Supplementary information

of

Large daytime signals of N_2O_5 and NO_3 inferred at 62 amu in a TD-CIMS: chemical interference or a real atmospheric phenomenon?

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1 Interference tests of PAN and HNO_3 to the TD-CIMS

Due to the relatively high abundances and similar pattern of daytime concentration peaks, PAN and HNO_3 are considered as the most possible compounds that had interference to the daytime N_2O_5 signals in this study. During and after the field campaign, a series of field tests were conducted to examine their interference to the detection of our CIMS.

The interference tests of PAN were performed for four times (Oct. 29, Nov. 8, Nov. 15 and Nov. 23 2012) by adding a stable trace flow (40 sccm) of synthetic PAN into the zero or ambient air samples. The experimental set-up is illustrated in Fig. S1. PAN was generated by an on-line PAN calibrator (*Meteorologie Consult GmbH*), in which excess acetone carried by ultrapure air was photolyzed with a Penray lamp and then reacted with NO and NO_2. A NO standard containing 4.83 (± 2%) ppmv NO balanced with nitrogen (*Scott-Marrin Inc., California, USA*) was used. The output PAN concentrations were determined by the NO concentration, the production efficiency of PAN and the dilution coefficient with zero air, and finally were quantified by using two gas analyzers of NO_x and NO_y. After standard addition of this synthetized and highly concentrated PAN to the sample flow, the changes in the signals of PAN at 59 *amu* and NO_3+N_2O_5 at 62 *amu* were inspected. Thus the interference of PAN to the NO_3^- signal in our CIMS could be determined.

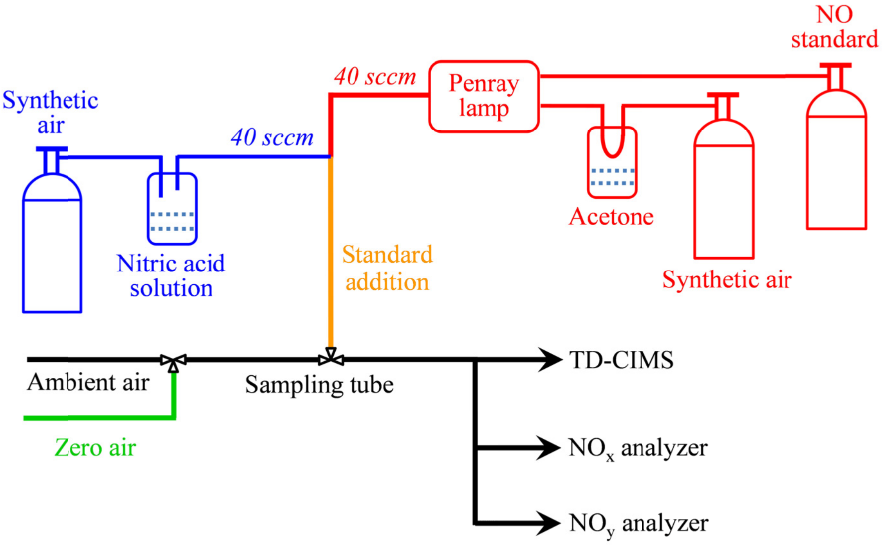

Fig. S1. Schematic of PAN and HNO_3 interference tests.

The interference tests of HNO_3 were conducted for three times (Nov. 08, Nov. 19, Nov. 23 2012), with similar standard addition method. A MFC-controlled synthetic airflow (40 sccm) was introduced into a bottle filled with nitric acid solution (5%, volume concentration), carrying out the HNO_3 gas volatized. The concentrations of HNO_3 were first quantified with a NO_y analyzer with and without a Nylon filter, and were also simultaneously measured by the NO_x and NO_y analyzers during the standard addition. After this trace flow of HNO_3 was added into the ambient sample flow, the changes in NO_3+N_2O_5 signals at 62 *amu* were examined. Considering that CH_3COO^- (the proxy of PAN in TD-CIMS) could react with HNO_3 to produce NO_3^- and thus interfere the N_2O_5 measurement, the test by adding both HNO_3 and PAN simultaneously was conducted once on Nov. 23, 2012.

