

## ***Interactive comment on “High concentrations of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub> observed in daytime with a TD-CIMS: chemical interference or a real atmospheric phenomenon?” by X. Wang et al.***

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Anonymous Referee #1 (Received and published: 14 September 2013) General Comments: This paper describes measurements of NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub> in a dense, urban area of Hong Kong. The paper reports the unusual occurrence of daytime peak signals for these compounds, which are normally present at much larger concentrations at night. However rather than focus on the scientific implications of this finding, the paper primarily discusses the potential for measurement artifacts with a chemical ionization mass spectrometer (CIMS) that can lead to artificially high daytime NO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub> signals. The paper quantifies several interferences and concludes that the most severe is

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that due to the interaction of PAN and NO<sub>2</sub> within the instrument or its inlet. Daytime N<sub>2</sub>O<sub>5</sub> signals are attributed partially to the interference signal, and partially to a real daytime maximum in NO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub>. In general, the consideration of interferences for measurements at 62 amu using I reagent ion in the CIMS is a useful contribution to the literature. Prior reports have indicated the utility of this mass for detection of the sum of NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>. Although some more recent papers have suggested that the cluster ion (I- N<sub>2</sub>O<sub>5</sub>) is more specific, it is worthwhile to have an understanding of potential artifacts at the NO<sub>3</sub>- mass. In particular, the interaction of PAN with NO<sub>2</sub> has not been previously considered as an interference, and is a new contribution to the literature. As such, I recommend publication in AMT subject to some minor comments.

Reply: We would like to thank the Referee #1 for the constructive and helpful comments. The detailed replies will be listed below point by point.

The two general comments for revision are as follows: First, the paper lacks some detail that would be useful in understanding the measurements and the potential for real daytime maxima in N<sub>2</sub>O<sub>5</sub>, which are inferred in the paper. The daytime steady state in NO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub> is straightforward to calculate. See, for example, Geyer 2003 (Geyer, A., et al., J. Geophys. Res., 108, doi: 10.1029/2002JD002967, 2003) or Brown 2005 (Brown, S. S., et al.: J. Photochem. and Photobiol. A, 176, 270-278, 2005.). The calculated daytime steady states should be plotted together with the case studies in Figure 4. That would give some sense for how unusual the daytime measurements really are and the level of the predicted N<sub>2</sub>O<sub>5</sub> signal relative to the measured one. Second, the calibration scheme should be described in somewhat more detail, graphically if possible. The authors should more explicitly consider whether there is any potential for errors in the gas phase calibration scheme to explain any remaining discrepancy between the predicted and measured daytime NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub>.

Reply: We have made significant amendments in response to above suggestions. A figure is added in the revised manuscript (Figure 12) to show the source strength and loss frequency of NO<sub>3</sub> and the predicted N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> levels for the six polluted

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episodes. This figure is shown below (Fig. 1). In brief, the reaction of NO<sub>3</sub> with NO is the dominant loss pathway at the study site. In most cases, the NO concentration was relatively high and the calculated values using steady-state assumption were much lower than the observed values (after correction for interference due to PAN+NO<sub>2</sub>). There is one exception in the late afternoon on 24 October. For example, at 16:00 when O<sub>3</sub>, NO<sub>2</sub> and NO concentrations were 96.1, 49.1 and 0.3 ppbv, respectively, the predicted NO<sub>3</sub> and N<sub>2</sub>O<sub>5</sub> concentration (5 min average) could reach 321 pptv if all major removal pathways are considered. In comparison, the measured N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> concentration was 286.5 pptv (with correction for PAN + NO<sub>2</sub> interference). The agreement between observation and prediction under the condition of very low NO in this case indicates that the elevated N<sub>2</sub>O<sub>5</sub> in daytime is possible at the study site. We have included the above text in the revised manuscript.

The detailed descriptions on the calibration procedure have been added in the revised manuscript as follows. "90 sccm of 2.5 ppmv NO<sub>2</sub> in nitrogen gas was mixed with 480 sccm of 2.1 – 4.6 ppmv O<sub>3</sub> generated by UV photolysis of O<sub>2</sub> in zero air (Model 111, TEI) in a glass reaction chamber in a commercially available calibrator (Model 6100, Environics). The reactions happened during a time period of one minute, and then the output was diluted to 6 slpm by zero air." We also modified Figure 2 to include the calibration part. A more detailed figure is provided below (Fig. 2) but not included in the revised manuscript because it provides little additional information.

