

Response (text in blue) to comments from Referee #1 (text in black)

Anonymous Referee #1 (Received and published: 14 September 2013)

General Comments:

This paper describes measurements of $\text{NO}_3 + \text{N}_2\text{O}_5$ 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 $\text{NO}_3 + \text{N}_2\text{O}_5$ signals. The paper quantifies several interferences and concludes that the most severe is that due to the interaction of PAN and NO_2 within the instrument or its inlet. Daytime N_2O_5 signals are attributed partially to the interference signal, and partially to a real daytime maximum in $\text{NO}_3 + \text{N}_2\text{O}_5$.

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 $\text{NO}_3 + \text{N}_2\text{O}_5$. Although some more recent papers have suggested that the cluster ion ($\text{I}^- \text{N}_2\text{O}_5$) is more specific, it is worthwhile to have an understanding of potential artifacts at the NO_3^- mass. In particular, the interaction of PAN with NO_2 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_2O_5 , which are inferred in the paper. The daytime steady state in $\text{NO}_3 + \text{N}_2\text{O}_5$ 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_2O_5 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 $\text{NO}_3 + \text{N}_2\text{O}_5$.

Reply: We have made significant amendments in response to above suggestions. A figure is added in the revised manuscript (Fig. 12) to show the source strength and loss frequency of NO_3 and the predicted $\text{N}_2\text{O}_5 + \text{NO}_3$ levels for the six polluted

episodes. This figure is shown below (Fig. R1). In brief, the reaction of NO_3 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 $\text{PAN} + \text{NO}_2$). There is one exception in the late afternoon on 24 October. For example, at 16:00 when O_3 , NO_2 and NO concentrations were 96.1, 49.1 and 0.3 ppbv, respectively, the predicted NO_3 and N_2O_5 concentration (5 min average) could reach 321 pptv if all major removal pathways are considered. In comparison, the measured $\text{N}_2\text{O}_5 + \text{NO}_3$ concentration was 286.5 pptv (with correction for $\text{PAN} + \text{NO}_2$ interference). The agreement between observation and prediction under the condition of very low NO in this case indicates that the elevated N_2O_5 in daytime is possible at the study site. We have included the above text in the revised manuscript.

