

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

Further comment on Wang et al. by Gavin Phillips (27/08/13, Mainz)

I would like to thank Professor Tao Wang for the rapid reply. The amtd/acpd systems normally do not seem to operate as discussions as both reviewers and authors place reviews and replies into the discussion at the last moment undercutting any discussion.

Reply: We thank Dr. Gavin Phillips for his interest in our work and for constructive comments. The discussions have helped authors to better convey their messages and to improve the quality of the manuscript.

My issues with the paper remain. I find it difficult to understand the precise point that the authors are trying to make (which in fairness may be my problem). The main message I get from the paper that, in the CIMS system as deployed, the signal at 62 mass units is an unreliable measure of $\text{NO}_3 + \text{N}_2\text{O}_5$ and has interference from (somehow) NO_2 and PAN. The authors do not really know why this comes about and seem not to be able to correct the signal satisfactorily. I think they should show more evidence to support the contention that N_2O_5 seems to be being produced during the daytime at the levels they state and discuss the chemistry in the manuscript. To me it seems more likely that, for whatever reason, the signal at mass 62 is more likely to come from these (acknowledged) interferences and not from $\text{N}_2\text{O}_5 + \text{NO}_3$. I think the paper title is not accurate. High levels of daytime $\text{N}_2\text{O}_5 + \text{NO}_3$ have not been observed and the authors have not demonstrated this. Contrary to authors' statement that "We never say that the 1000 pptv at 62 atm is the real signal of $\text{NO}_3 + \text{N}_2\text{O}_5$ ", they state in the paper conclusions "Surprisingly, concentration peaks of $\text{NO}_3 + \text{N}_2\text{O}_5$ were frequently observed in daytime at 62 amu channel in the TD-CIMS, which is in contrast to our current understanding of reactive nitrogen chemistry".

Reply: We acknowledge that we could have better worded the text in order to convey more clearly our key message and to distinguish the "raw" and "corrected" signals of 62 amu. We would like to state the key message of our paper as follows.

The TD-CIMS technique had apparently been successfully used in the US to measure the sum of N_2O_5 and NO_3 in ambient atmosphere, as indicated in two papers published in main-stream journals (Slusher et al., 2004; Huey et al., 2007). These studies have shown high-degree correlations between the signal at 62 amu and the measurement from a Cavity Ring-down Spectrometer, suggestive of the validity of the

signal of 62 amu in representing the sum of N_2O_5 and NO_3 . Although a subsequent study (Krecher et al., 2009) and a recent review (Chang et al., 2011) mentioned that the background signal at 62 amu could be high and variable, there were no detailed reports on the interferences contributing to the background and no clear conclusion to indicate invalidly of the use of 62 amu for measuring N_2O_5 and NO_3 .

In the present study, we deployed a TD-CIMS to an urban site (and later to a sub-urban and a rural site) in Hong Kong with the same model of CIMS and the same instrument configurations as in the previous studies. To our surprise, large signals were observed at 62 amu during daytime with equivalent N_2O_5 and NO_3 up to 1000 ppt. Such high daytime values cannot be explained by our current understanding of $\text{NO}_3/\text{N}_2\text{O}_5$ chemistry. Is this due to interferences, or a part of the signal is real? We have carried out detailed interference tests on possible compounds including PAN, HNO_3 , O_3 , and NO_2 . These results are valuable to the N_2O_5 CIMS community on the use of 62 amu. For the first time, it is discovered that the $\text{NO}_2 + \text{PAN}$ can significantly increase the interference at 62 amu. In the same time, we have found some evidence of daytime N_2O_5 at our study site with concurrently high NO_2 and O_3 . Although we cannot quantify with absolute certainty the relative contribution from interferences and real N_2O_5 signal, we think it is justified to report these findings to the community and to call for attention to re-examine the possibility of the presence of daytime $\text{NO}_3/\text{N}_2\text{O}_5$ in some environment.

In summary, the key message of our paper is (1) not use 62 amu for measuring $\text{NO}_3/\text{N}_2\text{O}_5$ in high NO_x environment and (2) elevated daytime N_2O_5 may be possible in some conditions.

Because we cannot determine the exact fraction of 62 amu from real $\text{NO}_3/\text{N}_2\text{O}_5$, we think it is inappropriate to use the data to discuss detailed chemistry. This is also the advice from referees who reviewed a previous version of this paper which contained much more discussions of the chemistry and implications of daytime N_2O_5 .

On page 7479, lines 18 and 19 the authors state “The time series of hourly mixing ratios of $\text{N}_2\text{O}_5 + \text{NO}_3$ measured in urban Hong Kong from 15 October to 4 December 2010 is shown in Fig. 3”. To me this is a statement that the authors contend that they measured 1000 pptv of $\text{NO}_3 + \text{N}_2\text{O}_5$. If that is the case, then showing time series of the signal at 62 and labelling them as $\text{N}_2\text{O}_5 + \text{NO}_3$ with calibrated units suggests to me that the authors have already corrected the data for the artefact. Is that the case? Is figure 3 corrected and calibrated data? If not, then the y axis should not be labelled

N₂O₅ + NO₃. The units should read “amu 62” and should be in counts or arbitrary units.