Specific Comments and technical corrections: Page 7475, line 18: Suggest removing the word "emerged"

Reply: Revised.

Page 7475, lines 28-89 – page 7476, lines 1-2: There is no comparison between CRDS and CIMS instruments in the Slusher 2004 reference, although there is one given in the Chang 2011 reference.

Reply: It has been revised by replacing "Slusher et al., 2004" with "Chang et al., 2011".

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Page 7478, line 9: Figure 3 erroneously referenced. There does not appear to be a figure showing the mass spectrum in this paper.

Reply: It has been revised by adding the correct "figure 3".

Page 7478, line 27: Figure 4 also incorrectly referenced. The actual figure appears to be figure 5.

Reply: Figure 4 is now correctly referenced. The position of "Figure.5" has been changed.

Page 7478, last paragraph: The NO<sub>3</sub> + N<sub>2</sub>O<sub>5</sub> calibration technique is critical to the arguments about daytime N<sub>2</sub>O<sub>5</sub> and warrants a figure. A demonstration of an example calibration (e.g., counts at 62 amu plotted against titration of NO<sub>2</sub>, O<sub>3</sub> or both from the calibration source) would be helpful to demonstrate the stated 3% accuracy of the measurement.

Reply: Fig. 3 shows the data points of signal at 62 amu versus the product of NO<sub>2</sub> and O<sub>3</sub> concentrations for N<sub>2</sub>O<sub>5</sub> calibration on 4 December 2010. When 3012 Hz of 62 amu signal was detected by TD-CIMS, the NO<sub>2</sub> concentration from a chemiluminescence analyzer equipped with a photolytic NO<sub>2</sub>-converter and O<sub>3</sub> concentrations from a UV photometric analyzer were 35.5 and 169.4 ppbv (after reaction), respectively. For the 5685 Hz of 62 amu signal, the simultaneous NO<sub>2</sub> and O<sub>3</sub> concentrations were 31.3 and 362 ppbv, respectively. For more recently N<sub>2</sub>O<sub>5</sub> calibrations, about 100 ppbv of NO<sub>2</sub> and 40 ppbv of O<sub>3</sub> were used, generating about 5 ppbv of N<sub>2</sub>O<sub>5</sub>. Similar sensitivities of N<sub>2</sub>O<sub>5</sub> in our CIMS were obtained with the two slightly different production sources of N<sub>2</sub>O<sub>5</sub>. In the revised manuscript, we added a sentence of "When inputted 36.7 ppbv of NO<sub>2</sub> and 170.4 ppbv of O<sub>3</sub> (initial concentrations before reaction), the generated N<sub>2</sub>O<sub>5</sub> was in level of 1.08 ppbv" instead of providing a figure. Note that the precision of 3% for 1000 pptv N<sub>2</sub>O<sub>5</sub> was obtained based on the relative standard deviation of the 62 amu signal when inputting 1000 pptv of synthetic N<sub>2</sub>O<sub>5</sub>.

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Page 7481, line 8: The definition of “ambient” signal is not clear – all signals are recorded during sampling of ambient air, presumably. Suggest referring to this as the “total” signal, or the “total signal in ambient air.”

Reply: As suggested, “ambient signal” has been changed into “total signal in ambient air”.

Page 7481, line 18-20: The association between PAN and greater than calculated daytime N<sub>2</sub>O<sub>5</sub> in the Brown and Osthoff studies is not necessarily related to the potential for PAN interference on the CIMS, since the cited studies use a different detection principle (CRDS). The authors should add a sentence to this effect.

Reply: It has been revised by adding “of using a different technique of CRDS” immediately after “In the previous studies”.

Page 7481, bottom: Should there be a reference to figure 6 somewhere in this text?

Reply: There is a reference to Figure 6 at Line 16 on Page 7482.

Page 7482, line 5: Suggest rewording: “ $23 \pm 4$  pptv of apparent NO<sub>3</sub>+N<sub>2</sub>O<sub>5</sub> signal per ppbv of PAN”

Reply: Revised.

Page 7482, line 11: Suggested wording: “The mechanism for the interference of PAN on the NO<sub>3</sub>- signal is unclear.”

Reply: Revised.

Page 7482, line 16: Figure 6 called out after Figure 7.

Reply: Revised.

Page 7483, line 2: Specify which section of the paper will have the analysis of the PAN interference (rather than “later”).

Reply: Revised.

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Page 7483, line 4: Delete “the” before HNO<sub>3</sub>.

Reply: Revised.

