Atmos. Chem. Phys. Discuss., 7, S987–S991, 2007
www.atmos-chem-phys-discuss.net/7/S987/2007/

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.

E. J. Dunlea et al.

Received and published: 4 April 2007

Response to Anonymous Referee #2:

This paper provides a useful summary of the current situation regarding the quality of "NO2 measurements" as obtained with chemiluminescent instruments. I recommend it be published in ACP after attention to the following:

>> The authors thank the referee for his/her insightful suggestions. Responses to individual comments are listed below and denoted with ">>"

Most important, NO and O3 measurements are almost always available simultaneously with NO2 measurements. A comparison of the two different measurements of NO2 with calculations of NO2 based on a steady state model would be very useful. Estimates of RO2/HO2 and their effect on the calculation could be made with the same accuracy as

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some of the other calculations presented in this paper. Of course this wouldn't work at night, but it would during the day. Evaluating the errors based on this calculation would allow every site in the world to do a comparative assessment.

>> The suggestion from the referee that steady-state model calculations of NO2 be included here along with the measurements is beyond the scope of this paper. We agree with the referee's point that this would add value to these measurements and help generalize these results to other locations. We note that the proposed calculations require a great attention to detail as well as information from other measurements (for example, JNO2, which was only available at one of the measurements sites in MCMA-2003). Volz-Thomas et al. (JGR-Atm, 108, D4, #8248, 2003) describe such modeling difficulties during the BERLIOZ campaign in Berlin. Additionally, an upcoming paper from Steinbacher et al. (accepted by JGR-Atm) addresses this issue of generalization much better. They have measurements of this interference to CL NOx monitors with molybdenum oxide converters for more than 10 years at two rural locations. They develop and assess a method for post-correcting the measured NO2 concentrations to account for this interference. It is obvious that further work along these lines is warranted if these molybdenum oxide converters are going to be used in the future.

I disagree with the other referee about the need to establish representativeness. The authors reinforce our understanding of established chemical mechanisms for these interferences. A reader who wants to estimate the interference somewhere else can make use of this chemical explanation and estimates of NOz and its partitioning. I doubt we will ever be able to use the NO2 measurements from chemiluminescent NOx monitors for precise scientific work, but we may be able to use them for approximate work and this paper contributes to reviving the issue of whether and to what extent we can use such measurements. I note that the subject has largely been dropped and that for more than 20 years the regulatory community has continued to endorse these instruments while the scientific community has entirely given up on them. Given the scope of the existing networks, a renewed dialog, to which this paper contributes is

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sorely needed-even if at it does is inspire renewed public criticism of the technique.

>> The authors agree with this referee concerning the scope of this paper in that it is not intended to present representative measurements of this NO2 instrument interference, but that the hope is that this paper rekindles a dialog concerning the continued use of these NO2 monitors.

I recommend adding some clarification to the discussion of PANĚ

>> The wording in the section concerning PAN (and in the abstract and conclusions) has been altered to make the point clearer: low ambient PAN levels mean that PAN does not contribute significantly to the observed interference in this location, not that PAN does not contribute to this interference in all locations. A paper discussing ambient PAN levels has just been published in ACPD (Marley, N. A., Gaffney, J. S., Ramos-Villegas, R. and Cardenas Gonzalez, B.: Comparison of measurements of peroxyacyl nitrates and primary carbonaceous aerosol concentrations in Mexico City determined in 1997 and 2003, Atmos. Chem. Phys. Discuss., 7, 1421-1448, 2007), and this reference has been added to the manuscript.

Pg 574. There are other recent intercomparisons already included in the authors reference list e.g. Thornton et al. 2003

>> It is not clear what the referee was suggesting here. Thorton et al., 2003 has been added to the list of papers that show intercomparisons.

The discussion of TILDAS as a “absolute method” ignores a large history of improvements to uncalibrated direct absorption methods that occurred after people tried to calibrate in the fieldĚ

>> We agree with the reviewer that calibration in the field greatly improves the confidence in the measurement and assists in evaluating the overall performance of the instrument. Though it has become routine now, via permeation sources and gas cylinders on the Mobile Lab platform, it was not during the MCMA-2003 field campaign. On

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the particular instrument that did go to MCMA-2003, however, the second channel of the instrument was used to measure HCHO; calibrations for this species demonstrated the pathlength was correct, and laboratory measurements of the pathlength using a pulsed light source indicate the cell was correctly aligned. Fortunately, for NO2 measurements, the spectroscopy (and potential other absorbers) near 1600 cm-1 is fairly well understood by virtue of being used so commonly. This discussion has been added to the revised manuscript.

In addition, attention to positive (NO+O3, PAN or HNO4 decomposition) and negative (losses to walls? to O3) interferences should be given in the instrument section not distributed through the paper as they currently are.

>> The discussion of these interferences has been moved to the experiment section as suggested.

The organization of the paper should be inverted. The most important interferences to the chemiluminescent NOx instrument should be discussed first and then the minor and remote possibilities. Discussion of NH3, olefins and particulate nitrate should be shortened dramatically.

>> The organization of the paper has been changed as suggested. The discussion of NH3 and olefins has been shortened and condensed into one section.

Pg 584-585 HNO3 formation is not dependent on the competition between reactions 2 and 4Ĕ

>> This sentence has been removed.

In the conclusion the suggestion is advanced that manufacturers pursue methods that allow multiple species to be measured, I see no justification for multiple species or for identifying any specific strategy at this pointĔ.

>> The recommendations section has been altered to reflect this point. The new recommendations are: (1) Possibly retrofitting NOx monitors that currently have molybde-

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num oxide converters with photolytic converters. (2) Suggesting that instrument manufacturers pursue low-cost, interference-free techniques for measuring NO2. (3) Possibly using NOx monitors with molybdenum oxide converters to measure NO and NOy instead of NO and NO2. (4) A cautious recommendation to look into post-correcting NO2 measurements from CL NOx monitors with molybdenum oxide converters with reference to a recently accepted JGR paper that discusses this idea in detail, which the authors were just made aware of (Steinbacher et al., 2007).

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