

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.

Anonymous Referee #2

Received and published: 30 March 2009

The present study by Melamed et al. reports on simultaneous measurements of total atmospheric NO₂ (by DOAS - Differential Optical Absorption Spectroscopy) and in-situ measured NO₂ (chemo-luminescence) from a field campaign in Mexico City. Even though both techniques do not provide the same information about NO₂ within the boundary layer, the data clearly show similarities in the amount of pollution detected, which can be interpreted with respect to the actual NO₂ concentration and boundary layer height. As it stands the study does, however, not yet provide tremendously new amount of new information or scientific content on air pollution and/or photochemistry within a megacity, but it may become acceptable for publication after a revision of the points listed below.

C103

Major comment:

Most unsatisfactory points in the present study are the crude treatment and discussion of (a) the residual absorption of the background spectrum, (b) the way air mass factor and (c) the diurnal variation of stratospheric NO₂ is dealt. While the effects of (a) and (c) on inferred NO₂ VCD and its error can easily be estimated, more accurate air mass factors can easily be assessed using existing RT models. In particular, approximating air mass factor by the secant of the solar zenith angle (SZA) largely increases the uncertainty in measured total atmospheric NO₂ for SZA > 60° and hence unnecessarily increases the error in inferred tropospheric vertical column amounts. Therefore I mandate a revision on these technical aspects of the study. Also in forthcoming studies I largely recommend to exploit better the full potential of ground-based DOAS measurements for trace gas and aerosol detection c.f., to include off-axis observations, which may nicely provide more information on the height distribution of the targeted parameters.

Minor comments:

1. Section 3.1 first paragraph: I guess you are over-interpreting your data, i.e. the narrowness of the two peaks. What effects do you expect with respect the spatial resolution of your measurement and what is with dispersion and mixing?
2. Why were the DOAS measurements not able to detect the first plume shown by the in-situ data? What is your detection limit of your instrument? C.f. if I take you numbers MLH = 312 m, [NO₂] = 27 ppb for the surface then the vertical column amount in the MLH could reach VCD = 2.1*10¹⁶/cm², which correspond to an optical thickness of 0.001. Using a similar type of spectrometer in one of our experiments indicate a detection limit somewhat lower for this instruments (a factor of 2). What do you expect for the vertical mixing, i.e. how far is the most prominent NO₂ source located?
3. I found it rather difficult to decipher what you mean with these sentences: Therefore the DOAS NO₂ VCD should increase between Plumes 2 and 3 as the number of

C104

NO₂ molecules in the atmosphere increases due to increased emissions from morning traffic. The surface NO₂ mixing ratio stayed more or less equal because the total number of the NO₂ molecules occupied more space due to the increase in MLH between Plumes 2 and This highlights the difference between surface and column density measurement and the importance of having both measurement techniques at an urban research site. In effect the total amount of NO₂ which you may detect boundary layer is a matter of both, the NO₂ concentration and the location of MLH. So please reformulate your statement accordingly.

Some technical comments:

1. Abstract: change from In addition, we show the effectiveness of how DOAS measurements ... to In addition, we show how suitable ground-based DOAS measurements are for monitoring....

2. Section 2.1, line 22: skip the reference Marquard et al. (2000) and Platt (1994) and include instead c.f.,

- Noxon, J. F. Nitrogen Dioxide in the Stratosphere and Troposphere Measured by Ground-Based Absorption Spectroscopy, *Science* 189, 547–549, 1975. - Platt, U., J. Stutz Differential Optical Absorption Spectroscopy; Principles and Applications, Springer-Verlag GmbH, Heidelberg, Germany, 2008.

