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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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1) During the same field campaign in March 2006 flux measurements of benzene and toluene using a PTR-MS and the DEC technique were conducted in a busy urban district close to the center of the city, referred as T1-2006 in this paper (see Figs. 1b and 5). The measurements were made above the urban canopy at 42 m of height. The average toluene and benzene fluxes at midday were 4.9+-1.0 and 0.5+-0.2 mg m-2 s-1, respectively. The fluxes reported by Karl et al. are 3.2 and 9.3 higher. Considering the highest peaks from the tower-based measurements, the airborne toluene and benzene fluxes are still 1.4 and 3.7 higher, respectively. Direct comparisons of the measured fluxes at ground level with the 2006 emissions inventory (SMAGDF, 2008) indicate that the predicted emissions in the inventory for the analyzed species (CO2, olefins, C2-benzenes and methanol) and specific district of the city, in general are in

good agreement, and do not support an under-prediction hypothesis. In addition, the results from the ground level fluxes are consistent with those of Lei et al. (2008), who by indirect comparisons between modeled and observed VOCs mixing ratios determined that the city-emissions of aromatic compounds need to be adjusted by factors from 1.1 to 1.5 depending on the compound. The authors need to investigate the reasons for these discrepancies in order to demonstrate the usefulness of aircraft flux measurements to address the emissions spatial distribution in a city. They need to review also if their measurements in fact represent the toluene and benzene emissions from the entire city.

Response: We agree with the reviewer that the C130 flight legs across MCMA were conducted above the Northern part of the city and therefore reflect emissions over an industrialized area. We will state that these measurements only reflect emissions over this part of the city. The flux footprint needs to be considered in this discussion and is illustrated by the size of the circles in figure 5. Confining emissions along our flight track improves the comparison between flux measurements and emission inventories. When comparing ground based flux measurements to airborne fluxes it also needs to be recognized that the flux footprint on the ground is typically only 100s of meters during daytime. The mentioned ground based fluxes of 4.9+-1.0 and 0.5+-0.2 mg m-2 s-1 for toluene and benzene would result in a toluene/benzene ratio of 9 (g/g); this is a factor of 3-4 higher than typical emission ratios expected from urban / exhaust emissions. Considering fairly heterogeneous surface emissions over a city as recognized by the reviewer our results are not necessarily at odds with their earlier findings. It is also noted that for aromatic compounds (and only these are considered here) Lei et al. (2008) report a significant underestimation of emissions (e.g. 50% see their Table 2, ARO1 and ARO2) and would therefore support our findings that emissions of aromatic compounds are underestimated in the CAM04 emission inventory. We also performed detailed model analysis using WRF-CHEM. These model results independently demonstrate that emissions of toluene and benzene are underestimated. For example, modeled toluene concentrations using the CAM2001 emission inventory shown

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in Figure 7 (left panel) are significantly lower than measured toluene concentrations (e.g. by 70%). Based on the adjusted CAM2004 emission inventory (right panel) the model/measurement comparison for toluene concentrations improves, but the model still tends to underpredict toluene concentrations (e.g. by 32%). These findings are qualitatively similar to Lei et al. (2008) and give some independent means for assessing the validity of our flux measurements. Both suggest higher emissions of toluene. The fact that our toluene/benzene flux ratio (3.2 g/g) reflects typical urban emission ratios supports the idea that measured airborne fluxes are internally consistent with expected urban emission ratios. We do not know the reason why the ground based flux ratio of toluene to benzene is so high (e.g. 9 g/g), but these results would argue for a significant underestimation of toluene fluxes in the emission inventory. The SMAGDF inventory predicts an annual toluene emission of 45351 t/y. Assuming daytime fluxes on the ground of ˜5 mg/m2/h (emitted over 8 hours according to a typical diurnal cycle reported by Velasco et al., 2007) and extrapolating this value to the whole basin (˜1290 km2), the yearly total toluene emission would amount to ˜18800 t/y (˜41% of SMAGDF); it is argued that ground based measurements agree with the SMAGDF inventory. Assuming this is correct it also suggests that the mean daytime toluene flux over T-1 is below the city average. Airborne fluxes provide an emission snapshot during this study over a large portion of the city; the average toluene flux measured on the airplane is within ˜30% of the adjusted CAM04 emission inventory. This is within the uncertainty stated for our flux measurements. Since toluene emissions in the adjusted CAM04 emission inventory and the SMAGDF inventory agree to within 20%, we can conclude that airborne flux measurements are within the range predicted by the newer SMAGDF inventory. The difference between ground based and airborne flux measurements can therefore be explained by the fact that different parts of MCMA were sampled. We will include a new table summarizing the comparison between 5 emission inventories (EDGARv2, EDGARv3.2, CAM2001, adjusted CAM2004 and SMAGDF, 2008) and put this in context of the above discussion. In particular we will clarify our statement on what area of the city was sampled by the aircraft. We conclude that our flux measure-

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ments are within the range predicted by the adjusted CAM04 but suggest that older emission inventories significantly underestimate emissions.

