

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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Reply to Anonymous Referee # 2:

Major Comments: The authors have added in the text the stratospheric NO₂ column density over Mexico City during the MILAGRO 2006 campaign derived from SCIAMACHY limb satellite data (personal communication Andreas Richter) on the day of the background spectrum, 18 March 2006. On this day at 10:00 CDT, the stratospheric NO₂ column was 2.5×10^{15} molecules cm⁻². Thus the background spectrum chosen in this analysis accounts for this NO₂ stratospheric column and the DSCDs represent enhancements due to an increase in the tropospheric NO₂ column density or an en-

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hanced path length through the atmosphere due to changes in SZA and multiple scattering due to clouds and aerosol. On the other two days analyzed in this study, 13 March and 28 March 2006, the measured stratospheric NO₂ column density were 2.26×10^{15} molecules cm⁻² and 2.38×10^{15} molecules cm⁻² respectively. The small variation in the measured stratospheric NO₂ column density will have a negligible effect on the large tropospheric NO₂ column densities measured in this study. In addition, the diurnal variation of stratospheric NO₂ at 28° N has been shown to be on the order of 1.4×10^{15} molecules cm⁻² (Tie et. al, 2009) and the authors assume a similar diurnal variation in stratospheric NO₂ above Mexico City. The small diurnal variation in the stratospheric NO₂ column does not change the analysis presented in this study, which presents plumes with maximum column densities between 1.7 to 9.7×10^{-16} molecules cm⁻². This analysis has been included in the manuscript.

The authors have clarified their method to derive and interpret the AMF for this study and do not agree with the reviewer that a RT model is necessary in order to interpret the results presented in this study. The authors now apply the AMF of the sec(SZA) only when the SZA < 60 degrees and the O₄ AMF indicates no increase in the optical path length due to multiple scattering, i.e. on 13 and 18 March 2006. The AMF of the sec(SZA) is also used on 28 March 2006 when the O₄ AMF indicates no increase in the optical path length. On 28 March 2006 from 12:50 to 14:50 CDT a thunderstorm cloud is detected by a combination of a large enhancement in the DOAS O₄ AMF, by a decrease in DOAS intensity and by the ceilometer on site. The ability of RT models to calculate the optical path length of photons traveling through such a cloud is very limited, especially in determining where the NO₂ resides within the cloud and whether the enhancement in the photon path length through the cloud occurs where the NO₂ resides within the cloud. Therefore, the authors believe using the measured O₄ AMF to qualitatively restrain the interpretation of the DOAS NO₂ enhancement in the cloud is a better approach than applying a RT model with low confidence to the interpretation of a measurement.

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Finally, the authors appreciate the reviewer's comments and our considering using MAX-DOAS measurements in the Mexico City Metropolitan Area in the future.

Minor Comments:

1. The authors have eliminated the interpretation of the two distinct peaks in Plume 1 as it does not add to the overall analysis of 13 March 2006.
2. As the referee pointed out, if the ML was completely mixed, the expected NO_2 VCD should reach 1.9×10^{-16} molecules cm^{-2} , which should be detected by the spectrometer assuming that the intensity of the photons reaching the spectrometer was maximized and NO_2 was present at 29 ppbv throughout the entire mixing layer. However, 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 tropospheric column density below the detection limit of the spectrometer. Therefore, Plume 1 is not seen in the DOAS measurements due to a combination of these two factors. With increased surface temperatures, convective mixing increases resulting in a well-mixed ML in the late morning. In this same section, the authors present a method to determine the extent of mixing within the ML using total tropospheric DOAS NO_2 VCDs, in-situ NO_2 surface mixing ratios and ceilometer MLH. The results presented by the authors show the ML becomes well mixed on this day during Plume 2 and remains well mixed during Plume 3. The authors have changed the manuscript to reflect this analysis more accurately.

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3. The authors have added a paragraph in sec. 3.1 to highlight the difference between surface mixing ratio measurements and DOAS column density measurements as well as the importance of having both measurement techniques at a research site. The paragraph reads, "A comparison between Plume 2 and Plume 3 highlights the difference between surface and column density measurement and the importance of having both measurement techniques at an urban research site. The DOAS measurements show that between Plume 2 and Plume 3, the total tropospheric NO_2 VCD increases from 1.7×10^{-16} molecules cm^{-2} to 4.8×10^{-16} molecules cm^{-2} . However, the maximum surface NO_2 mixing ratio stayed more or less equal, 29 ppbv during Plume 2 and 32 ppbv during Plume 3. This is because due to an increase in the MLH from 300 m to 1200 m, the increase in number of tropospheric NO_2 molecules between Plume 2 to Plume 3 as detected by the DOAS measurements occupy more space due to an increase in MLH, resulting in similar surface NO_2 mixing ratios."

Technical Comments:

1. This change has been noted in the manuscript.
2. The references Noxon, 1975 and Platt and Stutz, 2008 have been added.
3. A long list of references that have used O_4 to study optical path lengths and aerosol properties has been added, including the those mentioned by the referee.
4. Changed wording.
5. Done.
6. Done.
7. As the referee pointed out, the NO_2 mixing ratio the authors are inferring is an upper limit. In section 2.3 the paragraph on inferring NO_2 mixing ratios now reads,

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“In the following analysis, the surface NO₂ mixing ratio is estimated from the NO_x and NO measurements ($[\text{NO}_2]=[\text{NO}_x]-[\text{NO}]$). However, commercial NO_x chemiluminescence monitors are able to partially reduce more oxidized nitrogen compounds (HNO₃, HONO, PAN, PPN). Therefore, the NO₂ mixing ratio inferred from the above equation in this study is an upper limit dependant on the catalyst design and temperature, input pipe length and photochemical age of the polluted air parcel being observed.”

8. see 9.
9. All figures are now in military time and the times on the graphs coincide with the times mentioned in the text.
10. see 12.
11. see 12.
12. Section 3.1 has been re-written and the reviewer's comments on wording were taken into consideration. Specifically, since the authors are doing an analysis of the tropospheric NO₂ column densities and assume the stratospheric NO₂ column density is accounted for in the background spectrum, the authors now refer to the measurements as the total tropospheric NO₂ VCD throughout the text.
13. Where appropriate, references to figures were changed from, Fig. 2 to (Fig. 2)
14. References Erle et al. 1995 and Pfeilsticker et al. 1999 were added.
15. Changed.
16. Changed.

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17. This sentence has been changed to, “DOAS measurements of NO₂ and SO₂ can provide important information regarding the influence of NO₂ produced from lightning and biomass burning, as well as SO₂ emissions from volcanic activity, on pollution events within the Mexico City Metropolitan Area.”
18. Figure 14 has been removed because, as the referee point out, the figure is not clear without further explanation and it does not add to the interpretation of this section of text. However, another figure was added in this section to show the location and time of lightning strikes detected by the WLN.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 4769, 2009.

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