Thus, the concentration of mass 89 in this work has been adjusted to account for the fragmentation loss, as verified in our laboratory experiment. Previous studies which did not evaluate all VOCs but rather a limited number (Warneke et al., 2003) did not show any compound 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 ppb 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 2 summarizes the peak concentration, time of occurrence, duration, and 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 will allow for some insights regarding the

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source of the ethyl acetate plumes.

The top ten ethyl acetate peaks all happened during the early morning hours between 01:00—07:00 LT 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 LT when traffic generally switched from light to heavy and one of these four extended into the heavy traffic time period after 06:00 LT. 60% of the plumes occurred during periods of light traffic earlier than 05:00 LT.

A series of graphs depicting the temporal changes in mass 89 signals is displayed in Fig. 7 for the evenings during which these peaks took place. On all four 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 occurred. Examination of the meteorology conditions also revealed that during many of the ethyl acetate plume episodes when winds were light (<0.5 m/s) there was a tendency of the wind gauge to turn to approximately a 100° heading (which was a somewhat debatable measurement due to the low wind speed but nonetheless slightly skews the average wind direction). Therefore, it was concluded that these plumes likely originated from a specific area, which seemed to have been located at around a 230–260° heading from the IMP facility. It was 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 that 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 that were encountered on 29 March. Figure 8 shows the mass 89 measurement results of both instruments during the early morning hours of 29 March. 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

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data on the Aerodyne measurement. The two instruments detected the three separate peaks on that evening and the magnitudes of the three peaks were 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.

5 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 $(1.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ (Atkinson, 1994) which is approximately a factor of four lower than ethylene $(8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ (Atkinson, 1994). The peak that occurred at 06:00
10 on March 29 was observed within an hour of sunrise and was 183 ppb above the background level and would have been a significant source of ozone precursors.

4 Conclusions

A large number of ambient VOC concentrations were measured by a PTR-MS instrument on a rooftop in the urban mixed residential and industrial area North Northeast of downtown Mexico City as part of the MILAGRO 2006 campaign. The purpose of the
15 VOC measurements was to gain a better understanding of the type of VOC species present in the particular area of the MCMA, their diurnal patterns, and their origin.

The highest average VOC concentrations that PTR-MS measured were from methanol. Methanol peaks averaged approximately 50 ppb during the morning rush hour time period. Aromatics were the second most abundant class of species measured by PTR-MS with toluene, C_2 benzenes and C_3 benzenes averaging 26, 18 and 11 ppb, respectively, during the morning rush hour. The oxygenated VOC acetaldehyde was also found to peak at approximately 12 ppb on average during the late morning hours. Biogenic VOCs achieved a daily maximum of about a few ppb in the morning
20 hours, and decreased to several hundreds of ppt in the afternoon hours.

The diurnal patterns indicate that the highest mixing ratios of most VOCs were found between 06:00–09:00 LT and the VOC concentrations decreased as the boundary layer

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rose during the mid-morning timeframe. No afternoon VOC peak was observed. Aromatic VOC mixing ratios maintained a higher level on weekdays compared to weekend/holidays throughout the day indicating the influence of vehicular emissions. 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 ppb and had time durations varying from 10 min to 2 h. 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 one block West of the To 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 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 impacts of the toluene and ethyl acetate plumes relevant to ozone and secondary organic aerosol formation in this area need to be further assessed. Also, further work to integrate the present measurements with other VOC measurements conducted during the MILAGRO 2006 campaign is required to develop a better understanding of both the overall spatial pattern of VOCs in the MCMA as well as its variability.

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Table 1. Summary of occurrences of toluene plumes observed during MILAGRO 2006: The magnitudes, backgrounds (mixing ratios outside of the plume), wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the ten highest peaks.

