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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.

W. Stremme et al.

stremme@atmosfera.unam.mx

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Response to referee 2:
We would like to thank the comments from this referee for his helpful remarks which aim at improving the content of this manuscript. 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.

General comment:
Referee 2:
These are nice and potentially very useful measurements. The attempt, however, to

demonstrate the usefulness of these observations to infer mixing height is generally not convincing. CO column observations are compared to ground based CO point measurements to infer a quantity called "mixing layer height (MLH)". While some initial comparisons with modeled mixing height are presented, no significant agreement between measured and predicted MLH appears to be observed (R^2=0.37). The value of the approach to estimate MLH as it is currently presented remains unclear, and some speculative suggestions as to how this poor agreement with the model could be improved remain untested. These are nice measurements, but the interpretation of the data needs to be improved.

The authors would need to make a credible claim that demonstrates the value of CO columns as a tracer to quantify a meaningful parameter that helps understand the state of the atmosphere. Then the paper would be well within the scope of ACP. Without a convincing demonstration of how these measurements are useful to learn about the state of the atmosphere, the paper appears to be rather instrument focused, and would as such be better placed in a Journal like "Atmospheric Measurement Techniques". The reviewer has included several suggestions how the fit with ACP could be improved..

AC:

We have followed the suggestions of the referee and worked further to interpret the data in order to make the retrieved quantity of mixing layer height more convincing in the revised manuscript. Further filtering of the data, like reducing the time periods and applying a restriction to low wind intensities, improved the correlation between the reconstructed MLH from FTIR and the model considerably. Also the model used to calculate the MLH from FTIR data was extended and included the presence of a residual layer. This also showed to be beneficial to the correlation, which altogether improved from R^2=0.37 up to R^2=0.68. So as it is explained in the revised manuscript, the MLH can be used as a key parameter to portion the CO column between fresh and residual contributions.

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The MLH is usually not well described in the evening when horizontal transport affects the vertical dispersion of CO and since different phases can be identified during a day, we have added a section on the "Diurnal and nocturnal behavior of the CO column". We think that through the appropriate and constructive suggestions from referee 2, we could exploit the data further and extend the interpretation of the results as in this above mentioned section.

Specific comments:

Referee 2:

1) There is virtually no information how the model converts the observed slant column densities into vertical column densities. While this step is straightforward for direct sunlight/moonlight column observations such as the ones presented here, this is an important logical step that is currently not described in the text.

AC:

The description of this step is included in the revised manuscript: "SFIT2 assumes a horizontal homogenous layer to retrieve the direct vertical column. The slant path length of the sunlight in each layer is determined by the RAYTRACE program. This program calculates the curvature of the sunlight in the atmosphere for a given astronomical solar zenith angle, wave number and location and produces the input files for the SFIT2 program."

Referee 2:

2) Do the authors have any idea whether the background CO column at Altzomoni is representative over the city? The CO residual layer over the city seems to add significantly to the total column (factor 2 from Fig 10). How sensitive are the MLH estimates to changes in the background CO column? What is the error of assuming background CO to be constant?

AC:

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a) Local coincidence: Altzomoni is located almost directly at the outskirts of the Mexico City metropolitan area (Fig. 1). Because a column measurement is the integration of the CO density in the vertical, local effects as air masses from Mexico City or Puebla, which reach the altitude of Altzomoni (2 km over the basin) are strongly reduced in comparison to in situ measurements. Using an average restricted to morning data, when MLH is low, eliminates this local effect and minimizes the direct influence from pollution sources. b) Representability of measured background: We have taken advantage of the time since the submission from the first manuscript, and have included in the revised version data from a second measurement campaign at the end of 2008. We show that the background value doesn't noticeably change between both campaigns. We know from other ground based stations, MOPITT measurements and also models, that CO has a yearly cycle in the troposphere with a maximum in spring. Our dataset covers October/November to February and the error due to the seasonality in the background CO is expected to be low, as it has been mentioned in the manuscript. Nevertheless, one cannot exclude possible anomalies from regional events such as biomass burning during this time. c) The sensitivity of the MLH: The sensitivity of the MLH is dependent on the state of the atmosphere, contamination and MLH. This is discussed in point 6): We have done an intensive study to obtain the error and sensitivity from the MLH and have added this in the revised manuscript.

