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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Using ground-based solar and lunar infrared spectroscopy to study the diurnal trend of carbon monoxide in the Mexico City boundary layer" *by* W. Stremme et al.

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Response to referee 1:

Below are the responses to the specific issues and the proposed modifications for a revised manuscript. General comments are also addressed in a general response document.

Major comments:

Referee 1: *1. The introduction lumps together a string of citations 11503-10. This should be expanded to mention the insights from these papers relevant for the current paper.*

AC: Done for the revised manuscript. "Rinsland and Levine (1985) used for the first time the CO Band at 2100 to study the tropospheric CO column; Pougatchev and Rinsland (1995) retrieved a vertical CO profile from solar spectra; Barret et al. (2003) improved the CO profile retrieval strategy and provided a error estimation; Edwards et al. (2004) estimated the global CO sources with space-borne and ground-based CO column measurements. Yurganov et al. (2004, 2005, and 2008) improved the retrieval strategy, studied the annual cycle and identified biomass burning events based among others on CO column measurements of various NDSC/NDACC sites. Sussmann and Buchwitz (2005); Dils et al. (2006) compared ground-based solar-FTIR column measurements with SCIAMACHY CO column retrieval; Turquety et al. (2008); Clerbaux et al. (2008) used recent space born CO column retrieval to study CO sources and a CO emission inventory on global scale. Senten et al. (2008) recently presented CO column measurement at Reunion-Island used together with the inverse-transport model Flexpart to identify CO sources."

Referee 1: *2. In particular, Burton et al., have done lunar spectroscopy before, and their work should be discussed in addition to the reference at the end of section 2.3.*

AC: Included the following in the revised manuscript. "Burton et al. (2000) have done lunar spectroscopy to investigate the emission of SO2 from volcanoes during the night analyzing at 2500 cm-1. They report that thermal emission of the instrument has to be removed. The correction for CO (near 2100cm-1) is more pronounced since the analysis is at lower energy (the maximum of a black body with normal temperature is around 1000 cm-1)."

Referee 1: *3. a) The question of the emission inventory has received considerable attention before please do a more thorough review of past work and conclusions, including current discussion of the MILAGRO campaign (e.g. Tie et al., 2009 ACPD). b)*

11524-5 says "opens the possibility". It would be nice to see a more complete review of this question along with some estimates based on this paper. In connection with this, I think it would be worth expanding the discussion of CO concentration and emission trends. (11503-25) "It would be nice to see some estimates based on this paper".

AC: a) We mention and cite the most recent model studies using an inventory for Mexico: West et al. 2004, Tie et al 2009 and Zhang, 2009.

b) We agree with the referee's comment and believe that the strength of these measurements (time series of CO columns with high temporal resolution in a megacity) is that it opens the possibility for a top-down estimation of the emissions and even emission trends. However, a top-down estimation based on the CO column growth rate needs two ingredients more to get a value which could compare with the CO emission values of Mexico City: 1) The over the mixing layer integrated horizontal transport of CO and 2) the relative horizontal distribution of the emissions.

Both parts can be estimated based on observations, but the lack of coincident measurements of vertical wind profiles deny a reliable reconstruction of the horizontal CO flow. Alternatively, a statistically approach could help. The estimation of the mean advection of CO and the mean horizontal distribution of the CO emissions, columns and concentrations in Mexico City can be estimated for particular weekdays (7) and classified in various ventilation patterns (6 according to Foy 2008). The dataset with measurements on 62 days is not enough for a statistical analysis of maybe 42 different CO column growth rate classifications. Even if we assume that the emission rates are similar for all weekdays as well as their diurnal patterns, the dataset would be too small as not always the entire morning is covered.

Alternatively, the CO column measurements could be used for top-down checks of models, but this is not the focus of this work as it wouldn't prove if an error in vertical o horizontal transport is compensated by an error in the emission inventory. Here we present new CO column measurements and reconstruct an atmospheric parameter like

the MLH. We address only one aspect, the vertical CO distribution and it can be used for a cross validation FTIR-measurements versus NCEP-NARR-model. But the model is only used to extrapolate one quantity, MLH, which is only coincidently measured at 6:00 and 18:00 LT, at which time our measurement density has its minima.

Nevertheless, the slopes in figs. 10,11,12 during the morning reflect typical CO column growth rates, which are between the rates which we would get considering the cited emission inventories and with the assumptions that the emission rate is constant within the metropolitan area and during the day.

For these reasons and because this is the subject of a more comprehensive study, we exclude the direct estimation of CO emission in this work. We however will pursue this goal based on a larger dataset and coincident measurements of the MLH with a LIDAR system now installed at the rooftop.

Referee 1: *4. Fig. 8 shows a big difference between Nov and Feb. This should be discussed in the text. Also please put the background level on the fig, which makes the contrast even more striking.*

This issue is discussed in the general response document. The difference is no longer apparent when the new retrieval version is used since more days (62) passed the quality control. We included a solid line for the adopted background column as suggested and a dashed line for the overall mean during this period.

