

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.

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 amu 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".

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 $\text{N}_2\text{O}_5 + \text{NO}_3$. The units should read "amu 62" and should be in counts or arbitrary units.

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 $\text{I}(\text{ClNO}_2)^-$. There are still outstanding issues.

In the case of the ClNO_2 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* ClNO_2 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 ClNO_2 ?

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.

One reason for my confusion is that the authors also seem to discuss the data as if the signal at amu 62 is entirely N₂O₅ + NO₃. For example, page 7486; lines 10 to 20 discuss the possible ClNO₂ yields from the N₂O₅ measured at amu 62. The N₂O₅ 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 N₂O₅ + NO₃. In any case any value of N₂O₅ can be generated when assuming the value of three or more variables in a calculation, such as gamma, ClNO₂ production efficiency, and aerosol surface area.

How is the absolute calibration of N₂O₅ achieved? There is a description in the manuscript of the production of N₂O₅ by the reaction of NO₂ with O₃. However the efficiency of N₂O₅ production is not mentioned. There are likely to be large NO₃ losses in this system and the output should be verified independently by measuring N₂O₅ 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.

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.