Referee 2:

3) a) Is "mixing layer height" really what the authors infer about the state of the atmosphere? It seems to be a confusing choice of language, as it suggests active mixing of the air column over this height. What is the mixing mechanism at night to explain a 3 km deep mixed layer (Fig10)? b) The authors have unique capabilities to quantify the time constant at which the night time jet cleans out the air column above Mexico City. This is not mentioned in the current manuscript. An attempt should be made to quantify this very useful, and presently unconstrained parameter. In particular, every night the authors' data appears to show a repeated pattern of continually decreasing CO columns from midnight into the morning hours (Figs 12 and 13). This data should

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be exploited, rather than the ambiguous approach to estimate a quantity MLH that is a convolution of multiple processes (emissions, pollution export, chemical production of CO etc), and for which the meaning is unclear.

AC:

a) We define MLH as the effective trace gas mixing height, which it is not a meteorological parameter, but this terminology is being used in related literature. The effective mixing layer height is the height until where convection mixes the air so that the VMR of inert gases and other quantities which are constant for a vertical displacement have almost the same value. We agree that at night the reconstructed effective MLH should be used more carefully and rather be seen as an index. However, the good agreement with the observed PBLH (Planetary Boundary Layer Height) in the NARR model, shows that the MLH, particularly in the morning to early afternoon, can be a useful physical quantity.

b) We agree that the measurements have a unique capability to investigate the night time jet that should be discussed independently of the MLH. We have added a section about the diurnal and nocturnal trend in the CO column in the revised manuscript. We found that the surface wind speed, its average and its correlation with the CO column, allows identifying a phase (9-13 LT) where the MLH and the vertical transport are dominant and another (16-22 LT) when the interpretation should focus on horizontal transportation.

Referee 2:

4) How much CO is produced from the oxidation of hydrocarbons in Mexico City?

AC:

In comparison with the local sources from the transportation sector, CO from photochemical sources has virtually no contribution. We explain this by a rough estimation (i) and make reference to a study which addresses this issue (ii).

(i): The oxidation of CH4 and other HCs is globally the main source of CO adding to

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1000Tg CO/yr (Holloway,2000), which results in a mean CO production of 2Tons/(yr km^2). In a megacity, the production due to oxidation of hydrocarbons is surely increased due the higher concentrations of HCs, but the estimated production due to direct anthropogenic emission is around 225, 300 or 500Tons/(yr km^2) (West et al. 2004; Tie et al. 2009; Official inventory,2003; Foy et al. 2007, ...). We assumed a homogeneous emission over the MCMA. Enhancements of methane in the morning hours in Mexico City can reach 6 ppm (Gutter et. al 2003) with a background around 1.8ppm, but this factor of 4 is not big enough to increase the production of CO due to oxidation of hydrocarbons to a pertinent level. We assume that in this environment the photochemical source can be neglected in comparison to the direct emission. (ii): A statement in a recent work of Tie et al. (2009), ACP Page 4625,Sec. 3.1, is cited: "The chemical lifetime of CO is of order of months, thus over the few days relevant here it can be considered as a passive tracer which is emitted from the surface, mixed in the PBL, and transported with prevailing winds."

Referee 2:

5) In order to use the CO columns to estimate MLH, it appears that the authors need to isolate the portion of the CO column that is due to emissions from the residual CO column. Can the authors make an effort to parameterize the different processes contributing to CO columns for a case study where they observe a larger mismatch between MLH from the model and their estimate, and demonstrate the value of CO columns to estimate MLH under such conditions?

