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

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General comments

It is only in the past decade that eddy covariance (EC) techniques started to be used to measure fluxes of trace gases from urban footprints. Up until now all of these measurements had been made at ground level using tall towers. Karl et al. presents the first airborne flux measurements of volatile organic compounds (VOCs) over a severely polluted urban region. Fluxes of toluene and benzene were measured by the disjunct eddy covariance (DEC) method and a proton transfer reaction mass spectrometer (PTR-MS) placed in the NCAR-C130 aircraft during the MILAGRO field campaign in March 2006 in Mexico City. The experiment demonstrated the feasibility of EC measurements from an aircraft flying over a city. The flux measurements were compared to the local emis-

sion inventories from 1998 and 2002 (base years), finding that the predicted emissions of toluene and benzene are underestimated. This result is opposite to the findings from EC fluxes of selected VOCs and CO2 measured at ground level in two residential districts of Mexico as part of the MCMA-2003 and MILAGRO field campaigns (Velasco et al., 2005; 2007b). Both studies showed that generally the emissions of those species in the inventory are correct; even the toluene fluxes measured in 2006 suggest that the toluene emissions in the inventory are slightly over-estimated. This discrepancy may arise from the monitored sector of the city by Karl et al., which corresponded more to the industrial than the residential area of the city. A second concern is the height at which the flights were made, which is just few meters lower than the boundary layer height reported in previous studies during midday in Mexico City (Whiteman et al., 2000; Velasco et al., 2008).

Specific comments

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

ACPD

8, S5704–S5709, 2008

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.

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.

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.

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.

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

ACPD

8, S5704–S5709, 2008

emissions inventory (SMAGDF, 2008). In the same context the C2-benzenes contribution from fuel evaporation and industry is very high.

Technical corrections

1) Page 14274, Line 26: Volkamer instead of Volkhamer.

2) Page 14275, Line 8: See Wenfang et al. (2008) for further discussion above the VOC versus NOx sensitivity for ozone production in Mexico City.

3) Page 14275, Lines 27-29: It must be: Their work was contrasted by Velasco et al. (2005) who argued that the urban emission inventory for Mexico City was generally consistent with their eddy covariance flux measurements.

4) Page 14276, Line 17: (Karl, 1999) is missing in the reference section.

5) Page 14278, Line 16: (Lindinger et al., 1998) is missing in the reference section.

6) Page 14280, Line 10: The 1998 emissions inventory for Mexico City was published by the Comisión Ambiental Metropolitana (CAM) in 2001, and the 2002 emissions inventory by the same agency in 2004. With the aim of avoiding confusion in regard to the years, we suggest referring to them as 1998 and 2002 emissions inventories, instead of CAM01 and CAM04.

7) Page 14280, Line 12: (Guenther et al., 2006) is missing in the reference section.

8) Page 14281, Line 2: The sentence "At 5 m/s wind speeds this would relate to spatial scales of 9" is not completely clear within the text. According to Mann and Lenschow (1994), the indicated spatial of 9 km refers to the sample length if the measurements were made by EC in a tower at ground. Is this correct?

9) Page 14281, Line 8: The DEC acronym was defined previously in page 14276, line 16.

10) Page 14285, Line 6: Same as comment 6.

ACPD

8, S5704–S5709, 2008

Interactive Comment

11) Page 14285, Line 18: Note that the toluene/benzene ratio of 8.8 is in ppbC/ppbC.

12) Page 14286, Lines 6-7: It must be: 19°29'97"-19°49'85" N and 99°26'67"-98°88'93" W.

13) Page 14286, Line 23: The toluene mixing ratio of 70 ppbv reported for T0 is extremely high for midday. Concentrations above 30 ppvb are only observed during the morning rush hour. At midday concentrations below 15 ppbv are expected.

14) Page 14287, Line 26: Same as comment 11, the toluene/benzene ratio of 4.9 is in ppbC/ppbC.

15) Page 14288, Line 9: Must be Andreae and Marlet, 2001.

16) Page 14292, Line 1: Remove "bibitem"

17) Page 14294, Lines 20-29: Review the alphabetic order.

18) Page 14302, Fig. 1b: To better observe the flight tracks and ground sites in the map the panel should enclose a smaller area, similar to the area depicted in Fig. 7.

19) Page 14304, Fig. 3: To be consistent with the text, the legend in the bottom panel should indicate the bandwidths as 0.1-32 s and 0.1-64 s.

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ACPD

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Interactive Comment

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