

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

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The authors thank the comments and suggestions made by this reviewer. The specific comments are discussed below.

1) 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, 2008).’

As indicated in the manuscript the Fast Isoprene Sensor (FIS) does not respond specifically to any single olefin, instead it responds to a variety of olefins. For a direct comparison of the eddy covariance fluxes and ambient concentrations measured by the FIS with the olefin emissions reported in the emissions inventory and the ambient concentrations obtained from numerical models, the calculated emissions and modeled concentrations of alkenes need to be weighted by their sensitivity responses to the FIS. However, 52% of the species responding to the FIS in the atmosphere of Mexico City have not been identified, and a factor of 2.08 needs to be applied to the modeled emissions and concentrations to compare the entire budget of propene-equivalent alkene concentration measured by the FIS. This is a factor to adjust the instrument signal for the particular atmospheric composition of Mexico City and not a factor to adjust the emissions inventory.

The modeling studies conducted by Lei et al. (2007, 2008 and 2009), as well as indirect comparisons using speciated ambient concentrations of VOCs (Velasco et al. 2007) suggest that the emissions of olefinic and aromatic VOCs reported in the emissions inventory are in reasonable agreement, but not the emissions of alkanes, which might be underestimated by factors between 2 and 4. The revised manuscript emphasizes that the 2003 measurements showed that only for the olefins and aromatic species measured in that residential district of the city the emissions inventory was generally accurate.

2) 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.

Certainly the footprint for some nocturnal periods included to the Chapultepec park located at 1.4 km to the northwest of the tower. During daytime the footprint included only urban neighborhoods, where the vegetation cover represents 5% of the total surface, as shown in Fig 1b. The revised manuscript indicates that only during daytime the monitored footprint corresponded to an urban neighborhood with scarce vegetation.

Interactive  
Comment

3) 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.

The flux measurements were conducted in a district where the official emissions inventory reports the highest VOC and CO<sub>2</sub> emissions for a residential area of Mexico City. Higher VOC and CO<sub>2</sub> emissions can be expected from industrial sectors, as those emissions reported by Karl et al. (2009) and Fortner et al. (2009). The revised manuscript states clearly that the reasonable good agreement between estimated emissions and measured fluxes is valid only for the monitored districts in 2003 and 2006.

4) Page 8008, line 14, Figure 5: It is argued that benzene and C<sub>2</sub>-benzenes show good correlation with CO<sub>2</sub> fluxes and that olefins exhibit a poorer correlation with CO<sub>2</sub>. Looking at Figure 5 I would argue that the correlation between C<sub>2</sub>-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 CO<sub>2</sub> more than the correlation between aromatic compounds and CO<sub>2</sub>? Both compound classes are highly volatile and present in gasoline. I would not expect a significant difference between these two VOC categories.

It is true that benzene and C<sub>2</sub>-benzenes fluxes correlates slightly better than olefins flux with CO<sub>2</sub> flux. The slightly weaker correlation between olefin and CO<sub>2</sub> fluxes might be due to the variations of the FIS response to different alkenes and not to the evaporation of olefins from fuel tanks and engines. This statement has been fixed in the revised manuscript.

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Interactive  
Comment

5) 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.

On page 8010 (lines 11 - 13) 27% and 45% are the mobile sources contributions to the toluene emissions during the resin application period and the rest of the day, respectively. These contributions were calculated by the ratio between the toluene to benzene ratios for the Mexican vehicular fleet (1.9) and the measured fluxes (7 during the resin application and 4.2 for the rest of the day).

We agree with the reviewer that the toluene and C2-benzenes emissions from mobile sources are overestimated in the emissions inventory. However an overestimation of

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the evaporative emissions cannot be ignored, in particular of toluene, considering that the resin application on the sidewalks near the tower occulted a larger overestimation of the emissions inventory. The revised manuscript has been properly modified to include these observations.

6) 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.

Using modeled and measured VOC concentrations Lei et al. (2007, 2009) found that the emissions of aromatic species needed adjustment factors from 1 to 1.5 and the olefin emissions factors between 0.8 and 1.0 depending on the compound. Through a relatively simplistic comparison of early morning concentrations and total emissions Velasco et al. (2007) found that some aromatic and olefinic species might be overestimated in the emissions inventory.

Some studies have suggested that the variability on toluene emissions within the metropolitan area of Mexico City is due to the large fraction of emissions sources belonging to the informal sector (e.g. workshops, car street-painting, cleaning, etc.) and to industries burning banned fuels and using not reported industrial processes, in particular during nighttime. The large concentrations of toluene and other VOCs reported by Fortner et al. (2009) corresponded to plumes from those industries, and are not completely representative of the daily emissions of Mexico City. The target of this study was the average fluxes from a typical residential district.

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