

Interactive comment on “High concentrations of N_2O_5 and NO_3 observed in daytime with a TD-CIMS: chemical interference or a real atmospheric phenomenon?” by X. Wang et al.

X. Wang et al.

cetwang@polyu.edu.hk

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Response (text in blue) to comments by Dr. Gavin Phillips (text in black)

The cause of the observations is almost certainly an artefact arising from some error in the operation of the mass spectrometer. There are issues with the measurement approach and the lack of investigation of possible chemical routes to account for up to 1000 pptv of daytime N_2O_5 . It is highly unlikely that these levels of N_2O_5 and NO_3 were actually observed during the day and it is therefore the responsibility of the authors to demonstrate that they have properly considered alternative reasons for the

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signals measured in this study. There are studies which report daytime N_2O_5 , but these report much lower (100s of times lower) concentrations. In my opinion, the authors are reporting some fraction of PAN as N_2O_5 and this not a matter for publication in a journal as it most likely arises from the way the CIMS was operated which is not immediately apparent from the manuscript.

Reply: We think Dr. Phillips may have mis-understood the main message of our paper. We never say that the 1000 pptv at 62 amu is the real signal of $\text{NO}_3 + \text{N}_2\text{O}_5$. To the contrary, we have shown that a large fraction of it comes from interferences from PAN + NO_2 (and other untested compounds/reactions). In the same time, we present some evidence indicating the possibility of daytime N_2O_5 at the study site. It is an unsolved issue as to the relative contribution by interference to 62 amu from the real signal. We want to point out that we have noticed this very unusual daytime NO_3 and N_2O_5 signal at 62 amu at the very beginning and have done a lot of tests in the past two and half years. We do not believe that the signal at 62 amu is a fraction of PAN, both because the mass peak at 62 amu was well separated from that at 59 amu and because the increase in 62 amu signal was small when a standard of PAN is added. Our result show that the 62 amu signal increased from 29 Hz to 105 Hz when we introduced 1.6 ppb of synthetic PAN to the TD-CIMS (with 59 amu signal (PAN) reaching ~8000 Hz).

The production of NO_3 and N_2O_5 From the data presented in the paper, it should be possible to see that the loss of NO_3 would be on the order of a per second via photolysis and reaction with NO. Simply taking a back of the envelope calculation of NO_3 production using data presented in the paper will give a steady state max of NO_3 of the order of one ppt. It is very difficult to see how N_2O_5 and NO_3 would reach the levels (up to 1000 pptv) reported in this paper. Nocturnal measurements of N_2O_5 and NO_3 struggle to reach these levels even in the absence of sunlight and with minimal NO. These concentrations are a little unbelievable and the authors need to attempt to explain where they arise from.”

Reply: Again we didn't say that 1000 ppt at 62 amu is all from the real contribution of

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N₂O₅ and NO₃. During the time periods of most daytime N₂O₅+NO₃ peaks (12:00 – 16:00 LT), the loss rate of NO₃ was 0.02 – 0.2 s⁻¹ via photolysis and 0.2 – 50 s⁻¹ via reaction with NO. This indicates that reaction with NO and NO₃ is the dominant loss pathway at the study site. In most cases, due to the relatively high NO, the calculated values using steady-state assumption were much lower than the observed values (after correction for interference due to PAN+NO₂). There is one exception. At 16:00 on 24 October when O₃, NO₂ and NO concentration was 96.1, 49.1 and 0.3 ppbv, respectively, the predicted NO₃ and N₂O₅ concentration (5 min average) could reach 534 pptv when only loss by photolysis and NO reaction are considered and 321 pptv if all major removal pathways (including VOCs oxidation and N₂O₅ hydrolysis) are considered. In comparison, the measured N₂O₅ + NO₃ concentration was 286.5 pptv (with correction for PAN+NO₂ interference). The agreement between observation and prediction under the condition of very low NO in this case indicates that the elevated N₂O₅ in daytime is possible at the study site.

The actual origin of the instrument artefact? I have the following questions and points about the setup of the CIMS and the checks made on the data. 1) What is the mass resolution of the instrument? Ideally it should be shown with the areas of the spectrum zoomed in to check the peaks to see if there is any “bleed” into neighbouring peaks. No figures of the mass spectrum during periods of interest are presented in the paper.

Reply: The mass spectrometer (Extrel 150-QC, 2.1 MHz, 9.5 mm, 1-500 amu) used in our CIMS has high resolution – 2000 (M/ΔM FWHM). Figure R1 shows the mass spectra of ambient air during daytime and at night by our TD-CIMS. Figure R2, the magnifying mass spectrum, clearly indicates that the mass peak at 62.00 amu was well separated from that at 59.00 amu.

