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Atmospheric Chemistry and Physics Discussions

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

T. Karl et al.

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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.

Response: We will include actual times during city overpasses - our PBL heights were based on measurements conducted by Shaw et al. (2007). Measurements were con-

ducted in March 2005. Shaw et al. (2007) measured PBL heights from March 5 on, but only concentration measurements were conducted during RF1. For all flights where DEC measurements are reported, PBL heights are based on experimentally determined values reported by Shaw et al. (2007).

- 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 over flights and on the discrepancies with the ground-based measurements.

Response: We will expand the discussion on differences between ground and airborne measurements and also put these in context of a new emission inventory, which has just been released for 2006 (see detailed response to reviewer 1). Flux measurements are subject to a much smaller footprint than concentration measurements. Differences between ground and airborne flux measurements therefore reflect differences in their footprints. For example typical footprints of ground based flux towers are on the order of 100s of meters. Median fluxes measured on the C-130 are within ˜30% of the adj. CAM04 emission inventory. The adjusted CAM04 toluene emissions are comparable to a new emission inventory (SMAGDF, 2008) which has just been released. Our measurements indicate that emissions along the city transect were significantly higher than suggested by the CAM01 and the CAM04 emission inventory. However they appear to be within the uncertainty when compared to the adjusted CAM04 and the SMAGDF emission inventory. We will add a table comparing various emission inventories with our measurements in more detail and remove figure 6. Emissions according to the EDGAR database, which are low compared to the SMAGDF inventory, will also be added. The relative apportionment between urban (mobile exhaust) and industrial (area/point) sources between our regression analysis and the latest emission inventory for toluene (SMAGDF) is in reasonable agreement and will also be included

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in a table.

- 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?

Response: We realize that more discussion on the regression model will help clarifying our point on the influence of biomass burning for BTEX compounds. In a revised manuscript we will add a column listing slopes of the actual regressions obtained from the data. We will also clarify Table 2 and list best estimates of source emission ratios that were compiled from a literature review (rather than giving the total range). In this context (also in response to Erik Velasco) we note that source emission ratios for C2-benzenes in our original manuscript were not reported correctly. This will result in a revised regression for C2-benzenes showing a higher contribution from exhaust emissions than previously calculated. This change however does not influence our conclusion on the impact of biomass burning. Regressions were based on a robust (=x/y weighted) regression model using iteratively reweighted least-squares. Rather than adding another figure we propose to list the correlation coefficient for each VOC pair as a measure of how well they correlate with respect to MTBE and CH3CN. Observations clearly indicate much better correlations between MTBE and BTEX compounds than between CH3CN and BTEX compounds. For example the correlation coefficient

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between CH3CN and benzene is 0.37 compared to a coefficient of 0.82 between MTBE and benzene. Here we mainly focus on BTEX compounds. The C-130 dataset contains evidence that biomass burning exerts some influence on the distribution of BTEX compounds (e.g. up to 13% for Benzene). The question whether the fraction is large enough to play an important role for other trace gases is interesting but goes beyond the scope of the present manuscript. Our approach shows that MTBE and CH3CN can provide useful tracers to constrain urban vs biomass burning emissions. We note that Yokelson et al. (2007) estimate that about 20% of CO originates from fires in the MCMA. Another paper on the distribution of PAN type compounds is in preparation and will investigate the influence of biomass burning on these compounds. Preliminary results show little influence of biomass burning above 1 ppbv ambient mixing ratios (Flocke, personal communication).

- 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 “total observed NMHC” 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)

Response: We will add recommended references and correct typos. The uncertainty for shorter flux flight legs can be assessed based on eq. 6. Due to the limited flux dataset we can not accurately apportion the flux data into "industrial" and "urban" components. This would only be possible with a more extensive flux dataset. Emission sources are also co-located throughout the city; we believe that a more accurate way

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for apportioning urban and industrial emissions can be achieved by the tracer correlations presented in section 3.3. We agree that oxygenated compounds can add a significant amount of reactivity to the urban VOC mix. We will clarify that the total observed NMHC reactivity was based on a dataset containing only primary hydrocarbons available from canister sampling which included the most abundant (38) NMHC species. A paper by Apel et al. is in preparation and will specifically investigate the influence of oxygenated VOCs on the total reactivity. We will reference the fraction of BTEX reactivity relative to the total observed VOC reactivity in a revised version of this manuscript.

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