Reply: We agree. As indicated above, we will better define the raw and corrected signals of 62 amu. The data of N₂O₅ + NO₃ shown in Fig. 3, Fig. 4 and Fig. 10 have not been corrected for the interference from PAN + NO₂.

I agree with the authors that the MS seems to have unit mass resolution clearly separating the peaks at 59 and 62 Da and those at 208 and 210 for I(CINO₂)-. There are still outstanding issues.

In the case of the CINO₂ the plot shown in the SI (figure S4) implies that it is generated from calibration data. Is this the case? If so, this does not preclude the inference of a daytime artefact near these masses. Can the authors show the equivalent scatter plot during a period of measurable *daytime* CINO₂ signal? Does the isotopologue ratio hold? Also figure 5 in the authors’ reply (C2220) does not preclude the presence of a daytime artefact on a near mass. Do the authors have an equivalent plot during a period of measurable daytime CINO₂?

Reply: In Figure S4, the signals at 208 and 210 amu were from ambient air covering periods of both daytime and night-time. Figure R1 shows the scatter plot of 210 amu signal versus 208 amu signal for ambient air during a daytime period from 13:00 to 17:00 LT (local time). The slope is 0.31, very close to the natural ratio of 0.32 for ³⁷Cl: ³⁵Cl, indicating insignificant artifact of 208 amu signals from near mass peaks.

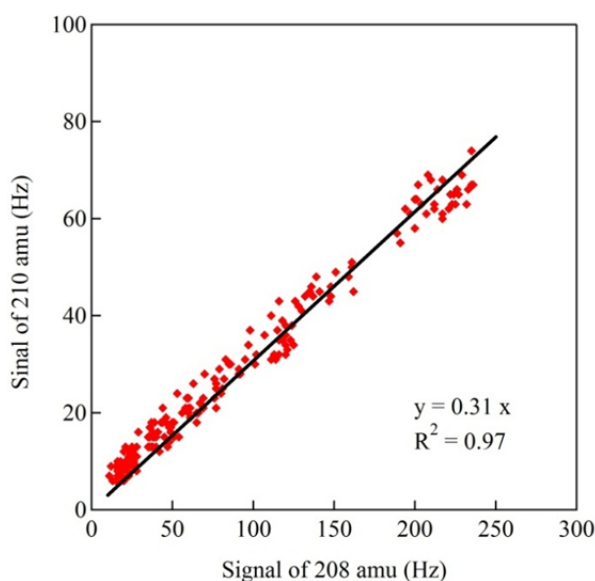


Fig. R1. Scatter plot of 210 amu signal versus 208 amu signal for ambient air during a daytime period of 13:00 – 17:00.

One (or two) piece of nice evidence for me would be the signal at 62 Da (corrected for artefacts and also maybe uncorrected) plotted versus the raw signal at 235 Da during the daytime period described by the authors in section 6 of the discussions paper (page 7485, lines 16 onward). Just because a particular signal responds to a standard addition it does not mean it does not also responds in the same way to atmospheric constituents present during ambient measurements. These two plots (uncorrected and corrected amu 62) may indicate the effectiveness of any attempted mass 62 correction for PAN in addition as to whether the two signals are indeed from the same molecule. In the future it might be an idea to reduce the degree of declustering and increase the proportion of the N₂O₅ signal observed at 235 and investigate whether or not concomitant changes in amu 62 are consistent with the authors contention that amu 62 measures N₂O₅ during the day.

Reply: Only in a cold CIMS, there are measurable 235 amu signals. When a cold inlet is used, the signal of 59 amu is very low and do not change with PAN concentration. Therefore, we did not conduct the interference tests for a cold CIMS and thus correction is unavailable. As suggested, Figure R2 shows the scatter plot of 235 amu signal versus uncorrected 62 amu signal for ambient measurements for the daytime period from 6:00 to 18:00 LT (the same day as that in Fig. 9 of the Manuscript). From Figure R2, it can be seen that the 235 amu signals exhibited generally good correlation with the 62 amu signals.

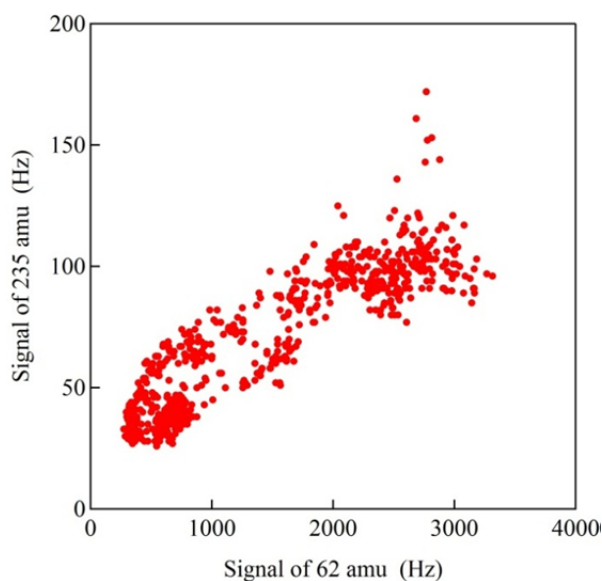


Fig. R2. Scatter plot of 235 amu signal versus 62 amu signal for ambient air during a daytime period of 06:00 – 18:00.