2) If the PAN signal at amu 59 is detected at 62 due to bad resolution, this would explain why the N₂O₅ time series presented in figure 8 look identical to the PAN series. It would seem that the PAN is insufficiently accounted for. In my opinion the entire signal comes from PAN.

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Reply: Figure R2 shows that the mass peak at 62 amu was well separated from that at 59 amu, so the signal at 62 amu was unlikely detected from the PAN signal at 59 amu due to bad resolution. In addition, the low 62 amu signals (29 – 105 Hz) when performing PAN calibrations (~8000 Hz for 59 amu) further suggests that the 62 amu signals were not from the PAN signals at 59 amu. Figure R3 is an example showing relatively low 62 amu signals (average 95 Hz for 8743 Hz of 59 amu) when synthetic PAN was introduced to the TD-CIMS in the night of 4 November 2010.

3) Photolytic PAN sources are likely to contain PA radicals in excess and other components such as peracetic acid in the effluent. Does the addition NO₂ after the PAN source somehow increase the PAN from the source resulting in the increase in the signal 62?

Reply: Yes, photolytic PAN sources contain PA radicals in excess or other components such as peracetic acid in the sample flow, as indicated by a significant offset when we performed multi-point PAN calibrations. For the second question, the addition of NO₂ after PAN source increased the 62 amu signal but did not increase the PAN signal at 59 amu (see Fig. R4).

4) If the signal at 62 arises from 59 then any interference on PAN will result in interference on 62, e.g PAA

Reply: As discussed previously, we do not think the 62 amu signal arose from 59 amu.

5) What is the effect of adding NO₂ to the inlet on the PAN signal at 59? Does it increase? Does the increase in NO₂ somehow compensate for wall losses of PA inside the TD region?

Reply: When adding NO₂ to the synthetic PAN sample flow, the PAN signal at 59 amu decreased slightly (see Fig. R4). We attribute this phenomenon to the reaction between NO₂ with PA radicals in the TD region (Slusher et al., 2004, JGR, 109(D19): D19315).

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6) It also seems that the measurement of CINO₂ may also be affected by an artefact also resulting from poor instrument resolution (figure 10). It would be interesting to see levels of nighttime N₂O₅ measured with the CIMS and the concurrent CINO₂ observed.

Reply: We do not think the measurement of CINO₂ was affected by artifact resulting from poor mass resolution, because the mass resolution of our CIMS was high – 2000 (M/ΔM FWHM) and the mass peak at 208.30 amu was well separated with those around as shown in Fig. R5 below. The very strong correlation between 210 amu and 208 amu (two isotopes of CINO₂, see the Supplementary Information) provides additional evidence for the presence of daytime CINO₂. During the night-time of the same day (28 August 2011), the peak value of N₂O₅ concentration was ~200 pptv and the concentration peak of CINO₂ was ~600 pptv (see Fig. R6). Strong correlation between CINO₂ and N₂O₅ with a slope of 2.6 pptv/pptv (see Fig. R7) suggests the formation of CINO₂ via N₂O₅ hydrolysis in this coastal environment.

7) The N₂O₅ data presented at amu 235 look like a photochemically produced species related to the daytime HO_x cycle and not arising from the reaction of NO₃ and NO₂. If the instrument resolution is sufficiently low for the amu 59 signal to appear at amu 62, then it is also likely that signal out at 235 mass (and for that matter 208) units also includes signal coming from other species detected at near mass-to-charge ratios.

Reply: As stated above, our CIMS has sufficient mass resolution to resolve 62 amu and 235 amu from neighboring mass-to-charge ratios. Fig. R8 shows a mass spectrum for an ambient sample during daytime around 235 amu.

Figure captures:

Fig. R1. Mass spectrums of ambient air in urban Hong Kong at day and night by iodide TD-CIMS with heating the inlet tube to 180 °C.

Fig. R2. Magnifying mass spectrums of ambient air by TD-CIMS at day and night.

Fig. R3. Signals of 59 and 62 amu when a PAN standard was sampled.

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Fig. R4. Changes of signals at 59 and 62 amu when adding NO₂ to the sample flow of synthetic PAN.

Fig. R5. Magnifying mass spectrums of ambient air by TD-CIMS at night.

Fig. R6. Time series of CINO₂ and N₂O₅ + NO₃ and other compounds or parameters from 12:00 to 24:00 LT on 28 August 2011 at a suburban site in western Hong Kong.

