

## ***Interactive comment on* “Emissions of volatile organic compounds inferred from airborne flux measurements over a megacity” by T. Karl et al.**

**Anonymous Referee #2**

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This paper describes the first airborne flux measurements of benzene and toluene, which were conducted over Mexico City during the MIRAGE-Mex campaign. Fluxes were determined using the disjunct eddy covariance technique using a PTR-MS instrument. The resulting fluxes are compared to the emission inventories CAM01 and CAM04 and indicate higher emissions than expected from the inventories. Furthermore source profile ratios and observed ratios were used to determine the emission sources for aromatic compounds and it was found that benzene and toluene are mainly emitted by vehicle exhaust followed by evaporative and industrial sources and to a lesser extent by burning activities. The data and analysis presented here about VOC emissions and source contributions are very relevant and important for the understanding of the air quality problems of Mexico City. The paper is clearly organized and well written, but

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I have some comments that need to be addressed.

- The uncertainties of flux measurements from the aircraft strongly depend on the accurate determination and the actual height of the boundary layer (BL). The discussion of the BL height determination in the paper is rather short. The BL height in Mexico City is changing very rapidly during the day and therefore it is important to state the time of day of the overflights for each research flight. The method of determining the BL height is also not given. Was that done with measurements on the flown profiles or taken from the Shaw et al paper? Especially the Shaw et al paper only shows data starting on April 5 and RF1 took place April 4. Also check the reference, it is Shaw et al 2007 not 2006.

- The fluxes resulting from this work indicate that benzene and toluene emissions are somewhat underestimated in CAM01 and CAM04. The ground-based measurements in an urban area during 2006 do not suggest an under-prediction. Does this mean that especially the industrial sources in CAM01 and CAM04 are under predicted? A more detailed discussion is needed on the distribution between urban and industrial sources during the overflights and on the discrepancies with the ground-based measurements.

- My main issue with this paper is the basically non-existing documentation of the regression model calculations. The model is described in detail and then only the results are given, but no explanation of how those results were obtained is presented. The conclusion that the concentrations of aromatic compounds is basically not influenced by biomass burning, but the result of exhaust and industrial emissions is very important and could possibly be in contrast to at least some previous results, such as Yokelson et al 2007 and deCarlo et al 2007. It would be important to show the correlation plots of the aromatics with MTBE and acetonitrile and document the quality of the regression that determines the source fractions. It is also important to bring the source contributions of the aromatics in context with other trace species. Does the small influence of biomass burning on aromatic compounds mean that there was no biomass burning influence for all other species or is this only valid for aromatics?

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Minor comments:

- Please check the references. There are some spelling mistakes, wrong dates and references missing in the list. - page 14278: The updated PTR-MS review paper should be added, this paper also gives a summary of the PTR-MS inter-comparisons. - page 14281: Is it possible to calculate the uncertainties for shorter legs as well, separated into the industrial and urban segments of the flight? - page 14287: The NMHC reactivity in Mexico City is not necessarily the main contributor to the total reactivity in the afternoon, which might be driven by compounds like formaldehyde and acetaldehyde. Please clarify which compounds are part of the &#8216;total observed NMHC&#8217; or use the total reactivity. - page 14289: please add references for the uniqueness of acetonitrile and MTBE as tracers (Millet et al 2004 and de Gouw et al 2003) and the exhaust emissions from acetonitrile (Holzinger et al 2001)

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 14273, 2008.

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