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Comment

## ***Interactive comment on “Chemically-resolved aerosol eddy covariance flux measurements in urban Mexico City during MILAGRO 2006” by R. Zalakeviciute et al.***

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We appreciate the careful review and comments from Dr. Klemm and the second reviewer. We have modified the manuscript according to these comments as outlined below:

p 11903, lines 18-19: The Nemitz et al (2012) citation cannot be accepted as is. Instead, other cities' results should be cited, see Atmos. Chem. Phys., 8, 7405-7417, 2008 This has been changed as suggested to read: Integral aerosol mass and number fluxes have been reported for a few urban sites (Dorsey et al., 2002; Vogt et al., 2011).

p 11904, l 25: provide also metric units for the diameter This has been changed as  
C5257

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suggested.

p 11909, lines 14 – 16: incomplete sentence: “The fractional contributions and the individual mass fluxes were used a least-squared residual minimization of (2) to yield the final organic flux components for HOA, OOA, and BBOA.” The correction has been made: “The fractional contributions and the individual mass fluxes were used in a least-squared residual minimization of Eq. (2) to yield the final organic flux components for HOA, OOA, and BBOA.”

Fig. 1 is not as informative as it could (should) be. Information about streets and land use would be helpful. We agree and we have added a more detailed map of the immediate area around the tower.

Fig. 2: The temp scale should be stretched to allow more precise reading. The wind direction should not be presented as a line graph to avoid vertical lines during the turn of the wind direction over North. Use a scatter plot instead. There seems to be a bug in the pressure data of 12 March. We have made improvements as follows: 1) the temperature scale was changed, 2) the wind direction data were binned into 8 groups (45-degrees each); the figure now shows winds from each sector more clearly; and 3) the pressure was corrected.

Table. 1: Some of the numbers are given with too high precision. Don’t use more than 3 significant digits. It would be preferable to use only 2 digits. We agree and have made this correction.

Fig. 3: Why is a color plot used here, but a b/w one in Fig. 2? Figure 3 displays aerosol concentrations and we used colors to be consistent with the convention used by the AMS community. We felt the meteorological graphs were clear in b/w since each component was plotted on a separate scale.

p 11912, line 20 and p 11916, line 11: suggestion to delete “error” as day-to-day variability is shown rather than errors. We agree and we have revised the text to read

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“bars indicating the day-to-day variability (one standard deviation)”

p 11912, lines 22 – 24: Is there independent support for the occurrence of the rush hour peak, for example from traffic count data or from the emission inventory? Does the stability of the boundary layer play a role here as well? We do not have traffic count data for this area of the city and we used the peak in CO<sub>2</sub> concentrations and fluxes to indicate the rush hour signature. The text has been slightly modified to reflect this. The stability of the boundary layer does affect the CO<sub>2</sub> concentrations, but the fluxes are a more direct measure of traffic activity.

Fig. 8, caption: The notion “Comparison of the diurnal profiles of PM<sub>1</sub> fluxes of primary aerosols. . .” is misleading, as F(HOA+BC) is shown. The last sentence of the section does not help. The text is clear, though. Please clarify the caption. We have revised the caption as “Comparison of the diurnal profiles of measured and estimated PM<sub>1</sub> fluxes of primary organic aerosols (based on HOA+BC) at the SIMAT flux tower site (grey solid line, shaded area is  $\pm$  one standard deviation) with the 2006 official emissions inventory for the monitored footprint around flux tower (black solid line) and the T0 supersite (black solid line with markers). . .”

## Responses to Review #2

1. p.11904, l.24: Could you add information about the length of the 5/8” copper sampling line, and about the sampling line from the copper sampling line to the AMS.

We have added additional details about the sampling line setup: The length of the 5/8” (1.6 cm) OD copper tubing included 1 m out towards the sonic anemometer, 26 m down the tower to the sampling pump with a tee prior to the pump where the AMS inlet line was attached (1/4”, 6mm OD stainless steel x 1 m)

2. From the PMF analysis, three organic aerosol factors (HOA, OOA, BBOA) were derived. Could you briefly discuss the relevance of a fourth factor (local primary nitrogen containing LOA) derived by Aiken et al. (2009) in the context of your measurements.

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The point raised by the reviewer highlights the differences in capabilities between the Quadropole-AMS used in this study and the High Resolution-AMS used in the study by Aiken et al. (2009). The Q-AMS cannot measurement multiple masses simultaneously, while the HR-AMS can. Thus, in order to make fast eddy covariance measurements with Q-AMS, we had to choose a limited amount of  $m/z$ 's (10). We chose  $m/z$ 's that would let us partition organic aerosol sources into 3 components: HOA, OOA, and BBOA. Even for lower time-resolution measurements it would be very difficult to identify the fourth N-containing factor identified by Aiken et al. (2009). The HR-AMS can effectively separate N-containing ions from other organic ions with the same unit  $m/z$ . Without this separation, isolating the LOA factor was not possible in this study.

3. p.11910, l.13: What exactly do you mean by “water correction”?

This refers to the standard Webb-Pearlman-Leunig flux correction for water vapor and temperature density effects. We have corrected the text to make this clear.

4. p.11913, l.4 and in Fig. 4: Concentrations of olefins are presented. How did you measure the olefin mixing ratios?

We used a fast chemiluminescent olefin sensor as described in Velasco et al. (2009, 2011). We have revised the text to reflect this.