Fig. R7. Relationship between CINO₂ and N₂O₅ + NO₃ for the night-time (19:00 – 24:00 LT) of 28 August 2011 at a suburban site in western Hong Kong.

Fig. R8. Magnifying mass spectrum of ambient air by cold CIMS at daytime.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/6/C2220/2013/amtd-6-C2220-2013-supplement.pdf>

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

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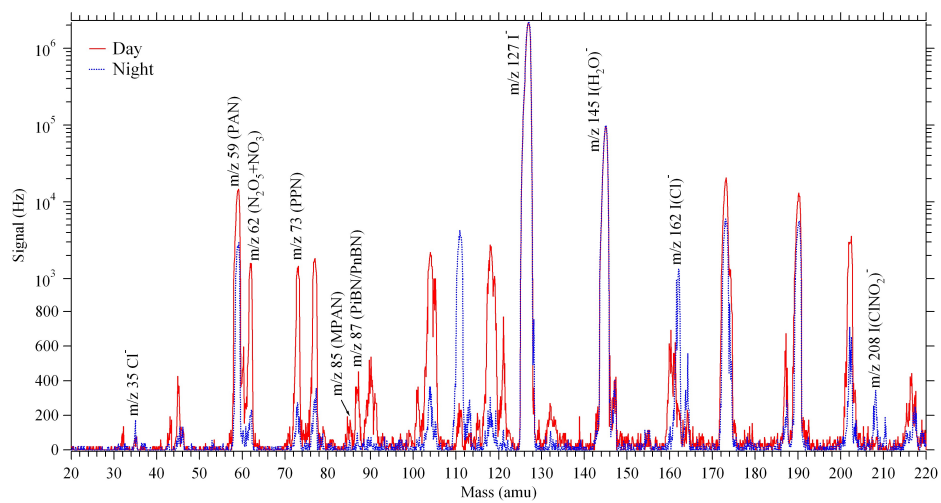


Fig. 1.

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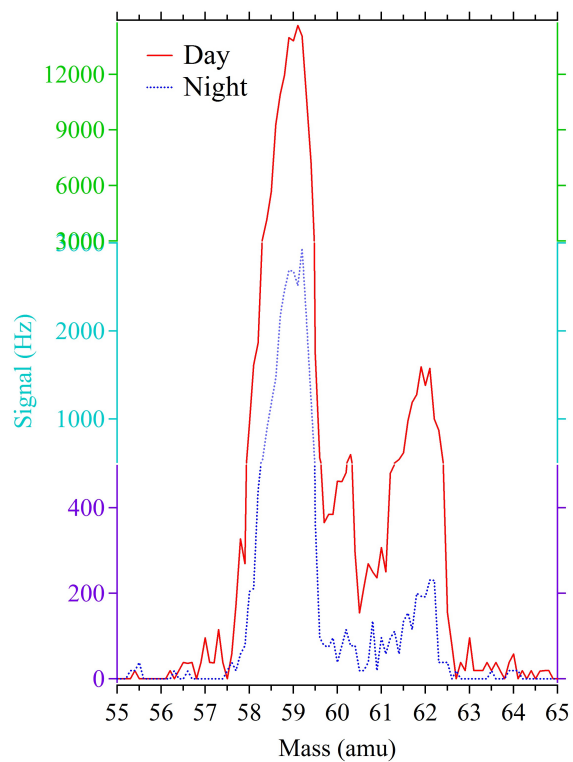


Fig. 2.

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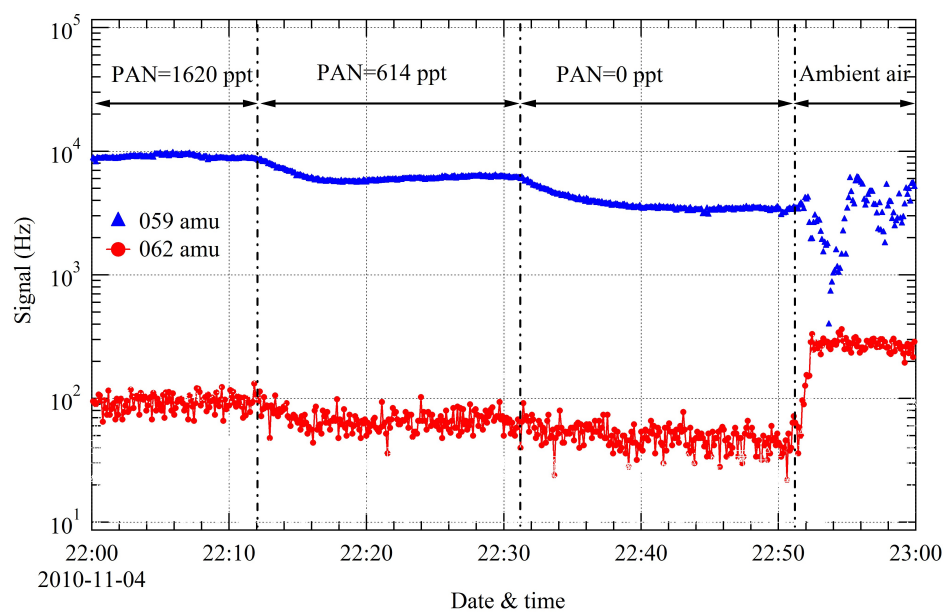


