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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Eddy covariance flux measurements of pollutant gases in urban Mexico City" *by* E. Velasco et al.

Anonymous Referee #1

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The manuscript describes eddy covariance flux measurements of a suite of VOCs and CO2 in an urban environment. Measurements conducted in 2006 are compared to an emission inventory and an earlier study in 2003. The main conclusion of the paper is that bottom-up emission inventories are consistent with VOC flux measurements, with the exception of methanol. The paper merits publication in ACP after addressing the following comments:

Page 7998, line 23: It is noted that olefin fluxes inferred from the FIS instrument have to be adjusted by a factor of 2. This adjustment factor could change depending on the ambient composition of olefins. The authors argue that after adjusting the FIS signal by a factor of 2 their flux measurements support findings by Lei et al. 2008, who have reported a significant underestimation for some olefins. This conclusion seems to be

at odds with the introductory statement (page 7994, line 15), where it is mentioned that conclusions by Velasco et al. (2005) were 'corroborated by ozone modeling studies by Lei et al. (2007, 2008a).'

It is stated that vegetation cover represents approx. 5% of the total urban surface, but from Figure 1a it appears that this fraction might be much larger within the footprint of the flux measurement location, which neighbors a large recreational park.

Page 7996, line 5: The SMA emission inventory reports highest urban VOC emissions in MCMA in an area surrounding the 2006 flux tower site. It is not mentioned that there could still be a significant discrepancy of VOC emissions for different parts of the city (e.g. the northern industrialized part). It is mentioned that Karl et al. 2009 (page 8007, line 27) for example observed higher toluene emissions above a different part of the city.

Page 8008, line 14, Figure 5: It is argued that benzene and C2-benzenes show good correlation with CO2 fluxes and that olefins exhibit a poorer correlation with CO2. Looking at Figure 5 I would argue that the correlation between C2-benzenes and olefins are comparable (e.g. between 0.4 and >0.8). The slightly smaller correlation coefficients for olefins could also be caused by the varying instrument response of the FIS. Also, why should evaporation from fuel tanks and engines change the correlation between olefins and CO2 more than the correlation between aromatic compounds and CO2? Both compound classes are highly volatile and present in gasoline. I would not expect a significant difference between these two VOC categories.

Page 8010, line 11: 27% and 45% only adds up to 72%. What about the remaining 28%? On page 8013 (line 1) it is mentioned that according to the emission inventory 72% of toluene on a daily average comes from traffic. Taking the statement on page 8010, the authors imply that other sources of toluene (e.g. evaporative sources such as painting) are underestimated by the SMA inventory based on concentration ratios (e.g. 45% vs 72% from traffic). On line 20-29 (page 8013) the authors argue that removing

evaporative emissions from the emission inventory would bring flux observations and emission inventory into agreement. This seems to contradict the earlier statement based on concentration ratios (page 8010). It is not clear why other source terms in the emission inventory could not be overestimated at the given location. In fact looking at Figure 9d, it seems that the evaporative component for toluene in the emission inventory (e.g. painting) is necessary to reproduce the diurnal toluene flux profile, which peaks between 9:00 and 18:00. It appears that the toluene contribution from gasoline vehicles might be overestimated: e.g. early morning hours (6-9am) before the painting started. From the presented evidence I don't see how the conclusion on page 8015 line 5 can be reached. On contrary from reported concentration ratios between toluene and benzene it seems that evaporative emissions from area sources (at least for toluene) are not under-predicted. From Figure 9d it appears that combustion/traffic sources (e.g. for toluene) are over-predicted. This issue needs to be addressed in a more systematic way. Right now conflicting arguments are presented and it leaves the reader wondering.

Page 8015, line 13. Reference Lei et al., 2008a is not listed in the reference section. What about Lei et al., 2007? It is argued that some modeling results might have grossly overestimated VOCs (e.g. by factors of 3-4, West et al. 2004 and ARriaga-Colina et al. 2004). What about the difference between Velasco et al. 2007 and Lei et al. 2007 who reported differences for aromatic compound emissions by a factor of 2.5? There is evidence from independent studies conducted in Mexico City (e.g. Fortner et al., 2008) suggesting that evaporative toluene sources are not accurately represented in current emission inventories. There is no discussion on these reports in the current manuscript.

Minor Comments

Page 7999, line 2: also cite one of the original publications on PTRMS (e.g. Lindinger et al., 1998 or Hansel et al., 1998).

Page 8000, line 16: A field intercomparison between EC and DEC for isoprene has been published in ACP (see Turnipseed et al., ACP, 2009).

Page 8002, line 24: Can the FIS response time be compared to the response time of the PTRMS?

Page 8004, line 17: I doubt that methanol is significantly produced from secondary photo oxidation in biomass burning plumes when compared to the primary emission from biomass burning as stated.

Page 8006, line18: change to 'During the second increment....'

Page 8007, line 4: It should be considered that night time flux measurements are uncertain due to advection. This could explain the fact that the nighttime increase was not as obvious for toluene and methanol.

Page 8007, line 19: change to 'This spike...'

Page 8013, line 15: Again, it should be noted that night time flux measurements are uncertain. Could this explain the underestimation?

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