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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment" *by* E. J. Dunlea et al.

Anonymous Referee #1

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The manuscript "Evaluation of nitrogen dioxide chemiluminescence monitors in a polluted urban environment" by Dunlea et al. discusses interferences in NO2 measurements in urban environments. Data of measurement campaigns in Mexico City are presented, and NO2 measurements of conventional NO2 instruments employing molybdenum converters is compared to those from Tunable Infrared Laser Differential Absorption Spectroscopy (TILDAS) and Differential Optical Absorption Spectroscopy (DOAS) instruments. These data indicated a bias of the conventional NO2 monitors even during episodes with severe pollution from nearby local sources, which is an interesting result; however, the presentation of the results may be improved considering the following major concerns are addressed below. The manuscript should only be published in ACP after addressing the following issues:

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General remarks:

The data presented raise some concerns about the representativeness of these measurements. The authors should add some remarks about the length of the campaigns and the meteorological conditions during the inter-comparisons. It should further be discussed how well these results can or cannot be transferred to other conditions and locations.

Specific comments:

The paragraph 'measurements' should also include the following information: Inlet materials, possible memory effects, residence times, use of inlet filters, meteorological conditions during the campaign(s).

Paragraph 3.2.1. and 3.2.2. Consider to shorten these paragraphs. The conversion characteristics of molybdenum converters are relatively well known, and interferences of olefinic hydrocarbons and NH3 are not expected (as confirmed by the results).

Page 582, line 5 to 24: It should be considered to shorten or re-write this paragraph. O3 is simply a proxy for photochemical processes; it is expected that the interference correlates with ozone; this result is not new.

Page 583, line 11 to 23 Particulate matter can evaporate and subsequently dissociate. What were the temperatures outside and in the labs? If there is a considerable fraction that is dissociating, the comparison with AMS results of PM1 can lead to misleading results.

Page 588, line 1 to 21 This approach is not feasible at least during the night.

Page 590, line 23ff

I do not agree that side-by-side comparisons of 'absolute' NO2 measurements with standard chemiluminescence NOx monitors will really help to further quantify these interference, simply because inlet loss and memory effects are too different for each

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instrument set-up. It will just give a broad idea of the range of these interferences, but this range is in principle already known from NOx/NOy ratios made with 'interference' free techniques. Also, a post-correction of the data will be very difficult. Furthermore, the question is how relevant these interferences are for science. In an urban environment, and especially in mega cities, day to day variability and dependence on the measurement location is expected to be significant. Such data is always only representative for the specific location and conditions.

Figure 2: when looking at the scatter plots, especially for CENCIA. There seem to be even more data with negative interferences than with positive interferences. As the authors already mention in there manuscript, a larger variability can be expected when comparing point measurements with open path observations. However, if the variability is as high as it is shown in Figure 2, I have severe doubts that the interferences can be reliably determined. Furthermore, it is PAN that shows no interference at all, but PAN will be converted to NO2 on any heated surface and should therefore be quantitatively measured in the CL NOx monitors. How can these results be explained?

Minor remarks:

Table 1: Consider to remove column 'R2' since the R2 are already given in parentheses. Instead values of the number of data points used should be given.

Page 571, line 18: don't use the term 'CL NOx' in the abstract

Page 584, line 1: pNO3 should be read as pNO3-

Page 586, line 3: Neuman et al. show HNO3 losses not only on steel.

Figure 1: Is it the whole campaign that is shown? If no, do the other periods look like the presented case study?

Figure 3 and 4: for which time periods have the diurnal profiles been calculated?

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 569, 2007.