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Atmospheric Chemistry and Physics Discussions

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.

E. C. Fortner et al.

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We are very grateful for the suggestions by this referee. The specific comments are responded below.

(1) "Objectives and implications of the VOC speciation and concentrations determined by the PTR-MS technique"

Generally, we agree with the referee's comments regarding PTR-MS technique. Several sentences have been added in the introduction to reflect the advantages of this method. In this manuscript, the primary objective is to present the general characteristic of VOCs at T0 site during the campaign. A detailed analysis of the origins of the VOC plumes, their reactivities, and implications in ozone and SOA formation will be

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needed in a future work, including calculations using chemical transport models.

(2) "Comparison with VOC data reported previously and collected during the same campaign"

We have included VOC intercomparison of our PTR-MS measurements with those from DOAS co-located at the T0 site and from another PTR-MS instrument on the Aerodyne mobile van available to us. The results show good agreement in the VOC measurements between ours and the others. We have now indicated that 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 ratio can change significantly within a industrial toluene solvent plume (Rogers et al., 2006). We found the toluene/benzene ratio was often larger than 5, and we suggested that the T0 site was affected by industrial emissions.

1) "Source Identification"

We have now stated that traffic conditions in the MCMA area were visually lightened during weekends or holidays, but industrial facilities in this region typically operated on a basis of twenty-four hours a day and seven days a week.

We have now stated that for methanol its diurnal profile was consistent with other OVOCs. It is possible that those OVOCs shared some similar formation mechanisms. Because vegetation is scarce within the city, especially in the northern portion, the biogenic components are negligible in the city. On the basis of the present measurements, it was rather inconclusive on the contribution of automobile emissions to the methanol observation.

We agree with the referee that acetonitrile was not only from biomass burning in the form of forest/vegetation fires but also from the domestic usage of biomass fuels, which is commonly used within the city. We have pointed out this feature in the manuscript. We also have corrected our acetonitrile measurements to remove interferences from

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mass 43.

We agree with the referee that isoprene was mainly originated from automobile emissions, since vegetation is very scarce within the city, especially in the north sector. This is also consistent with early findings in MCMA 2003 campaign. We have corrected the manuscript accordingly.

Indeed, ozone was depleted during nighttime by overwhelming NO emissions. This information has been included in the manuscript to support our monoterpene observations.

We agree with the referee that the VOC/CO ratio could provide valuable information regarding to the emission sources. However, CO measurement at T0 was not available. Thus, we cannot perform this analysis.

We agree with the referee that nocturnal PBL is more stable and make air pollutants easier to accumulate. Thus most highly elevated VOC plumes were encountered at nighttime. The toluene/benzene ratio was frequently higher than 5.0 during the campaign. Therefore, we believe the T0 site strongly affected by industrial sources. However, Figure 6a (now Fig. 7a) shows both industrial and traffic sources present around the IMP site. It clearly shows that the toluene plume was first dominated by industrial sources during the midnight and then gradually changed into a traffic emission dominated plume as the toluene/benzene ratio decreased from around 60 to about 5 at 8:00 am LT. Those points have been reflected in the revision.

We appreciate the suggestion made by the referee that it is important to identify the industry type responsible for the particular VOC emissions and their emission patterns are crucial to evaluate their impact on the VOC emission inventory within the MCMA. In this paper, we focus on the general characteristic of VOCs observed by PTR-MS at T0 site. One of our future studies will be conducting further analysis of the source origins using back trajectory calculation and VOC reactivities and their roles in ozone and SOA formation using simulations with chemical transport models.

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