2 Steady-state predictions

In the troposphere, the chemical formation and losses of NO_3 are dominated by the reactions of R1-R9, which together establish a near-instantaneous steady state during the daytime.

$$NO_2 + O_3 \xrightarrow{k_1} NO_3 + O_2 \quad \text{(R1)}$$

$$NO_3 + NO_2 \xleftrightarrow{K_{eq}} N_2O_5 \quad \text{(R2)}$$

$$NO_3 + NO \xrightarrow{k_3} NO_2 + NO_2 \quad \text{(R3)}$$

$$NO_3 \xrightarrow{j_4} NO_2 + O \quad \text{(R4)}$$

$$NO_3 \xrightarrow{j_5} NO + O_2 \quad \text{(R5)}$$

$$NO_3 \xrightarrow{k_6, VOC_i} products, k_6 = \sum_i (k_{VOC,i} \cdot [VOC]_i) \quad \text{(R6)}$$

$$NO_3 \xrightarrow{k_7, hetero.} products, k_7 = \frac{1}{4} c_{NO_3} \cdot \gamma_{NO_3} \cdot S_{aerosol} \quad \text{(R7)}$$

$$N_2O_5 \xrightarrow{k_8, hetero.} products, k_8 = \frac{1}{4} c_{N_2O_5} \cdot \gamma_{N_2O_5} \cdot S_{aerosol} \quad \text{(R8)}$$

$$N_2O_5 \xrightarrow{k_9, \text{homo.}} 2HNO_3, k_9 = k_I \cdot [H_2O] + k_{II} \cdot [H_2O]^2 \quad \text{(R9)}$$

The steady-state calculation based on the source and loss terms is a useful tool to predict the daytime concentrations of NO_3 (Geyer et al., 2003; Brown et al., 2005; Osthoff et al., 2006). The concentrations of NO_3 can be readily predicted by

$$[NO_3]_{calc} = \frac{k_1 \cdot [NO_2] \cdot [O_3]}{k_3 \cdot [NO] + j_4 + j_5 + k_6 + k_7 + (k_8 + k_9) \cdot K_{eq} \cdot [NO_2]} \quad \text{(Eq. 1)}$$

Similarly, N_2O_5 follows a rapid steady state via the fast equilibrium with NO_3 and NO_2 under warm conditions (R2). Thus the concentrations of N_2O_5 can be estimated as

$$[N_2O_5]_{calc} = K_{eq} \cdot [NO_2] \cdot [NO_3]_{calc} \quad \text{(Eq. 2)}$$

The reaction rate constants of k_1, k_{2f}, k_{2b} and k_3 were adopted from the Master Chemical Mechanism (MCM version 3.1; *http://mcm.leeds.ac.uk/MCM/*) (Saunders et al., 2003; Atkinson et al., 2004). The photolysis frequencies of NO_3 decomposing to NO_2 and NO (j_4 and j_5) were calculated as functions of solar zenith angles as described in the MCM, and were rescaled by the measured j_{NO2} values. The rate constants for the reactions of VOCs with NO_3 ($k_{VOCs,i}$) were taken from a review by Atkinson and Arey (2003). For the heterogeneous processes, the uptake coefficients of

NO_3 and N_2O_5 on wet aerosol surfaces (γ_{NO3} and γ_{N2O5}) were 0.004 and 0.03, respectively, which is considered to be suitable for coastal urban atmospheres (Evans and Jacob, 2005; Aldener et al., 2006). The mean molecular speeds of NO_3 and N_2O_5 (i.e. c_{NO3} and c_{N2O5}) were calculated from the gas kinetic theory (Aldener et al., 2006; Osthoff et al., 2006), and the surface area concentrations of aerosols were calculated based on the measured particle number size distributions. The loss rate of N_2O_5 via homogeneous hydrolysis with water vapor (k_9) was adopted from the measured value by Wahner et al. (1998). During the observations, only 29 VOC species (C2–C9) were measured. To get a more accurate estimation of the loss frequency of NO_3 by VOCs, we classified all of the VOC compounds into three categories: anthropogenic VOCs, terrestrial biogenic VOCs and DMS. The loss frequency of NO_3 by anthropogenic VOCs was calculated as the value of the measured 28 hydrocarbons (except isoprene) multiplied by a factor of 2; for biogenic VOCs, the loss was calculated from the rate for isoprene multiplied by a factor of 3.5 (according to the emission ratio of total terrestrial biogenic VOCs to isoprene in China (Yan et al., 2005)); the reaction rate with DMS was estimated as one fourth of the total rates for the oxidation of VOCs (R6), NO_3 hydrolysis (R7) and homogeneous and heterogeneous N_2O_5 hydrolysis (R8 and R9) (Aldener et al., 2006).

