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 NO3 + N2O5 and has interference from (somehow) NO2 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 N2O5 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 N2O5 + NO3. I think the paper title is not accurate. High levels of daytime N2O5 + NO3 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 NO3+N2O5”, they state in the paper conclusions “Surprisingly, concentration peaks of NO3 + N2O5 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 N2O5 +NO3 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 NO3 + N2O5. If that is the case, then showing time series of the signal at 62 and labelling them as N2O5 + NO3 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.

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(ClNO2). There are still outstanding issues.

In the case of the ClNO2 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 ClNO2 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 ClNO2?

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.