

***Interactive comment on* “Measurements of volatile organic compounds using proton transfer reaction – mass spectrometry during the MILAGRO 2006 Campaign” by E. C. Fortner et al.**

Anonymous Referee #2

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The manuscript reports concentrations of a number of volatile organic compounds (VOCs) in ambient air measured using a PTR-MS technique at a downtown site in Mexico City during two periods, 3/5–3/23 and 3/26–3/31, as part of the 2006 MILAGRO field campaign. Based on 38 masses monitored sequentially at 2 sec each, concentrations of key VOCs including methanol (m/z 33), acetonitrile (42), acetaldehyde (45), isoprene (69), benzene (79), ethyl acetate (89), toluene (93), styrene (105), monoterpenes (137) were determined. Also determined were the sum of acetone, propanal and glyoxal from mass 59, of methyl ethyl ketone and methyl glyoxal from mass 73, C2 benzenes from mass 107, and C3 benzenes from 121.

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Hourly averaged concentrations of VOCs show marked diurnal variations with maxima in early morning hours and minima in the afternoon, mainly caused by traffic emissions in early morning before the inversion was broken up and dilution resulting from increased boundary layer depth during the day. The maximum concentrations and the time they occurred were further examined by dividing the data into two categories, weekdays (WD) and weekends/holidays (WEH). Oxygenated VOC such as acetaldehyde reached their maxima later than did VOCs such as toluene, indicating the oxygenated compounds are also produced as photooxidant products. The observation that levels of methanol and C2 benzene during evening hours were lower on WEH but not toluene and ethyl acetate suggests that the latter compounds have sources other than tailpipe emissions.

Nighttime plumes of high concentrations of toluene and ethyl acetate that were greater than background values by a factor of 10 were intercepted with durations varying between 10 to 140 min. Using toluene/benzene ratios associated with the plumes, the authors argue the night time toluene plumes were of industrial origin. However, no additional information was provided to support that ethyl acetate plumes were due to industrial activities other than showing the timing of the occurrences were distinct from the early morning traffic emissions.

Overall comment: Measurement of selected VOCs using a PTR-MS techniques was conducted at an important site as part of a very large field campaign, providing potentially important data on speciated VOC in terms of concentrations, contributions to photooxidant formation, and, most importantly, sources. The time coverage and number of compounds measured are both substantive making this work important. In addition, the authors have demonstrated that the measurement work was performed with care regarding back ground characterization, signal calibration, and mass-compound assignment. However, the manuscript is weak in several areas: stating a major objective and achieving it, comparing with measurements that were made simultaneously and previously to cross check and to validate the data; and identifying the possible

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sources of the measured VOC compounds. This reviewer suggests that additional information be added to improve the scientific content of the manuscript for consideration for publication.

Some specific comments and suggestions are given below.

1. Objectives and implications of the VOC speciation and concentrations determined by the PTR-MS technique.

In the introduction, the authors give some motivations for making good VOC measurement for Mexico City as to help narrow the gaps between the measured and predicted quantities such as the VOC to NO_x ratios. An objective is also given as to "better elucidate the VOC emissions and chemistry in Mexico City area." Unfortunately, it didn't appear that these objectives were being fulfilled or addressed adequately. I feel the authors need to provide a more insightful analysis of the sources (which is discussed below) and the photochemical reactivities of the VOCs to reveal if the VOC mix of Mexico City is distinct or similar to that of other major urban areas regarding O₃ and aerosol production potential. While the PTR-MS technique is capable of rapidly determining quite a number of VOC's, with good sensitivity especially toward the unsaturated, it cannot detect many VOCs, mainly the saturated hydrocarbons. The authors might want to articulate on why this technique is beneficial for ground measurement, and the implications of the PTR-MS data having high a high temporal resolution.

2. Comparison with VOC data reported previously and collected during the same campaign.

It was mentioned in the manuscript that VOCs were also determined at the same TO site with a number of other techniques including canister-GC and DOAS. If the VOC data collected using these techniques are available, effort should be made to examine the agreement between the PTR-MS data and those obtained with the other techniques. The PTR-MS technique is relatively new, and determines compounds based primarily on parent ion masses, comparison with other techniques is needed to obtain

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corroborative evidence whenever possible. Although the PTR-MS technique has been characterized for many commonly observed VOCs in early works, and the authors have shown that they have exercised care in assigning the major compounds responsible for a given mass, there remain the possibilities of compounds not previously observed that could interfere with the identification. If this possibility exists at all, the Mexico City area is a prime candidate because of elevated emissions from a plethora of sources in this megacity.

