Atmos. Chem. Phys. Discuss., 9, C3468–C3472, 2009
www.atmos-chem-phys-discuss.net/9/C3468/2009/

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.

Anonymous Referee #2

Received and published: 2 August 2009

General comments:

The manuscript entitled "Using ground-based solar and lunar infrared spectroscopy to study the diurnal trend of carbon monoxide in the Mexico City boundary layer" describes the application of ground based FTIR to perform slant column observations of carbon monoxide (CO) to the sun as well as to the moon over Mexico City. 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.

Specific comments:

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.

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?

3) 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 3km deep mixed layer (Fig10)?

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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 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.

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

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?

6) 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.

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." 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? And due to any photochemical production of CO?

If the mixing layer is not homogeneous, is there indeed a relation between the inferred height, and the "effective Z_MLH"?

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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?

8) Error discussion: Page 11514, line 27: What is a "non-fitted parameter field of view"? Page 11515: What is the meaning of the following sentence? "We call the spectra which are prepared for a retrieval to be a measurement." 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?

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 Rˆ2 =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 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?

Minor comments: 10) Abstract, line 1: Define "main", while CO is abundant, it is not necessarily the most relevant. 11) Line 2: "challenging" 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." 13) Page 11503, line 6: "human" 14) Line 7: CO does not control the OH budget; it affects HOx partitioning. 15) Line 27: have there been previous column CO observations in Mexico City? If yes, this would be the place to mention this. 16) Page 11506, line 8: is there really a Opag 22 Bruker spectrometer? 17) Page 11507, line 14: "varies" not "variates" 18) Line 19: "totally" 19) Page 11509, line 18: delete "of" 20) Page 11511, line 16: "a current topic" 21) Line 23: do the authors mean to refer to the "constrained

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retrieval"? 22) Page 11515, line 17: "fitted" 23) Line 26: "analysis" 24) Page 11520, line 9: do the authors mean "where"? 25) Page 11521, line 7: "volume" 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.

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