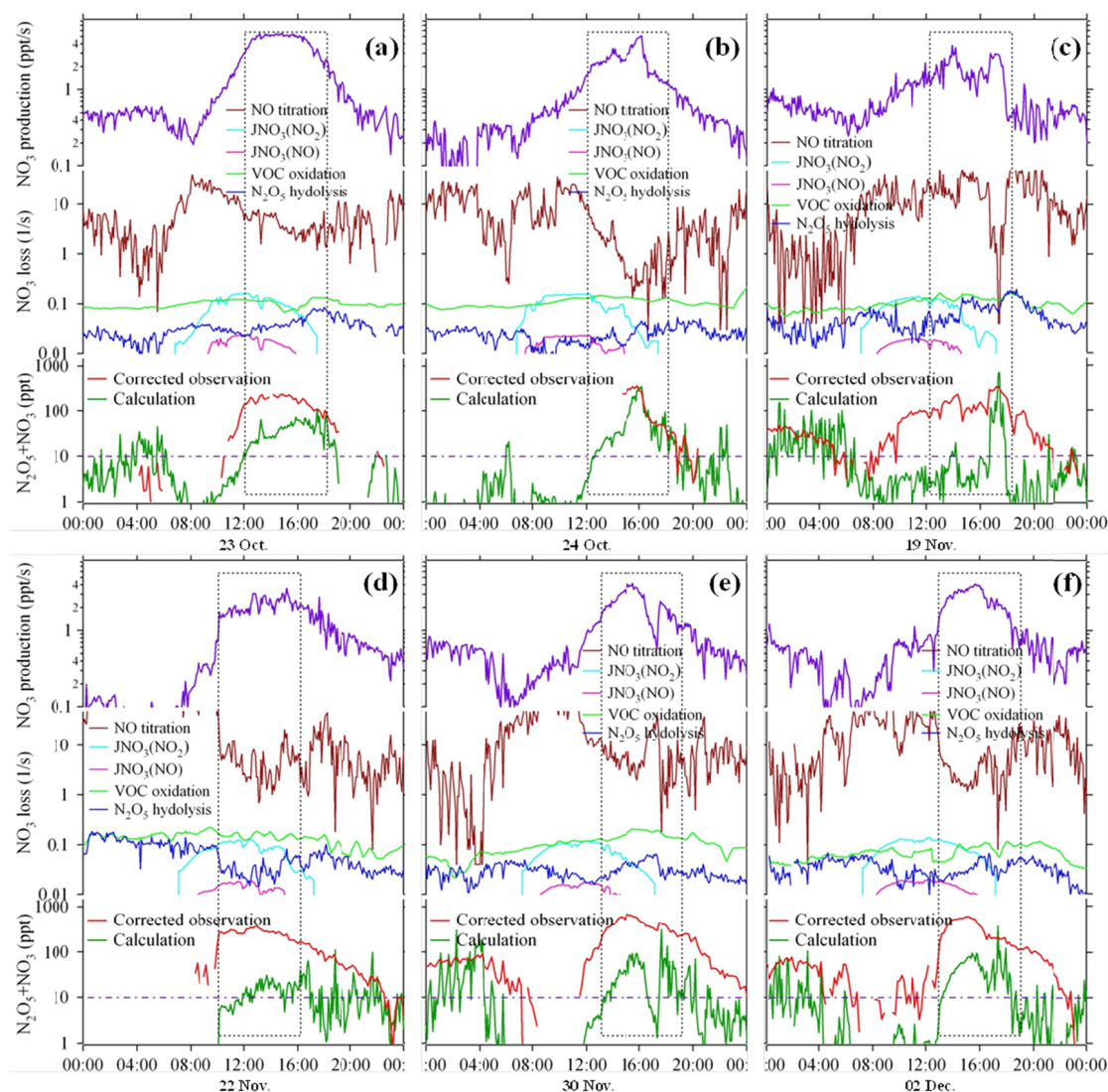


Fig. R1. NO_3 production rate from NO_2 and ozone, loss frequency of NO_3 from NO reaction, photolysis, VOC oxidation and N_2O_5 hydrolysis, steady-state calculated $\text{N}_2\text{O}_5 + \text{NO}_3$ and observed $\text{N}_2\text{O}_5 + \text{NO}_3$ after correction (for the interference from $\text{PAN} + \text{NO}_2$) for the six pollution episode days.

The detailed descriptions on the calibration procedure have been added in the revised manuscript as follows. “90 sccm of 2.5 ppmv NO₂ in nitrogen gas was mixed with 480 sccm of 2.1 – 4.6 ppmv O₃ generated by UV photolysis of O₂ in zero air (Model 111, TEI) in a glass reaction chamber in a commercially available calibrator (Model 6100, Envirionics). 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 Fig. 2 to include the calibration part. A more detailed figure is provided below but not included in the revised manuscript because it provides little additional information.

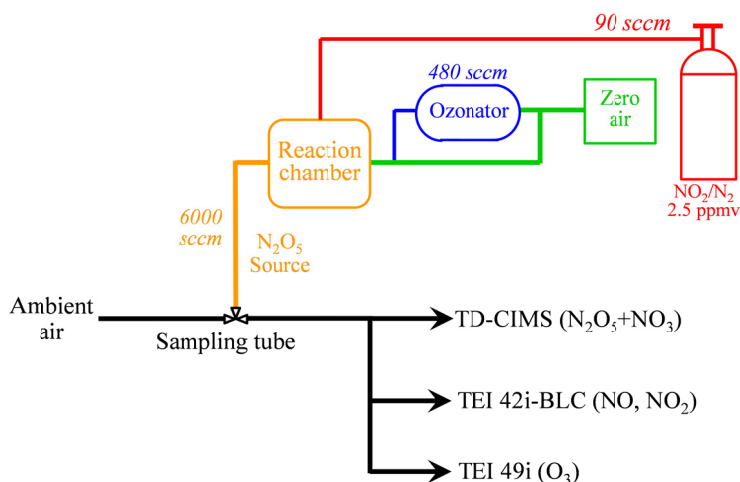


Fig. R2. Schematic diagram for N₂O₅ calibration using the on-line synthesis method.

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”.

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 “Fig.5” has been changed.

Page 7478, last paragraph: The $\text{NO}_3 + \text{N}_2\text{O}_5$ calibration technique is critical to the arguments about daytime N_2O_5 and warrants a figure. A demonstration of an example calibration (e.g., counts at 62 amu plotted against titration of NO_2 , O_3 or both from the calibration source) would be helpful to demonstrate the stated 3% accuracy of the measurement.