Page 7485, line 10: “are” instead of “were”.

Reply: Revised.

Page 7485, line 16: Delete the word “by”

Reply: Revised.

Page 7486, line 8-9, and Figure 9: It would be helpful to have the data for NO, NO<sub>2</sub>, O<sub>3</sub> and PAN together with the measured N<sub>2</sub>O<sub>5</sub> to understand how close to the predicted daytime steady state these measurements are.

Reply: The figure has been revised in the revised manuscript and is also shown below. Fig. 4 presents the data for NO, NO<sub>2</sub>, O<sub>3</sub>, Ox and PAN from GC-ECD together with the measured N<sub>2</sub>O<sub>5</sub> from the I(N<sub>2</sub>O<sub>5</sub>)- ion signal at 235 amu. From these data, it can be found that the predicted N<sub>2</sub>O<sub>5</sub> in steady state during the daytime will be very low, as the NO concentration was very high in urban Hong Kong in early winter.

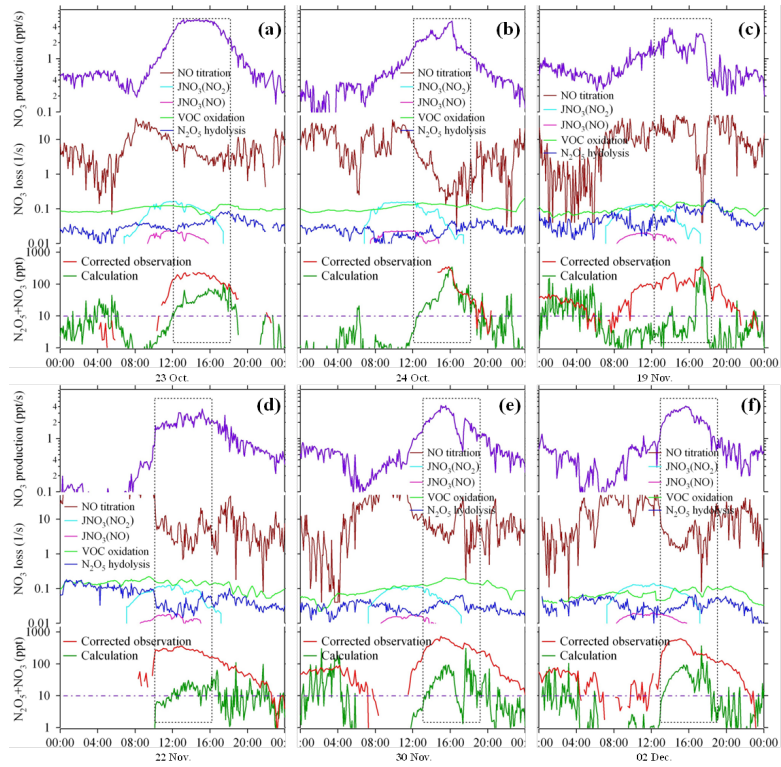
Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/6/C3245/2013/amtd-6-C3245-2013-supplement.pdf>

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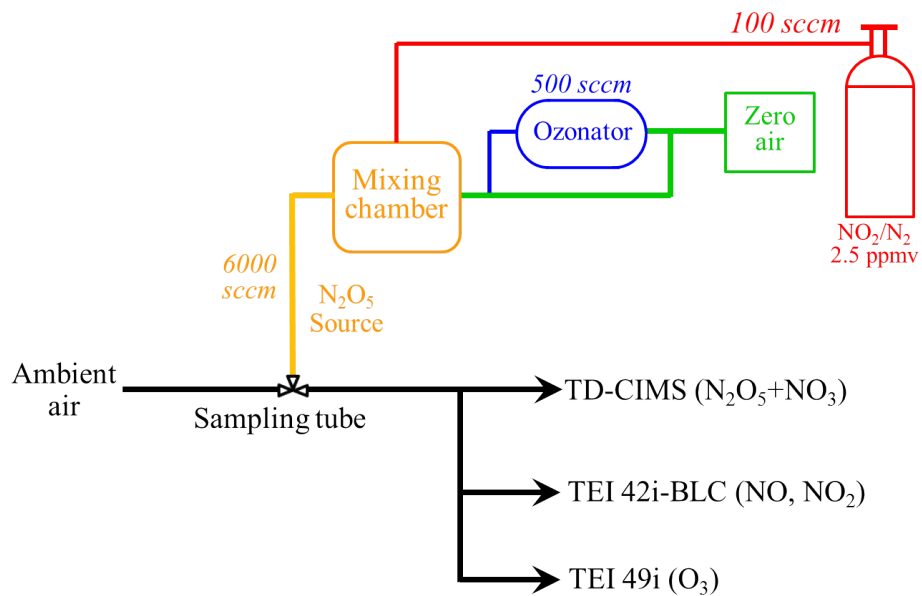
Interactive comment on Atmos. Meas. Tech. Discuss., 6, 7473, 2013.