3. Page 4773, line 23: add reference after this sentence: However, the retrieval of the oxygen collision complex (O₄) can provide important information in regards to the optical path length of the photons that have been scattered multiple times e.g,

- Pfeilsticker, K., B. Arlander, J. Burrows, F. Erle, M. Gil, F. Goutail, C. Hermans, B. A. Høskar, J.C. Lambert, U. Platt, J.-P. Pommereau, A. Richter, A. Sarkissian, M. Van Roozendael, T. Wagner, and T. Winterrath, Intercomparison of the influence of tropospheric clouds on UV-visible measurements during the NDSC intercomparison campaign at OHP in June 1996, *Geophys. Res. Lett.*, 26, 1169-1172, 1999.

C105

- Wagner, T., K., F. Erle, L. Marquard, C. Otten, K. Pfeilsticker, T. Senne J. Stutz, and U. Platt, Cloudy Sky Optical Paths as derived from DOAS Observations, *J. Geophys. Res.*, 103, 25307 - 25321, 1998.

4. Page 4774, line 20: change fromHowever, since the vertical profiles of NO₂ and O₄ differ, the O₄ AMF is used in this study to qualitatively restrain the interpretation of the enhancements of the NO₂ VCDs. ... However, since the vertical profiles of NO₂ and O₄ differ, in this study the O₄ AMF is used to qualitatively restrain the interpretation of the enhancements of the NO₂ VCDs.

5. Page 4774, line 22: change from ... NO₂ DSCDs are retrieved in the visible spectral window of 407–505 nm.to ... NO₂ DSCDs are retrieved in the visible spectral window of 470–505 nm.

6. Page 4775, line 6: change from Lavenberg ...to Levenberg

7. Section 2.3: Please explain NO_x (NO, NO₂, HONO, NO₃ ?) and how it is measured? (by UVA photolysis and as a difference between NO measured during by switching on and off a photolysis lamp ?). Accordingly, the in-situ NO₂ you are inferring is an upper limit, and it can be expected that sizable amounts of HONO are also existing in the very polluted air of Mexico City at daytime. In fact, you should be able to detect it with your instrument.

8. Section 3.1: In the figures you refer to 2:00 pm, than the text should also read 2:00 pm rather than 14:00.

9. In all Figures (4 – 12), please change 12 pm to 12 am on the horizontal axis

10. Section 3.1, line 21: change from ... Due to the shift in the wind direction, Due to the change in the wind direction,...

11. Section 3.1 and throughout the text: Please change the notation from 'total burden' and DOAS NO₂ VCD to 'total atmospheric NO₂', or if you mean that 'total tropospheric NO₂', or 'total boundary layer NO₂' et cetera and please name the same thing the

C106

same throughout the manuscript.

12. Page 4779, lines 15 to 23: Reformulate the whole paragraph!

13. Bracket the reference to Figures in the whole text body, i.e. change from ... by aerosol and clouds, Fig. 7.to... by aerosol and clouds (Fig. 7).

14. Page 4783, line 3: Include here the reference to Erle et al. (1995) and Pfeilsticker et al. (1999) and again after the sentence in line 23. e.g.,

- Erle F., K. Pfeilsticker, and Platt U., On the influence of tropospheric clouds on zenith-scattered-light measurements of stratospheric species, *Geophys. Res. Lett.*, 22, 20, 2725-2728, 1995.

15. Page 4784, line 23: change fromlocalized concentration... to ... local concentration

16. Page 4784, line 23: change fromTherefore, as shown in the analysis of 13 March 2006, surface mixing ratios across a variety of plumes can remain constant even though the DOAS column density measurements detect large changes in the total burden of NO₂ molecules in the atmosphere. ...to .. Therefore, as shown in the analysis of March 13, 2006, NO₂ within a variety of plumes can remain constant even though the remotely measured total atmospheric NO₂ may change.

17. Conclusions, Last sentence but one: What do you want to say ? Probably that remotely sensed SO₂ plumes provide better skills for forecasting volcanic activity related pollution events?

18. It not total clear what is shown in Figure 14. What are the black dots (the cloud bottom height?), and what is the gradient local minimum (of the backscatter signal?)

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