Mixing Ratio (ppb)	Baseline (ppb)	Date (Mar)	Local Time	Duration (min)	Day	Wind Dir. (Degree)	Wind Speed (m/s)
229	12.5	17	02:53–03:35 a.m.	42	Friday	109	0.6
215	13.8	11	02:49–01:17 a.m.	28	Saturday	239	0.5
202	23	21	04:29–04:56 a.m.	27	Tuesday	246	0.86
191	20	12	01:53–03:18 a.m.	85	Sunday	183	0.96
185	8	26	11:22–11:57 p.m.	35	Sunday	215	0.6
177	7	9	11:13–11:34 p.m.	21	Thursday	221	1.08
142	19.5	8	01:14–01:31 a.m.	17	Wednesday	148	1.27
124	30	7	07:06–07:38 a.m.	32	Tuesday	N/A	N/A
124	26	31	04:26–04:39 a.m.	13	Friday	N/A	N/A
123	11	6	03:36–05:20 a.m.	104	Monday	N/A	N/A

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Table 2. Summary of occurrences of ethyl acetate plumes observed during MILAGRO 2006: The magnitudes, backgrounds (mixing ratios outside of the plume), wind direction, wind speed, time of occurrence, duration, date and day of week pertaining to the ten highest peaks.

Mixing Ratio (ppb)	Baseline (ppb)	Date (Mar)	Local Time	Duration (min)	Day	Wind Dir. (Degree)	Wind Speed (m/s)
202	19	29	05:51–06:14 a.m.	23	Wednesday	224	1
152	15	17	02:03–02:58 a.m.	55	Friday	236	0.74
142	10	16	03:32–05:44 a.m.	132	Thursday	232	0.65
142	27	29	03:41–04:19 a.m.	38	Wednesday	215	0.7
127	23	31	01:27–02:05 a.m.	38	Friday	N/A	N/A
125	27	31	04:21–04:47 a.m.	26	Friday	N/A	N/A
121	12	23	05:25–05:36 a.m.	11	Thursday	194	0.45
119	18	23	03:25–03:57 a.m.	32	Thursday	246	1.19
117	29	29	02:15–02:45 a.m.	30	Wednesday	241	1.06
102	25	21	05:04–05:20 a.m.	16	Tuesday	258	0.94

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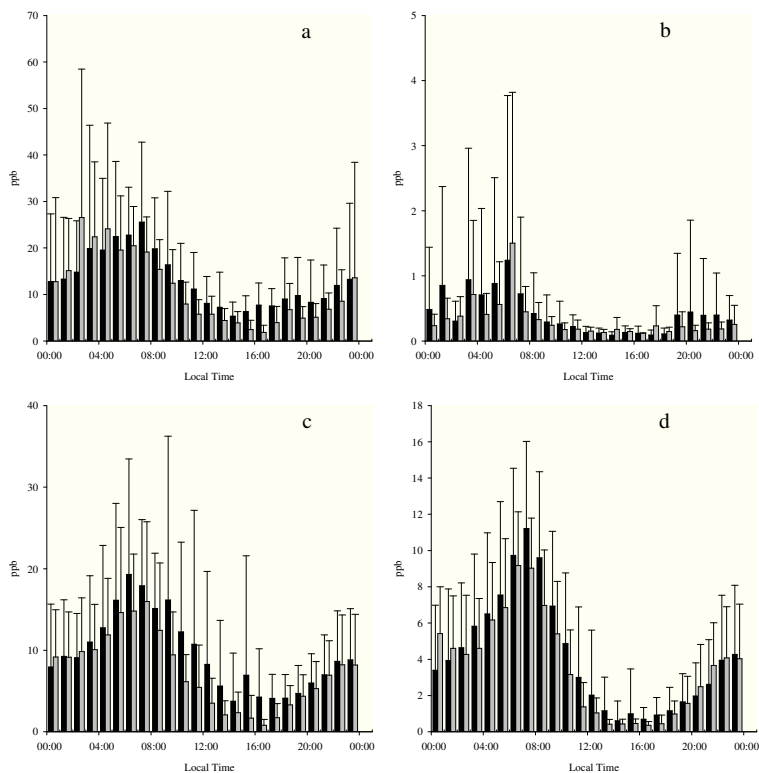


Fig. 1. The diurnal profiles of **(a)** toluene (m/e 93), **(b)** styrene (m/e 105), **(c)** C₂-benzenes (m/e 107), and **(d)** C₃-benzenes (m/e 121) for both week days (black) and weekend/holidays (gray).

