Atmos. Chem. Phys. Discuss., 7, S602–S604, 2007
www.atmos-chem-phys-discuss.net/7/S602/2007/

Atmospheric Chemistry and Physics Discussions

ACPD

7, S602–S604, 2007

Interactive Comment

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

Anonymous Referee #2

Received and published: 13 March 2007

Review of Dunlea et al.

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:

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 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.

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

I recommend adding some clarification to the discussion of PAN, obviously as the other referee notes PAN contributes to this interference with unit efficiency. PAN is not correlated with the false NO2 because it is small compared to that signal. I find this kind of odd, is PAN from the MCM similar to the observations?

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

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 field. People have found that their pathlength was mismeasured, that spectroscopic lines from other molecules were in the same window, and that the stability of their calibration was not at all what was predicted by their laboratory results for other reasons. I strongly urge the authors to calibrate under field conditions.

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 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.

Pg 584-585 HNO3 formation is not dependent on the competition between reactions 2 and 4. see the discussion of HNO3 in ACPD papers by Murphy et al or in JGR papers from the NOAA group for some guidance on a more accurate discussion of HNO3 production rates.

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 point. This paper only shows we have a problem with NO2 measurements not with the other species reported in the monitoring network. I suggest that only a recommendation to identify a cost effective solution to the problem be included in a revised manuscript.

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