2) The evolution of the convective boundary layer (CBL) in Mexico City is different from other places. It passes from 200 m at 7:00 h to 600 m by midday, then it grows rapidly reaching heights of 3000 m or more within the next two hours. This has been determined from previous studies (see Whiteman et al., 2000; Velasco et al., 2008b). Therefore, the heights being considered (3000 and 3600 m) during the flights could not possibly be consistent if the measurements were conducted at noon. However, if they were conducted within the next couple of hours, those heights could be correct. A table with the flights schedules would help to solve this uncertainty.

Response: Rather than using observations from previous studies, we base PBL heights on actual measurements conducted in 2006. (see Shaw et al., 2007, this issue). Shaw et al. (2007) measured PBL heights up to 4000m during MIRAGE-MEX. On average (during Mirage-MEX) they observe a PBL of 1200m at LST, which would already be a factor of 2 larger than suggested in the comment above. The onset of the evolution of the PBL on each individual day however can vary quite a bit. During C-130 city transects (typically conducted between 20 and 22 UTC) PBL heights (see Shaw et al.,2006) were measured between 2500 and 3600 m. We are therefore quite confident that PBL heights used in our analysis are accurate. We will include approx. times of city transects in a revised manuscript if accepted.

3) According to the equations used to calculate the systematic and random errors, a lower CBL results in smaller errors in the airborne fluxes. As a consequence, if the CBL heights are overestimated, the errors will decrease, and both types of errors will depend on the flight length. In this sense, if the land-use is heterogeneous in terms of emissions sources, such as Mexico City, the entire flight track cannot be used to estimate the errors, and shorter lengths will bring about an increase in errors.

Response: We do not believe that PBL heights were underestimated as outlined in

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response to comment 2). We will clarify issues on the systematic flux error using a sub-segment of each flight based on eq. 6. For example the systematic flux error for a flight segment of 5 km would be 12%. We also note that systematic errors result in a lower limit of our measured fluxes.

4) According to the flight trajectories depicted in Figures 1b and 7, the measurements were conducted mainly over the northeast sector of the city, where the greater number of heavy industries are located (see Fig. 4.1.1, page 67 of the 2006 local emissions inventory; SMAGDF, 2008). This could jeopardize the representativeness of the toluene and benzene fluxes presented here.

Response: We agree that measurements conducted onboard the C-130 were conducted across the more industrialized part of MCMA. This will be clarified in a revised version. The toluene/benzene flux ratio gives some indication of industrial influence. It is true that flux measurements are only representative within the given flux footprint (in our case shown by the size of circles in Figure 5). It is noted that this would apply even more so at a ground based flux site due to a rather limited flux footprint (typically only a couple of 100 meters during the daytime).

5) Benzene contribution from vehicle exhaust obtained from the source contribution analysis is low when compared to other studies in Mexico City and other urban areas (i.e., Fortin et al., 2005; Barletta et al., 2005; Velasco et al., 2007a), as well the local emissions inventory (SMAGDF, 2008). In the same context the C2-benzenes contribution from fuel evaporation and industry is very high.

Response: We believe that MCMA has its unique VOC mix; differences to US cities (eg.. Fortin et al.,2005) or Chinese cities (Barletta et al., 2005) can be expected and do not necessarily invalidate our findings. Velasco et al. (2007) report concentration ratios at different locations in MCMA based on ambient measurements. They assign industrial, rural and urban labels to VOC ratios (Table 4, 6) measured in different parts of the city. It is noted that any of these locations probably consisted of a mix of dif-

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ferent sources (e.g. more industrial and less urban or more urban and less industrial influence). It is hard to assign these VOC concentration ratios to City wide emission ratios. Observed concentrations ratios are a linear combination of all source ratios at any location in the City. A chemical mass balance model would therefore be required to quantitatively compare our results to Velasco et al. (2007). Our analysis is based on emission ratios reported for different source types as outlined. Due to similar emission ratios for evaporative gasoline and industrial emissions we were forced to lump these two source categories. However we realized that some values (in particular for C2-benzenes) listed in table 2 were not converted correctly; we reanalyzed VOC ratios with respect to revised emission ratios. Our revised lumped source profiles for exhaust and industry for C2 benzenes and benzene changed accordingly - in particular C2-benzenes agree better with work cited by the reviewer. Our main point however does not change and demonstrates that biomass burning emissions of aromatic compounds probably play a comparably small role in MCMA.

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