AC:

Yes, we did so and it works better than expected. Extending the model used for reconstruction of the MLH with a residual layer and adopting the residual concentration (and column amount) we can tune the MLH to obtain a better overall agreement. If we do this with the filtered dataset, we get a better dependence between MLH from model and FTIR data and the presence of the residual layer in the model takes care of the offset. The correlation R^2 quantifying the mismatch between MLH-FTIR and MLH-model

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does not necessarily needs to improve, but it did improve from 0.58 to 0.63.

We are not convinced that the MLH of the model is better than our estimation, but we learned that we can calibrate our reconstruction if we have reliable information of the true MLH. We thank the referee 2 for his useful hint and we would like to point out that this extension of the model can be used in another way as well. As the MLH-FTIR should match with other MLH measurements, it can be used to isolate the portion of fresh and background CO. This could be extended to other gases, as has recently been done for NO2 in a similar approach using DOAS measurements (Zhou et al. AMTD, 2009). That particular example, however, is far more complicated due to the active photochemistry, stratospheric background and limited lifetime.

This issue is addressed in the subsection added on the "Impact of the CO residual layer on the MLH-reconstruction" in the revised manuscript.

Referee 2:
6) a) The discussion of experimental error stands only in very remote relation to the authors estimate of MLH. The issues from points 4 and 5 should be addressed, and quantified. Also, error bars should be included into the MLH data shown in Figure 12, and 13. b) The assumption of a homogeneous mixing within the layer is fine, but is it really motivated in any meaningful way "by the short mixing time and the relatively long lifetime of CO." c) What is the sensitivity to changes in the residual CO column from previous days? And due to changes in CO background columns from spatial and seasonal variations? d)And due to any photochemical production of CO? e) If the mixing layer is not homogeneous, is there indeed a relation between the inferred height, and the "effective Z_{MLH}*"?*

AC:
a) We included a section "Error and sensitivity of the retrieved MLH "which is based on sensitivity studies. The result of the mathematical analysis is consistent with the obvious intuition that as CO is used as a tracer, a smaller error in the estimated MLH

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is present during days with high CO levels. The error bars, based on well defined errors in the input parameter from in situ and column CO measurements, have been added to the Figs. 10,11 and 12. b) Yes, in assuming a horizontal rather homogenous dispersion and if the only source is at the ground, the ratio between the time of mixing and the lifetime is relevant to determine the vertical profile. c) The remaining residual surface concentration might be in average around 0.33 ppm (as obtained by the study described in point 5). How much remains from one day to the other depends on the actual ventilation and is expected to vary considerably, as is shown by the time series of daily means. This question could only be answered with a statistics, and therefore a dataset with more consecutive measurements is needed. d) CO can be considered as a passive tracer, see above answer to question 4. e) This subject is discussed in original manuscript page 115221 line 22 to115222 line 6 and see also response to referee 1 (question 8) as well above to referee 2 (question 4 (ii)) .

Referee 2:

7) de Foy et al. 2007 used ground-based FTIR in a previous study. The authors limit themselves to comparing CO columns. However, as described in de Foy et al., 2007, the scientific value of CO columns lies in its use to constrain pollution export from the valley. How do the data from the authors compare in this respect?

AC:

The pollution export is directly related with the emission estimation. As also referee #1 pointed out, it would be very interesting to expand the discussion to the estimation of CO emission and even emission trends. This is a goal of ongoing work. Foy et al. (2007) used various measurements like metrological parameters, SO2, CO in situ and column measurements to calibrate their model and to proof the emission inventory. Here the measurements are used as a "top-down check" for all, vertical transport, horizontal transport and emissions. Their final conclusion is however limited as there had been neither a description nor a validation of the CO column measurements until

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now. We have concentrated on the quality of the CO measurements and obtaining a large data set until now and are aiming to reconstruct the CO emission in a top-down manner. Since the horizontal transport is rather unconstrained, we have limited this work on the reconstruction to a parameter (MLH) which can characterize the vertical transport in the morning to early afternoon period. We present implicitly a rough estimation of emission as given by the CO column growth rate in the morning hours (on days with low horizontal ventilation,) Fig. 10. 11 and 12 (see also response to referee 1, question 3b).

