Response (text in blue) to comments from Referee #2 (text in black)

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/NO_2 do significantly interfere at 62 amu. Nevertheless, it is argued that significant levels of daytime N_2O_5 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 at 62 amu) and scientific (daytime levels of N_2O_5) 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/NO_2 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 N_2O_5 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 N_2O_5 concentration is quantified by the signal of $I(N_2O_5)^-$ 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 NO_2 reacts with Criegee intermediate producing nitrate radicals (i.e., NO_3 radical production from the reaction between the Criegee intermediate CH_2OO and NO_2, 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.

Reply: This is a very good point. It is possible that the reaction between the Criegee intermediates and NO_2 contributed to NO_3 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 NO_3 and N_2O_5.

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, NO_2 was analyzed with a chemiluminescence instrument equipped with a photolytic NO_2-converter illuminated by ultraviolet light emitting diodes at 395 nm. The photolytic NO_2-converter is insensitivity to other NO_y species including HNO_3, N_2O_5, NO_3, HO_2NO_2, $ClONO_2$, PAN, CH_3NO_3 and minimizes the interference from HONO and $BrONO_2$ (*Ryerson et al, JGR, 2000*). Therefore, we do not think there are significant interferences to NO_2 measurement from other NO_y species.

Ryerson, T., Williams, E., and Fehsenfeld, F.: An efficient photolysis system for fast-response NO_2 measurements, J. Geophys. Res., 105, 26447-26461, doi: 10.1029/2000JD900389, 2000.

Finally, while the data do point toward high N_2O_5 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 N_2O_5 levels were mainly due to the simultaneous strong photochemical activity and high concentration of NO_2 in the afternoon. In particular, high levels of NO_2 put forward the equilibrium between NO_3 and N_2O_5 to produce N_2O_5, and thus led to high levels of daytime N_2O_5. This is likely a widely spread phenomena in mega cities suffered with heavy photochemical pollution and strong NO_x emission.

In conclusion, this is a nice piece of work.

Reply: Thanks a lot.