Comparison of the present PTR-MS results with previously reported VOCs in urban areas in the form of ratios involving benzene, toluene, C2 and C3 benzenes should also be made to reveal the reliability of the PTR-MS technique both in its assignment and quantification, and perhaps to contrast urban VOC mix characteristic between Mexico City and other major cities in North America.

3. Source Identification

The analysis of possible sources of the measured VOCs should be augmented. Even though the authors have tried to identify the major VOCs that can be attributed to four different sources: vehicular, industrial, biogenic, and biomass burning, based on their diurnal variation patterns divided into the two categories of WD and WEH, the analysis is vague and incomplete. Some questions and suggestions follow.

First of all, it should be clearly stated why the data are divided into the two categories of WD/WEH, and what differences are expected of these categories based on previous studies. Is vehicle usage known to be different in volume/mileage or the timing, or both? How about industrial emissions? Do they have different emission patterns because the industry also operates on a weekday/weekend basis? Or do they operate on a 24/7 basis? Without such a priori knowledge, the analyses are not well constrained.

By stating that methanol has a similar diurnal trend as acetaldehyde and MEK/methyl glyoxal, are the authors implying methanol is a photochemical product in addition to be among primary emissions from vehicles? Previous studies have shown methanol to be

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mainly governed by biogenic sources, and has it been identified to be also emitted from vehicles? If a finding is new and contradicting previously established understanding, it behooves the authors to provide convincing evidence to support their contentions.

Acetonitrile is a biomass burning marker which is derived not only from the episodic forest/vegetation fires that were either unintentional or prescribed, but also from the use of biomass fuels in populated areas. The latter is consistent with the observation that acetonitrile was building up during the night. The description of the diurnal pattern of acetonitrile, which is similar to essentially all other VOCs, of being "was likely controlled by the physical mixing processes" is too vague. It seems that the authors have only considered the "fire" episodes as they stated that "..several biomass burning events were visually identified", and then attributed the "normal looking" diurnal pattern to the physical mixing. The authors should consider the urban sources of this compound and try to explain its diurnal variations accordingly.

Isoprene has been identified to be a minor component of tailpipe emission, and has also been found to be a fugitive gas from petrochemical plants in Houston, the authors should try to assess the importance of these sources as well as that of biogenic emissions.

Since monoterpenes react rapidly with O₃, the accumulation of these compounds during the night may reflect a situation where O₃ has been depleted by NO. It will be informative to also report O₃ concentrations along with that of monoterpenes.

The use of concentrations of CO and NO_y to gain insights into the sources of the measured VOCs is mandatory. Vehicular emissions, and other combustion sources, contain CO concentrations significantly higher than that in industrial emissions such as that of solvent plants. Consequently, if the authors' contention is correct that they are derived from industrial emissions, the ratios of toluene and ethyl acetate to CO in those nighttime plumes should be significantly greater than that exhibited during morning rush hours which mainly reflect vehicular emissions.

Nighttime inversion makes mixing a slow process; emissions can be localized and undiluted for extended periods giving rise to high concentrations especially under low wind speeds of 1 m/s and less reported here. Despite the apparently high concentrations in these plumes, the sources responsible for these plumes may or may not represent important sources of these compounds. Other than inspecting CO levels in the plumes to rule out combustion origins, the importance of these compounds should also be investigated perhaps using the toluene/benzene ratio which the authors have used to differentiate "industrial" sources from vehicular emissions. If the daytime ratios of toluene to benzene are significantly increased over that observed during the rush hours dominated by traffic emissions (note toluene reacts with OH more rapidly than benzene), then one could argue for the importance of industrial contributions to these compounds in the region.

The authors should also make an effort to identify the types of industry that use these chemicals, and whether the releases may be accidental or on a regular basis. Attempts should also be made to identify the sources of the toluene and ethyl acetate plumes using air back trajectory calculations that may be available from the MILAGRO project.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 11821, 2008.

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