Referee 2:
8) Error discussion: a) Page 11514, line 27: What is a "non-fitted parameter field of view"? b) Page 11515: What is the meaning of the following sentence? "We call the spectra which are prepared for a retrieval to be a measurement." c) Page 11515, line 17: define "quality of a measurement". Is this the combination of statistical and systematic error sources in the instrument, software tools used in the retrieval, and literature data used for calibration?

AC:
a) With "non-fitted parameter field of view" we want to express that the FOV (field of view) parameter is important for the ILS, but as it is normally very well known, it is not fitted in SFIT2 or Linefit retrieval code). We rewrote this sentence anyway as the entire paragraph is changed according to the change made of the retrieval version. b) We removed this misleading sentence. The idea was that one has to choose on which data the analysis is based on, since the statistical error changes if a single spectrum or an average of half an hour is used. c) We replaced "quality" with "statistical error"

Referee 2:
9) Page 11522, Line 19: "For lower MLHs, the higher values of the model than the reconstructed MLH show a bias of about 700 m and slope of 0.5 with an overall correlation of R^2 =0.37, Fig. 13. This result may be improved considerably if data with higher time resolution from the model would be available and the days with strong convective

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or ventilation processes are filtered out." An attempt should be made to demonstrate this from applying the author's own suggestions to their own data. Do these suggestions improve the correlations?

AC:
This point is related with point 6) and we have included a section "Mixing layer height comparison: FTIR vs. Model (NARR)" in the revised manuscript . We filtered the data and reached a better agreement MLH-Model= 0.99 MLH-FTIR + 535 m and a $R2$ =0.58.

Minor comments:

Referee 2: *10) Abstract, line 1: Define "main", while CO is abundant, it is not necessarily the most relevant.* **AC:** Replaced with "important"

Referee 2: *11) Line 2: "challenging"* **AC:** done

Referee 2: *12) Line 14: a rather complicated sentence. Consider shortening. For example: "The total CO column within the city presents large variations that are caused mainly by fresh CO emissions at the surface, and transport or mixing processes within the field-of-view of the instrument."* **AC:** we made three sentences out of it

Referee 2: *13) Page 11503, line 6: "human" 14) Line 7: CO does not control the OH budget; it affects HOx partitioning.* **AC:** done

Referee 2: *15) Line 27: have there been previous column CO observations in Mexico City? If yes, this would be the place to mention this.* **AC:** Foy et al. 2007 is mentioned only some lines later, when the topic changes from emission inventory to the vertical constrain.

Referee 2: *16) Page 11506, line 8: is there really a Opag 22 Bruker spectrometer?*
AC: Yes, it is true.

Referee 2: *17) Page 11507, line 14: "varies" not "variates"* **AC:** done

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Referee 2: *18) Line 19: "totally"* **AC:** done

Referee 2: *19) Page 11509, line 18: delete "of"* **AC:** done

Referee 2: *20) Page 11511,line 16: "a current topic"* **AC:** done

Referee 2: *21) Line 23: do the authors mean to refer to the "constrained retrieval"?* **AC:** Yes, changed.

Referee 2: *22) Page 11515, line 17: "fitted"* **AC:** done

Referee 2: *23) Line 26: "analysis"* **AC:** done

Referee 2: *24) Page 11520, line 9: do the authors mean "where"?* **AC:** yes, done

Referee 2: *25) Page 11521, line 7: "volume"* **AC:** done

Referee 2: *26) Page 11522, Line 1: "The formation of a new mixing layer explains the second peak in the surface concentration of CO (Stephens et al., 2008)." How can the formation of a mixing layer explain a second peak? If the authors refer to a decrease in mixing height, while emission rates are constant, than this is different to what they say here.* **AC:** We removed this sentence

References

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