Atmos. Chem. Phys. Discuss., 9, C749–C753, 2009
www.atmos-chem-phys-discuss.net/9/C749/2009/

Atmospheric
Chemistry
and Physics
Discussions

Interactive comment on “Detection of pollution transport events southeast of Mexico City using ground-based visible spectroscopy measurements of nitrogen dioxide” *by* M. L. Melamed et al.

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Received and published: 12 May 2009

Reply to Anonymous Referee # 3:

We thank the critical observations made by the referee and used these to improve the quality of the manuscript. The authors believe that this manuscript provides critical information to the overall MILAGRO campaign. As noted in the manuscript, the Tenango del Aire research site was the only research site located to the south of Mexico City during the campaign. As can be seen by the authors' analysis of pollution transport events to the Tenango del Aire research site, as well as the analysis of de Foy et al. 2008, the pollution transport to the south of the city center occurred on the

majority of the days during the campaign. Therefore, the results presented in this study will aid in enhancing the ability of models to capture the overall pollution transport within the basin. Additionally, the authors' present a technique to determine the extent of mixing within the pollution plumes using their unique data set. As previous studies have shown, the ML in the Mexico City basin is complex and the analysis of the plumes on 13 March aid in unraveling this complexity. Finally, the authors show strong evidence for enhancements in NO_2 within the basin due to lightning on 28 March 2006. Although further studies are required to quantitatively determine the amount of NO_2 produced from lightning within the basin, this finding will aid in determining the pollution photochemistry in the Mexico City Metropolitan Area by explaining a possible NO_2 source not previously detected. Through observations and identifying pollutions events like we do in the present study, the modelers can verify the performance of their results. The chemical transformation, on the other side, is important, as pointed out by the referee, and a detailed analysis of the observations at this particular site is in preparation and the results from this study will aid in that interpretation. The authors have modified the introduction and conclusions of the manuscript to better reflect the importance of this work to the MILAGRO campaign and how the manuscript addresses previously unanswered scientific questions regarding the air pollution within the Mexico City Metropolitan area.

Minor Comments:

1. Page 4772, line 7: Changed “nitrous oxide” to “nitric oxide”.
2. Page 4773, line 2-3: The authors added “the particular background spectrum used in this study is discussed later”.
3. Page 4773, line 13: Changed to “It is important to note that since the background solar spectrum is taken from the ground and not outside the Earth's atmosphere, . . .”

4. Page 4774: The authors do explain the units for the O_2-O_2 complex in line 1-6 on this page, "It is important to note that since O_4 is an O_2-O_2 collision complex, the O_4 absorption cross section has the units cm^5 molecules^{-2}. The O_4 "column densities" will be expressed with respect to the quadratic O_2 concentration in the unit cm^5 molecules^{-2}. Since these units are not traditional units for a molecular absorption cross section nor a column density, the O_4 quantities will use the symbol DSCD* throughout the text to denote this specialty."
5. Page 4774 lines 12-13: Changed to "The O_4 DSCD* are then used to qualitatively restrain the source and cause of the NO_2 VCD enhancements as discussed in Sec. 3.1, 3.2, and 3.3.
6. Page 4775, line 1: The authors added the reference Grainer and Ring 1962.

   Page 4775, line 2: Changed to "A 'shift and stretch' is applied in order to align the laboratory cross sections acquired by a different spectrometer at different temperatures and air densities with the foreground spectrum."

   The authors feel further discussion of the DOAS method is not necessary since references to articles and books that thoroughly describe the DOAS method and how errors and detection limits are determined.

   The estimated detection limit of the spectrometer to measure the NO_2 column density in this study is 2.5 x 10^{15} molecules cm^{-2}, assuming the intensity of the photons reaching the spectrometer is maximized.
7. Page 4776, line 20: Corrected the spelling of artifacts.
8. NO_2 is converted to NO by a molybdenum NO_2-to-NO converter heated to about 325° C. The lower limit of detection, 50 pptv, applies to all 3 species. The above has been noted in the manuscript.
9. Page 4780: Plume 2 reaches a maximum of 1.7 x 10^{-16} molecules cm^{-2} and this has been corrected in the text.

The authors do not argue there is an increase in the surface NO_2 mixing ratio. The authors state that the total tropospheric NO_2 VCD increases between Plume 2 and 3 due to an increase in the total number of NO_2 molecules in the atmosphere. The authors then show that the surface NO_2 mixing ratio does NOT significantly change between Plume 2 and 3 because the increased total number of NO_2 molecules in the troposphere occupy more space due to an increased MLH for Plume 3. The measurement of the total tropospheric NO_2 VCD is completely independent of the MLH and therefore should not increase nor decrease as the MLH does.

In regards to the referee's comments about the possibility of the NO_2 molecules residing in a layer aloft and not within the ML, the analysis presented on Page 4781 is precisely a way to determine whether or not the NO_2 layer is within the ML, above the ML and/or whether the NO_2 is well mixed within the ML. IF the ML is well mixed and the NO_2 molecules reside within this layer, THEN the NO_2 mixing ratio calculated from the ceilometer MLH and the total tropospheric DOAS NO_2 VCD will be equal to the measured surface NO_2 mixing ratio. As shown, during plume 2 and plume 3 the calculated and measured surface mixing ratios are consistent. Therefore, the authors conclude the NO_2 is residing within the ML and the ML is well mixed.

The DOAS NO_2 measurements do not detect the first plume due to a combination of two factors. The first factor is that the maximum integration time was limited to 75 msec (which was not stated in the manuscript but has now been changed). With large SZAs during Plume 1, 64° to 75° , the amount of light reaching the spectrometer was small, resulting in a low signal-to-noise ratio. The second factor is the authors assume NO_2 has a strong source at the ground and in the early morning, mixing of the ML is limited due to a small amount of convective mixing and low wind speeds of 1.0 m s^{-1}. It is likely Plume 1 is a thin low lying NO_2 layer that has a high surface mixing ratio of 29 ppbv but a column density below the detection limit of the spectrometer. A combination of these two factors result in the column density of NO_2 during Plume 1 that cannot be detected by the DOAS instrument.

10. The authors appreciate the reviewer's comments and our considering using MAX-DOAS measurements in the Mexico City Metropolitan Area.
11. Page 4783 line 21: The sentence has been re-worded to say "an increase in NO_2 into the convective cloud from its surrounding."