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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 #2

Anonymous Referee #2 (Received and published: 27 September 2013) TD-CIMS measurements at Hong Kong are presented and their potential interferences analyzed. It is shown that PAN/NO₂ do significantly interfere at 62 amu. Nevertheless, it is argued that significant levels of daytime N₂O₅ have been observed. This manuscript is concise and well illustrated. To my opinion, data and possible interferences have been discussed in great detail. This paper conveys interesting technical (interferences

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at 62 amu) and scientific (daytime levels of N₂O₅) information, both of which warrant publication.

Reply: We would like to thank the Referee #2 for the comments. The detailed replies will be listed as following point by point.

Concerning the identification of possible interferences, it is stated that all possible interferences have been considered with only PAN/NO₂ mix leading to large signal not undergoing zeroing in their experimental procedure. I'm just wondering as Hong Kong is a densely populated region facing strong anthropogenic and biogenic emissions, if such a statement is really true? Organic nitrate are maybe more abundant and ubiquitous than thought, especially in organic aerosols. Could organic aerosols carry organic nitrate that may either directly or indirectly (through their possible, but not known partitioning between phases) interfere in these measurements?

Reply: It is possible that other organic nitrates in addition to PAN may have interferences to our N₂O₅ measurements by TD-CIMS. We have added this point in the revised manuscript.

For the present set-up, our CIMS is operated with a cold inlet with other modifications and the N₂O₅ concentration is quantified by the signal of I(N₂O₅)- cluster ion at 235 amu. The new set-up will be compared with a CRDS system in this fall.

As Hong Kong face both biogenic and anthropogenic emissions, I would have an unfair comment to the authors. In fact, a paper just appeared (after the submission of this AMT manuscript) stating that NO₂ reacts with Criegee intermediate producing nitrate radicals (i.e., NO₃ radical production from the reaction between the Criegee intermediate CH₂OO and NO₂, Phys. Chem. Chem. Phys., 2013, 15, 17070). Would reactions like that one be captured by these CIMS measurements? If yes, this would be a great outcome and a new start in characterizing the atmospheric importance of such processes.

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Reply: This is a very good point. It is possible that the reaction between the Criegee intermediates and NO₂ contributed to NO₃ production and the elevated 62 amu signals in our CIMS. We have added this point in the revised manuscript. Further tests and detailed calculations will be conducted to evaluate the role of Criegee intermediate reactions in the production of NO₃ and N₂O₅.

NO_x were measurement with a chemiluminescence instrument coupled to a photolytic converter. This could also be used to highlight HONO, HO_x, NO_y interferences in these measurements has this been investigated as it may also convey information about the CIMS interferences?

Reply: As described in Section 2 in the manuscript, NO₂ was analyzed with a chemiluminescence instrument equipped with a photolytic NO₂-converter illuminated by ultra-violet light emitting diodes at 395 nm. The photolytic NO₂-converter is insensitivity to other NO_y species including HNO₃, N₂O₅, NO₃, HO₂NO₂, ClONO₂, PAN, CH₃NO₃ and minimizes the interference from HONO and BrONO₂ (Ryerson et al, JGR, 2000). Therefore, we do not think there are significant interferences to NO₂ measurement from other NO_y species.

Ryerson, T., Williams, E., and Fehsenfeld, F.: An efficient photolysis system for fast-response NO₂ measurements, *J. Geophys. Res.*, 105, 26447-26461, doi: 10.1029/2000JD900389, 2000.

Finally, while the data do point toward high N₂O₅ day time levels, what would be the reason for that? Is it specific to Hong Kong or do the authors think it is a widely spread phenomena?

Reply: In our view, the high daytime N₂O₅ levels were mainly due to the simultaneous strong photochemical activity and high concentration of NO₂ in the afternoon. In particular, high levels of NO₂ put forward the equilibrium between NO₃ and N₂O₅ to produce N₂O₅, and thus led to high levels of daytime N₂O₅. This is likely a widely spread phenomena in mega cities suffered with heavy photochemical pollution and

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strong NO_x emission.

In conclusion, this is a nice piece of work.

Reply: Thanks a lot.

Please also note the supplement to this comment:

<http://www.atmos-meas-tech-discuss.net/6/C3238/2013/amtd-6-C3238-2013-supplement.pdf>

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

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