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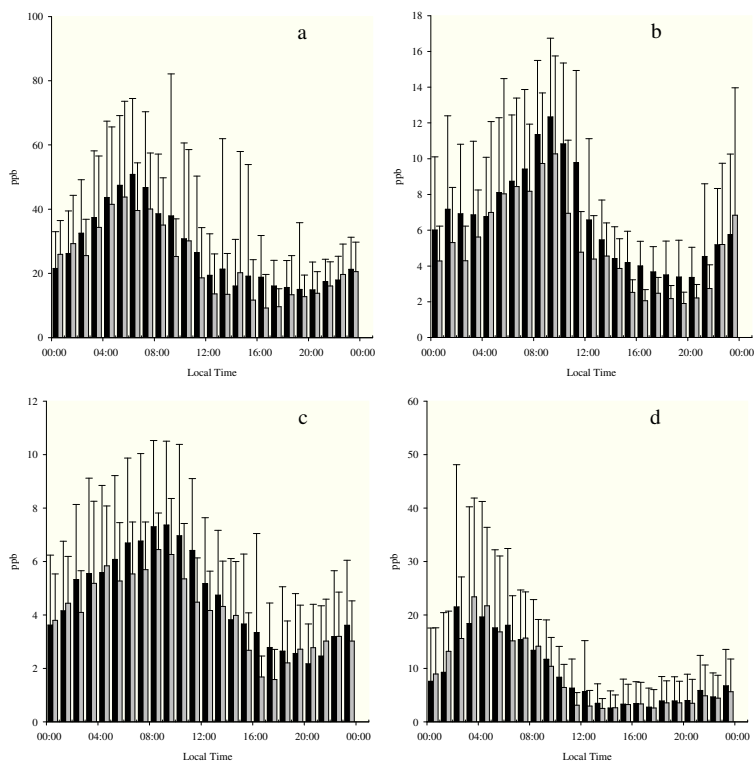


Fig. 2. The diurnal profiles of **(a)** methanol (m/e 33), **(b)** acetaldehyde (m/e 45), **(c)** methyl glyoxal + MEK (m/e 73), and **(d)** ethyl acetate (m/e 89) for both week days (black) and week end/holidays (gray).

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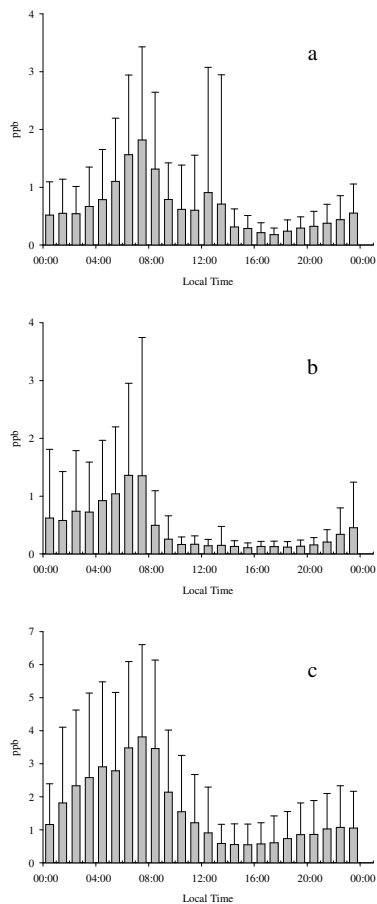


Fig. 3. The diurnal profiles of **(a)** isoprene (m/e 69), **(b)** monoterpenes (m/e 137), and **(c)** acetonitrile (m/e 42).