Fig. 3.

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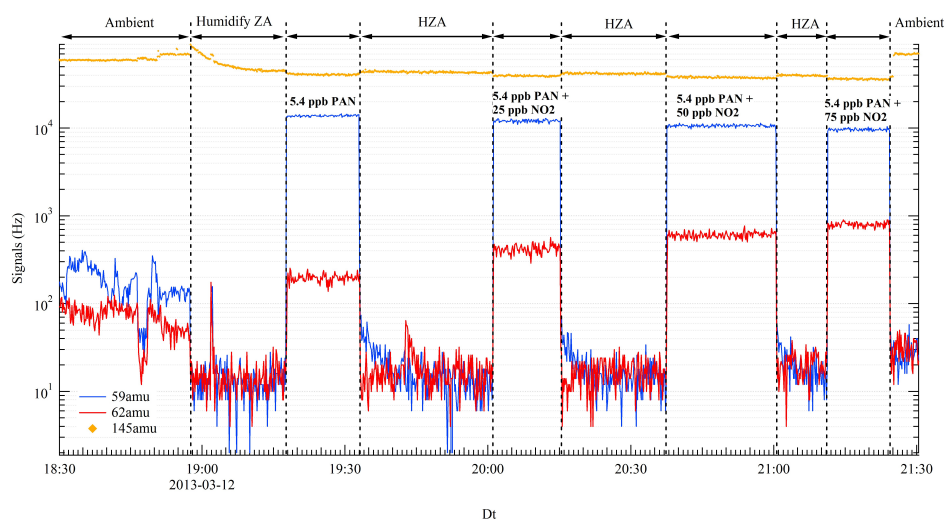


Fig. 4.

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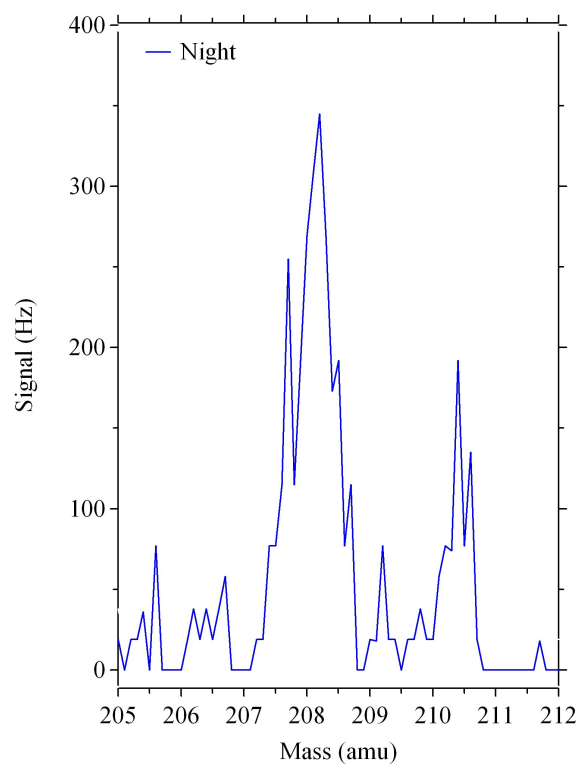


Fig. 5.

