Comment on Wang et al. (Gavin Phillips, MPI, Mainz, 21/08/2013)

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 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.

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.

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.
2) If the PAN signal at amu 59 is detected at 62 due to bad resolution, this would explain why the N_2O_5 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.
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 NO_2 after the PAN source somehow increase the PAN from the source resulting in the increase in the signal 62?
4) If the signal at 62 arises from 59 then any interference on PAN will result in interference on 62, e.g PAA
5) What is the effect of adding NO_2 to the inlet on the PAN signal at 59? Does it increase? Does the increase in NO_2 somehow compensate for wall losses of PA inside the TD region??
6) It also seems that the measurement of $ClNO_2$ may also be affected by an artefact also resulting from poor instrument resolution (figure 10). It would be interesting to see levels of nighttime N_2O_5 measured with the CIMS and the concurrent $ClNO_2$ observed.
7) The N_2O_5 data presented at amu 235 look like a photochemically produced species related to the daytime HOx cycle and not arising from the reaction of NO_3 and NO_2. 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.