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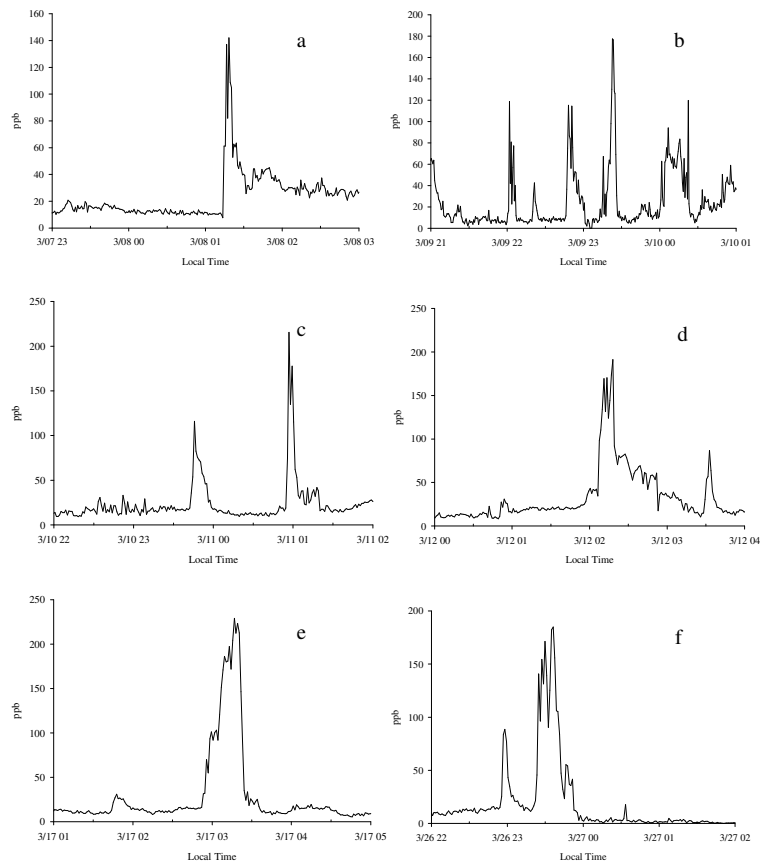


Fig. 4. Six overnight toluene plumes observed during the MILAGRO 2006 at T0 on 8 March (a), 10 (b), 11 (c), 12 (d), 17(e), and 27 (f).

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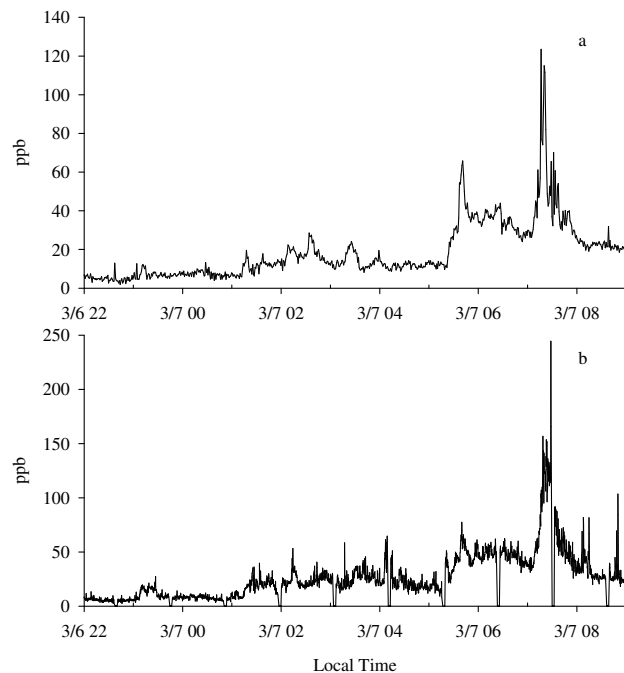


Fig. 5. Intercomparison of toluene observed at T0 **(a)** and on the Aerodyne Mobile Lab **(b)** on 7 March. Gaps in **(b)** were due to background checks.

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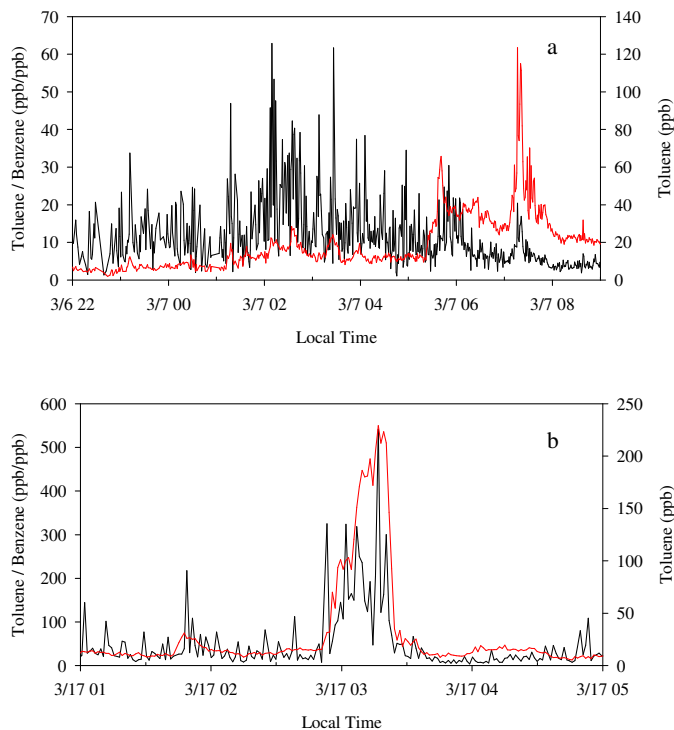