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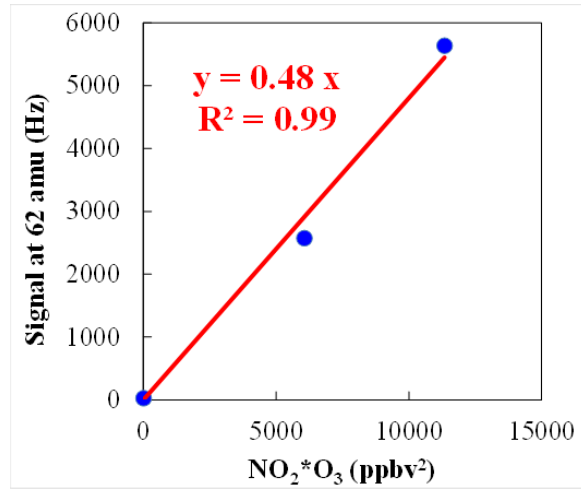
**Fig. 1.** NO<sub>3</sub> production rate from NO<sub>2</sub> and ozone, loss frequency of NO<sub>3</sub> from NO reaction, photolysis, VOC oxidation and N<sub>2</sub>O<sub>5</sub> hydrolysis, steady-state calculated N<sub>2</sub>O<sub>5</sub>+NO<sub>3</sub> and observed N<sub>2</sub>O<sub>5</sub>+NO<sub>3</sub> after correction.

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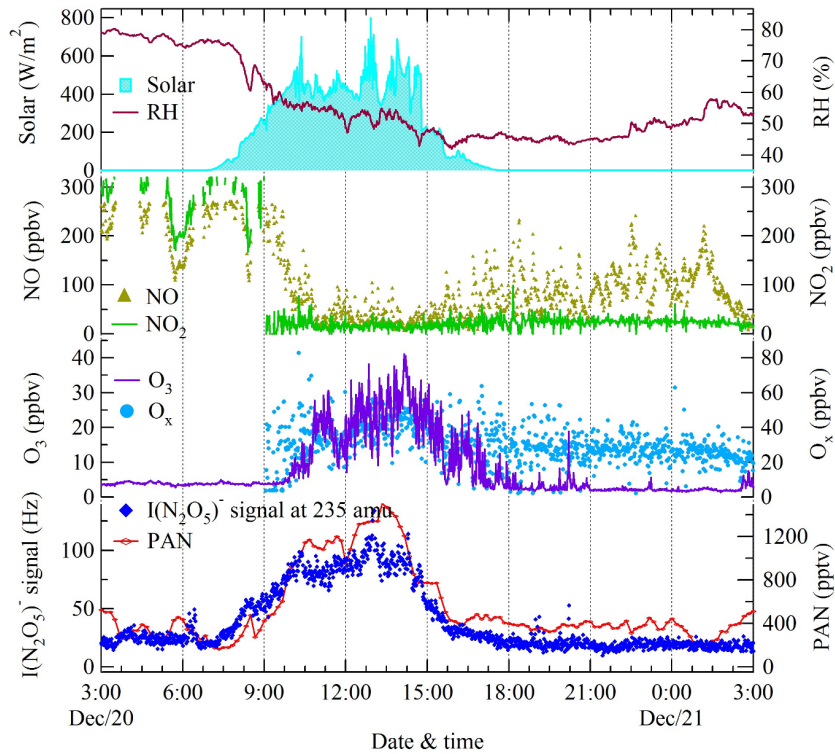
**Fig. 2.** Schematic diagram for N<sub>2</sub>O<sub>5</sub> calibration using the on-line synthesis method.

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**Fig. 3.** Plot of 62 amu signal versus the product of NO<sub>2</sub> and O<sub>3</sub> for N<sub>2</sub>O<sub>5</sub> calibration on 4 December 2010.

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**Fig. 4.** Time series of I(N<sub>2</sub>O<sub>5</sub>)- signal at 235 amu, trace gases and meteorological parameters in urban Hong Kong on 20 December 2010.

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