We have modified our CIMS to reduce the degree of declustering and have increased the sensitivity of the $I(\text{N}_2\text{O}_5)^-$ signal at 235 amu. The new set-up will be compared with a CRDS system in this fall.

One reason for my confusion is that the authors also seem to discuss the data as if the signal at amu 62 is entirely $\text{N}_2\text{O}_5 + \text{NO}_3$. For example, page 7486; lines 10 to 20 discuss the possible ClNO_2 yields from the N_2O_5 measured at amu 62. The N_2O_5 concentration is assumed to be approximately 600, but is this corrected? If the authors know the signal is largely due to other species why call it $\text{N}_2\text{O}_5 + \text{NO}_3$. In any case any value of N_2O_5 can be generated when assuming the value of three or more variables in a calculation, such as γ , ClNO_2 production efficiency, and aerosol surface area.

Reply: We agree the comments on inappropriate use of unit. Here the intention is to show that based on the daytime ClNO_2 , calculations support the presence of N_2O_5 at several hundred of ppts, although the calculations had to assume the values of uptake coefficient and ClNO_2 production yield, which we think are not unreasonable. We will further modify this part.

How is the absolute calibration of N_2O_5 achieved? There is a description in the manuscript of the production of N_2O_5 by the reaction of NO_2 with O_3 . However the efficiency of N_2O_5 production is not mentioned. There are likely to be large NO_3 losses in this system and the output should be verified independently by measuring N_2O_5 produced by the system, not by the loss of starting material. Was this done? If not, what was the efficiency of production assumed for the source? If there is an over estimate of production efficiency then is likely an underestimate of instrument sensitivity and consequently an over estimate of atmospheric concentrations before adding any effect from measurement artefacts.

Reply: N_2O_5 was synthesized with an online-method in which nitrogen dioxide (NO_2) was reacted with excess ozone (O_3) to produce NO_3 and then N_2O_5 . 90 sccm of 2.52 ppmv NO_2 (coexisting with 0.30 ppmv NO) in N_2 was mixed in a commercially available calibrator (Model 6100, Environics) with 480 sccm of 2.13 ppmv O_3 generated by UV photolysis of O_2 in zero air (Model 111, TEI) in a glass reaction chamber with a reaction time of about one minute, and then the output was further diluted to 6 slpm by the zero air. The outputting NO_2 , O_3 and N_2O_5 concentration was 36.7 ppbv, 169.4 ppbv, and 1.08 ppbv respectively. The produced concentration of

N_2O_5 was determined by the difference of NO_2 before and after adding O_3 with consideration of the interferences in NO_2 measurement from O_3 , NO_3 and N_2O_5 . The main interference happened in the photolytic NO_2 converter where a small fraction of newly produced NO by photolysis was oxidized by O_3 in the sample flow within the retention time of about one second. The N_2O_5 concentration determined from the NO_2 difference was further confirmed by the decrease in O_3 concentration.

We did not measure the absolute concentration of the produced N_2O_5 with another independent measurement technique as we did not have such an instrument. However, we concurrently measured the total reactive nitrogen (NO_y) with a chemiluminescence NO_x analyzer equipped with a molybdenum converter to check NO_y loss in the calibration system by comparing the signal with and without adding O_3 to NO_2 . The result showed no obvious decrease in concentration of total nitrogen in the calibration system. Here we acknowledge that a small fraction of N_2O_5 could be converted into gaseous nitric acid, but believe that the HNO_3 in the calibration system was insignificant (<10% of N_2O_5) with reference to the testing result by Bertram et al. (2009).

In our more recent studies, N_2O_5 is synthesized by reaction of O_3 with excessive pure NO_2 with subsequent dilution by synthetic air. The final concentrations of O_3 and NO_2 were 40 ppbv and 100 ppbv, respectively, 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 summary, I find the lack of clear distinction between the signals measured by the CIMS and the actual calibrated, corrected concentrations really confusing. I still think that the paper is describing some unfortunate cross sensitivity with a molecule or molecules unknown which gets photochemically produced in the day (maybe it's just PAN). It is unfortunate, but I think this needs more work in the lab. I am not completely against being persuaded, but I think there is more work that needs to be done as currently the paper raises more issues than it answers.

Reply: We understand the above concerns. In fact we also think that the result of daytime N_2O_5 phenomenon is most unusual. In this study, we present some evidence (235 amu and ClNO_2 signals) to support such a possibility, and we don't think the 62 amu signal is all due to PAN, as discussed in the paper. We welcome your and other colleagues' comments on our reported results, and we think this is a healthy way to further develop of our knowledge on not-well understood N_2O_5 chemistry in different

environments of the globe.

References

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