Reply: Fig. R3 shows the data points of signal at 62 amu versus the product of NO_2 and O_3 concentrations for N_2O_5 calibration on 4 December 2010. When 3012 Hz of 62 amu signal was detected by TD-CIMS, the NO_2 concentration from a chemiluminescence analyzer equipped with a photolytic NO_2 -converter and O_3 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_2 and O_3 concentrations were 31.3 and 362 ppbv, respectively. For more recently N_2O_5 calibrations, about 100 ppbv of NO_2 and 40 ppbv of O_3 were used, generating about 5 ppbv of N_2O_5 . Similar sensitivities of N_2O_5 in our CIMS were obtained with the two slightly different production sources of N_2O_5 . In the revised manuscript, we added a sentence of “When inputted 36.7 ppbv of NO_2 and 170.4 ppbv of O_3 (initial concentrations before reaction), the generated N_2O_5 was in level of 1.08 ppbv” instead of providing a figure. Note that the precision of 3% for 1000 pptv N_2O_5 was obtained based on the relative standard deviation of the 62 amu signal when inputting 1000 pptv of synthetic N_2O_5 .

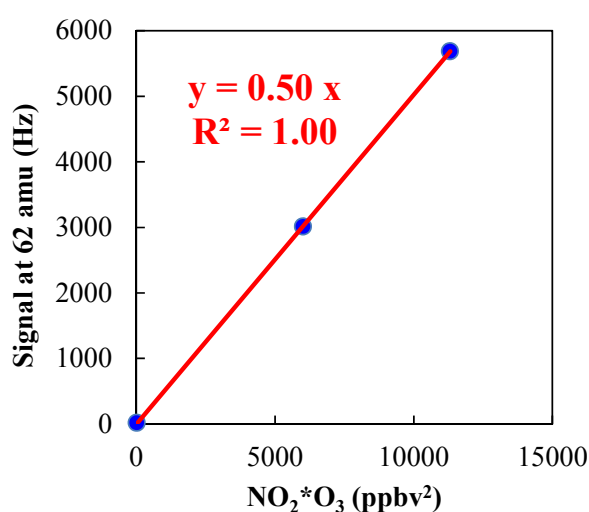


Fig. R3. Plot of 62 amu signal versus the product of NO_2 and O_3 for N_2O_5 calibration on 4 December 2010.

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_2O_5 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 Fig. 6 at Line 16 on Page 7482.

Page 7482, line 5: Suggest rewording: “ 23 ± 4 pptv of apparent $\text{NO}_3 + \text{N}_2\text{O}_5$ signal per ppbv of PAN”

Reply: Revised.

Page 7482, line 11: Suggested wording: “The mechanism for the interference of PAN on the NO_3 - 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.

Page 7483, line 4: Delete “the” before HNO₃.

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, NO₂, O₃ and PAN together with the measured N₂O₅ 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. R4 presents the data for NO, NO₂, O₃, O_x and PAN from GC-ECD together with the measured N₂O₅ from the I(N₂O₅)⁻ ion signal at 235 amu. From these data, it can be found that the predicted N₂O₅ in steady state during the daytime will be very low, as the NO concentration was very high in urban Hong Kong in early winter.

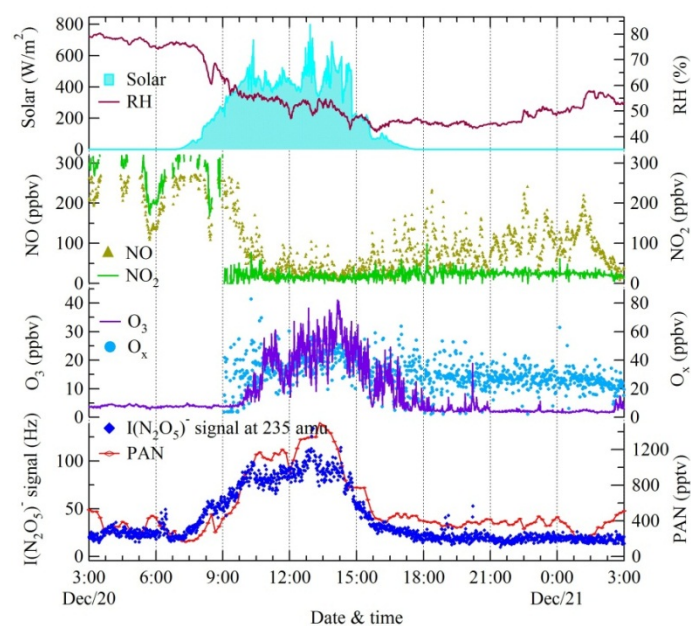


Fig. R4. Time series of I(N₂O₅)⁻ signal at 235 amu, trace gases and meteorological parameters in urban Hong Kong on 20 December 2010.