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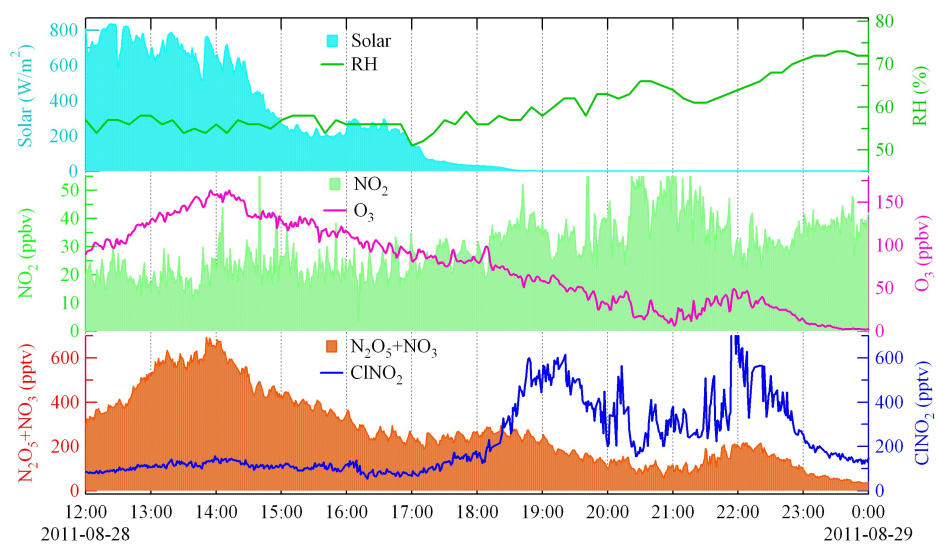


Fig. 6.

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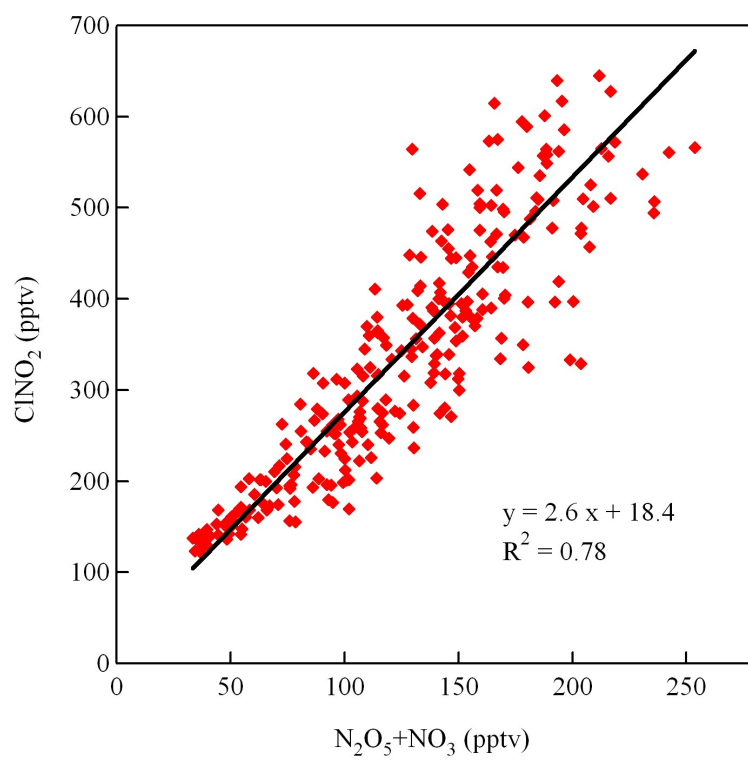


Fig. 7.

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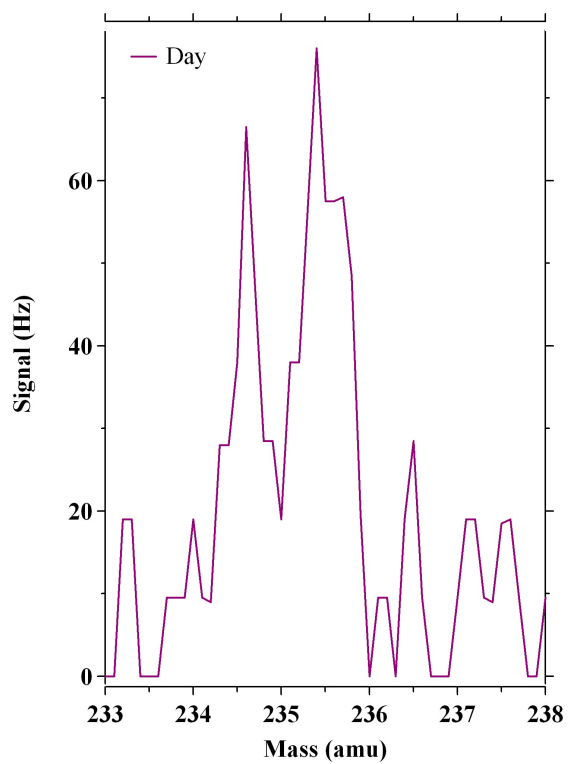


Fig. 8.

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