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Atmospheric Measurement Techniques Discussions

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.

Anonymous Referee #3

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This manuscript reports on measurements of N2O5 and NO3 using chemical ionization mass spectrometry (CIMS) at an urban site in Hong Kong from October 17th to December 4th in 2010. It was found that daytime concentrations of the species were higher than nighttime concentrations. Several potential sources for interference in these measurements were evaluated, specifically the chemical processes that could result in the formation of these species. On the basis of these investigations they found that peroxy acetyl nitrate (PAN) can contribute noticeably to the concentration of N2O5 and NO3 and in the presence of NO2 this effect was amplified and could account for up to 30%-50% of the average daytime N2O5 and NO3 signal measured. This was further

evaluated by introducing synthetic PAN to zero air as well as clean ambient air from a coastal site. The mechanism behind this was unknown but it has been observed that higher NOX levels caused significantly higher interference at 62 amu. Other possible sources of interference were ClONO2, BrONO2 and HO2NO2 were tested. In the case of ClONO2 and BrONO2, both recorded during measurements and interference from them was corrected in the data. ClONO2 would not affect their results because ClONO2 was thermally unstable and thus unable to pass through the heated inlet. To confirm these measurements a series of follow up measurements were made utilizing a cold version of CIMS, allowing for the measurement of I(N2O5)- which was expected to be free from the chemical interference affecting the NO3- ion. These measurements concurred with the previous field study, finding the peak in I(N2O5)- at the same time as a peak in solar radiation. Thus, the authors concluded that elevated N2O5 and NO3 were a real effect, but the interference in measuring them with the NO3- ion also added in a large variability that was difficult to correct, leaving 62 amu unsuitable for use in measuring N2O5 and NO3 with TD-CIMS in environments high in NOX. This paper was reasonably well written and referenced. Overall, this is a useful study to the CIMS community, and I suggest publication with several corrections below. 1: Page 7477, line 26: The comma is unnecessary. 2: Page 7478, Line 9-12: Refers to figure 3 as a graph showing the I- signal at 127 amu, NO3- signal at 62 amu and PAN signal at 59 amu, etc. However in figure 3 the only signal that appears present is the NO3- signal. If this line represents the summation of these ions it should be reflected in the comment below the figure, otherwise the other lines are absent from the figure. 3: Page 7481, Line 20: There is no need for the word 'the', should read as "was evaluated post field campaign by". 4: Page 7482, Line 17: Large in "A surprising finding was much large interferences at 62 amu" should read "A surprising finding was much larger interferences at 62 amu". 5. The title of the manuscript is a bit misleading. Perhaps, it should be changed to "Possible interference of measurements of N2O5 and NO3 by a TD-CIMS", since as they concluded that 62 peak cannot be trustable for NO3 and N2O5 because of possible interference.

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