Referee 1: *5. In relation to the two points above, you might consider looking at horizontal wind speeds to get a dilution factor.This could tell you if winds were stronger in Feb leading to lower columns. It could also be used in a first order calculation of expected columns based on the emission inventory.*

AC: In reference to point 3 (difference between Nov and Feb), we couldn't find a systematic wind dependent dilution for the morning means but rather, we find a significant dilution in the afternoons. We included a section "diurnal and nocturnal behavior of the

CO column" in the revised manuscript. For the analysis we gathered the mean and standard deviation values of the surface wind speed and from its correlation with the CO column, we see that there are different phases during a day: (a) When the horizontal transport is small and no systematic dilution appears during the mornings. At those times the dynamics of the atmosphere is dominated by the vertical transport and the growing of the mixing layer. (b) During the afternoon, when the horizontal transport is important and the city is typically cleaned up. The correlation coefficient between CO column and wind speed for 16-22 LT reaches R= -0.63 (R^2=0.4), while for 9-13 LT is only R=-0.15 (R^2=0.02).

The other two phases, early afternoon (13-16 LT) and night (22-9 LT), show a good correlation with relatively high wind speeds and no correlation with low winds, respectively.

Referee 1: *6. The discussion of night-time dispersion should be expanded.*

AC: We include a discussion of the night-time measurements in the new section mentioned before: "Diurnal and nocturnal behavior of the CO column". We have added error bars to the MLH estimation in Fig. 10, which shows the large uncertainties obtained during the night (see point 8).

Referee 1: *7. There are tethered balloon and Lidar measurements that could be used to expand the discussion.*

AC: Unfortunately, these are not coincident measurements and we can only use them as reference, as it was originally done (page 11521 lines 15-18).

Referee 1: *8. In particular, the high night-time values of MLH in Fig. 10 suggest that you are getting the residual layer aloft, not the surface CO.*

AC: We agree with this comment, and it is what has been noted in page 11522 line 3 of the original manuscript: "The air near the surface might be clean at times, but a polluted CO residual layer may be present above. An inhomogeneity like that would

result in an over-estimated MLH and could be a typical case in night time, for example on 25 February, Fig. 10."

Referee 1: *9. The model data of the boundary layer height is from the NARR model, please add a sentence about this. With a horizontal resolution of 32 km, it is not clear that the values are going to be representative with 3 cells across the basin.*

AC: We have included that important piece of information in the revised manuscript and have to mention that fortunately the grid point of the model is located very near to the measurement site.

Referee 1: *10. I would recommend comparing MLH values with readily available radiosonde data.*

AC: Unfortunately, the radiosonde measurements take place at 6:00 and 18:00 LT, which is when we do not have a lot of measurements and when the variation is small, so that an investigation of dependence or correlation would be difficult. We assume and hope that the model, by assimilating the information reported by the radiosondes, does the best possible inter/extrapolation for the times used for the measurements.

Referee 1: *11. Furthermore, the growth of the MLH in Fig. 10 seems slow and the maximum values low. Comparison with radiosonde data might suggest if this is because of the cold season or for other reasons.*

AC: Comparison of the MLH and its growth rate with days short before and afterwards showed that the MLH (Fig.10) is only a little bit smaller. The day is not colder and does not show different surface wind speeds. A comparison with Fig. 13 and other days shows that the 24th of February 2008 (Fig.10) might be considered as a typical day.

Referee 1: *12. 11518-18: The effect is very slight - if it is evidence of a residual layer, it would suggest that the residual layer does not have much CO. This paragraph should be either expanded based on discussion of known features of basin circulation, or the speculation should be limited.*

AC: We removed this paragraph and will investigate the small effect on a larger dataset in further work.

Referee 1: *13. 11519-25: different surface pressure might impact the background column value, but otherwise the resemblance is presumably due a match in the combination of emissions and horizontal ventilation.*

AC: We agree, that the same emission and similar ventilation of the two megacities should rather result in same fresh CO column amounts than into the same CO surface VMR values. We add in the revised manuscript that the statement refers to the background column.

Minor Comments:

Referee 1: *14. Please review the language, there are numerous errors that a spell checker would correct immediately, e.g.:* **AC:** done

Referee 1: *15. Challaging, dirunal, informartion, carfully, interferance, qunatities, diappeares, "from an in the laboratory", "goals of sought", "an current topic", "strongly variable" - use highly variable, 'if in contrary" - use in contrast* **AC:** done

Referee 1: *16. Sec. 4, first sentence is very vague.* **AC:** done

Referee 1: *17. Fig. 14 is referred to as fig 13 in the text.* **AC:** We corrected this

Referee 1: *18. Expand the caption for fig. 8 and 9 to say the location.* **AC:** done

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Interactive comment on Atmos. Chem. Phys. Discuss., 9, 11501, 2009.