Fig. 6. Toluene (red line) and toluene/benzene ratio (black line) of **(a)** a morning traffic plume observed on 7 March and **(b)** a solvent plume observed on 17 March.

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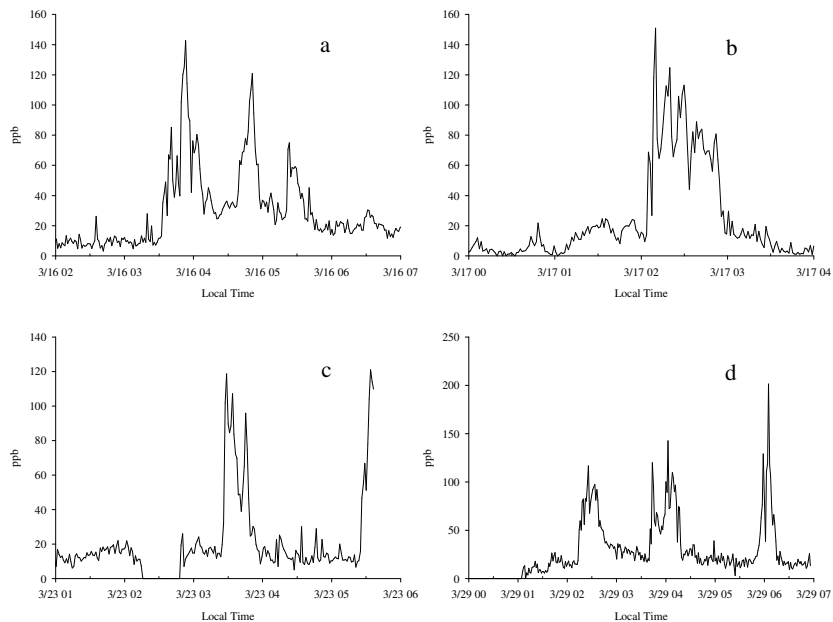


Fig. 7. Four ethyl acetate plumes observed during the MILAGRO 2006 at T0 on 16 March **(a)**, 17 **(b)**, 23 **(c)**, and 29 **(d)**.

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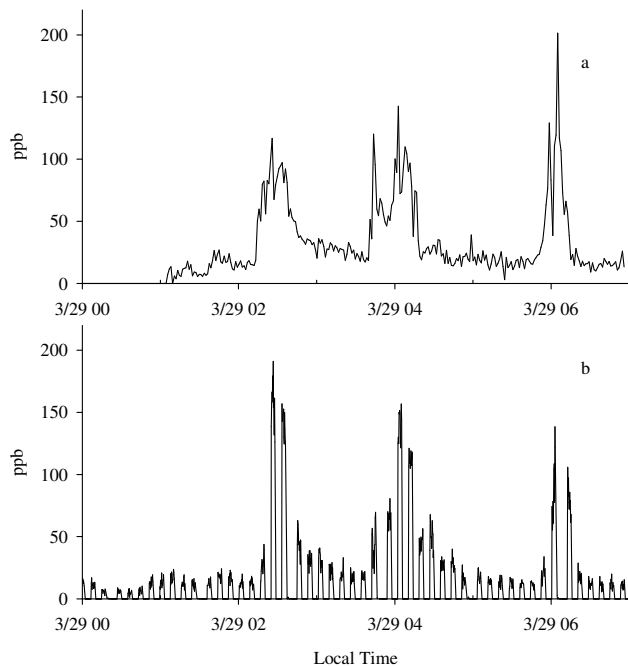


Fig. 8. Intercomparison of ethyl acetate observed at T0 **(a)** and on the Aerodyne Mobile Lab **(b)** on 29 March. Gaps in **(b)** were due to background checks.

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