5. In section 3.3, the local gridded emissions inventory of primary PM<sub>2.5</sub> is compared with the emission flux measurements of this study. I am not surprised that the temporal pattern of the inventory and the observations are different, and that the results are not consistent with earlier studies by Aiken et al. (2009) and Zavala et al. (2009). Many of the primary particles included in the inventory, i.e. black carbon, dust, and metals, were not directly measured with the AMS. Also, when using an average PM<sub>1</sub>/PM<sub>2.5</sub> ratio to estimate a PM<sub>1</sub> emission inventory, and when using an average correlation of HOA and BC to parameterize BC concentrations, an interpretation of the diurnal patterns is very difficult. This should be stated more clearly in a revised version of this section.

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These are valid points. We have substantially revised the text in 3.3, in the Conclusions and the Abstract to address this. In section 3.3, we now state:

Our comparison between the EC fluxes and the local emission inventory is thus complicated by the imperfect overlap between the AMS measurements and the emission inventory with respect to particle size cut-off (PM<sub>1</sub> vs. PM<sub>2.5</sub>) and the chemical components tracked (HOA vs. total particulate mass). To make a comparison, we first estimated the fraction of the inventory due to PM<sub>1</sub> emissions (80% of PM<sub>2.5</sub>) and second, we assumed the contribution of black carbon (BC) was 75% of the measured HOA flux. Querol et al. (2008) estimated that about 80 % of PM<sub>2.5</sub> consists of PM<sub>1</sub> at T<sub>0</sub>, while Moya et al. (2011) reached the same conclusion for the T<sub>1</sub> suburban site during MILAGRO, as did Salcedo et al. (2006) for a different urban site in a previous study. Aiken et al. (2009) reported that BC was approximately 75% of the HOA contribution (see their Figure 5a) and, thus, we estimate BC as 75% of our measured HOA fluxes. With these two assumptions, we can compare our measured PM<sub>1</sub> fluxes of HOA plus the derived BC emission with the derived PM<sub>1</sub> mass emissions from the inventory. The use of the measured fluxes may lead to an underestimate of the real emissions, as the deposition of some of the airborne material may partially cancel the local emissions, resulting in a smaller local net flux. Figure 8 shows the daily averaged profiles of the sum of measured HOA fluxes and estimated BC fluxes, and compares those with the estimated PM<sub>1</sub> emissions from the emissions inventory for the grid cells corresponding to the observed footprint at the SIMAT flux tower and T<sub>0</sub> sites. The gray-shaded area indicates the standard deviation-based upper and lower limits for the measured data. Overall, the mass emission rates for the flux measurements (including estimated BC) are in good agreement with the emission rate for the area around the tower in the emission inventory. The estimated PM<sub>1</sub> emissions from the emissions inventory for the monitored footprint yield an average emission of 0.16  $\mu\text{g m}^{-2} \text{ s}^{-1}$ , compared to the observed average PM<sub>1</sub> fluxes of 0.15  $\mu\text{g m}^{-2} \text{ s}^{-1}$ . However, it is important to recognize that the inventory emission rate includes dust and metal contributions, and thus it appears that the inventory underestimates the emissions of organic and black

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carbon aerosols as derived from the flux measurements. The degree to which this underestimate occurs cannot be determined from this comparison. Further, the temporal pattern in the inventory shows a sharp increase in emissions early in the morning, missing in our flux measurements, which suggests that the temporal profile used in the inventory overestimates the timing and magnitude of early morning emissions. Aiken et al. (2009) using measured ratios of PM<sub>2.5</sub> to CO at the T0 site concluded that the inventory was low by as much as a factor of four, and Zavala et al (2009) also found that the emission factors used for inventories were too low based on their on-road measurements. Our results also suggest that the inventory is low, although we cannot estimate the degree of this error from our results.

6. p.11921, l.1: The presented flux measurements are described as a useful method to directly quantify PM<sub>1</sub> emissions and deposition within a densely populated urban area. Taking into account my comment above, and the level of sophistication needed to perform those measurements, this statement should be softened.

This is a good point and we have revised the text using:

With the increasing number of megacities throughout the world, it is becoming increasingly necessary to characterize the particulate emissions in densely populated urban areas. This work demonstrates a powerful approach to directly quantify the near-surface fluxes of an important subset of particulate emissions- non-refractory PM<sub>1</sub>. While imperfect, this approach could provide a useful validation for the emissions inventories that are being implemented for these developing megacities.

7. p.11921, l.15: It is stated that “nitrate aerosol emissions were observed only during evening rush hours with peak levels of 0.4  $\mu\text{g m}^{-2} \text{ s}^{-1}$ ”. However, in Fig. 6d, the average diurnal pattern of the nitrate fluxes shows an emission episode at 6 AM in the morning. Please clarify!

There is a much larger uncertainty in the morning peak in nitrate due to much larger variability at that time in this measurement. Thus, we chose to point out the evening

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peak as a more meaningful part of the pattern.

#### Technical Corrections

p.11909, l.14/15: Please revise: “The fractional contributions and the individual mass fluxes were used squared residual minimization of...”.

This sentence has been corrected.

p.11915, l.13: Replace “MCMA” by “Mexico City Metropolitan Area”.

This change was been made.

Tab. 1: To be consistent with the rest of the manuscript, replace “chlorine” by “chloride”.

This change has been made.

Fig. 1: For reasons of clarity, please show additional tick marks indicating longitude and latitude.

These changes have been made.

Fig. 3: For the reader, a time series of the total submicron mass measured by the AMS would be an interesting addition.

This graph has been added as suggested.

Fig. 4: For the reader, the average diurnal pattern of the total AMS mass would be an interesting addition. Also, references for the NO<sub>x</sub> and CO<sub>2</sub> measurements should be included.

This has been added as suggested. The NO<sub>x</sub> measurements have not been published, but the CO<sub>2</sub> measurements are presented in Velasco et al. (2009).

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Interactive comment on Atmos. Chem. Phys. Discuss., 12, 11899, 2012.

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