

Interactive comment on “High concentrations of N₂O₅ and NO₃ observed in daytime with a TD-CIMS: chemical interference or a real atmospheric phenomenon?” by X. Wang et al.

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Response to comments from Referee #3

Anonymous Referee #3 (Received and published: 13 October 2013) 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

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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 NO_x 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 NO_x. 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.

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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.

Reply: Thank the anonymous Referee #3 for the helpful comments. Note that it is HO₂NO₂ instead of ClONO₂ that would not affect their results because it was thermally unstable and thus unable to pass through the heated inlet. 1: Corrected. 2: Corrected it with adding a figure (see Figure 3) in the revised manuscript. 3: Corrected. 4: Corrected. 5: The title has been corrected into "Large daytime signals of N₂O₅ and NO₃ inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon?". In addition, phrases like N₂O₅+NO₃ concentration or mixing ratio has been changed into apparent N₂O₅+NO₃ concentration or mixing ratio (N₂O₅+NO₃*) in the revised manuscript.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/6/C3242/2013/amtd-6-C3242-2013-supplement.pdf>

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