3 Measurements of N_2O_5 by the cold CIMS

In addition to the NO_3^- ion, the cluster ion of $I(N_2O_5)^-$ can also be used to quantify the concentrations of N_2O_5 by using a iodide CIMS with an unheated inlet (Kercher et al., 2009). In the cold CIMS, the N_2O_5 molecules in the sample air directly react with iodides in the flow tube to produce $I(N_2O_5)^-$ which are then detected by the mass spectrometer at 235 *amu*. Due to the apparent dependence of $I(N_2O_5)^-$ yield/sensitivity on the water vapor mediated cluster formation, a correction should be made for the obtained $I(N_2O_5)^-$ signal based on the humidity of the sample flow (e.g., the $I(H_2O)^-/I^-$ ratio). Because the $I(N_2O_5)^-$ ions only come from the N_2O_5, the signals of $I(N_2O_5)^-$ are believed to be isolated from interference and accurately reflect the true N_2O_5 concentrations. Given this advantage, this detection scheme has been adopted extensively in recent years (Bertram and Thornton, 2009; Bertram et al., 2009; Riedel et al., 2012; *etc.*). Parallel measurements of N_2O_5 with a cold CIMS and a CRDS in Boulder, CO on the night of 26 February 2008 have shown excellent agreement between the two principally different instruments (Kercher et al., 2009).

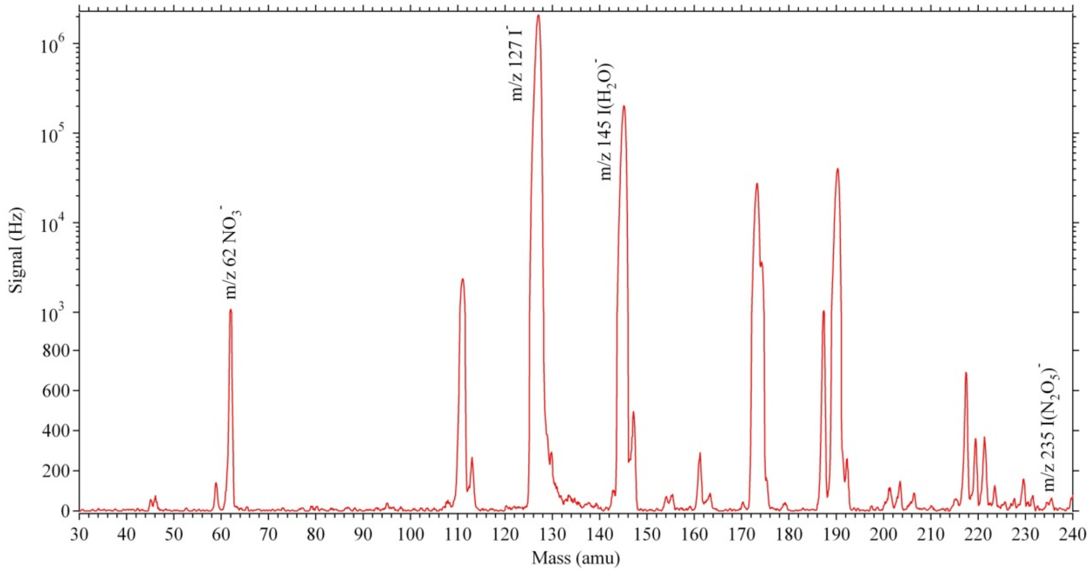

Fig. S2. Mass spectrum of the ambient air in urban Hong Kong at daytime by I^- CIMS with an unheated inlet tube.

To re-confirm the observed daytime concentration peaks of N_2O_5+NO_3 by the TD-CIMS, we also operated our CIMS with an unheated inlet tube during 6 – 21 December 2010, immediately after the present campaign. Figure S2 shows a piece of mass spectrum for ambient air sampled at daytime in urban Hong Kong, from which we can clearly see the I^- signal at 127 *amu*, NO_3^- signal at 62 *amu*, and $I(N_2O_5)^-$ signal at 235 *amu*. The calibration procedure was the same as that for the TD-CIMS as described in the section 2.2 of the manuscript. During the measurement period, the sensitivity of N_2O_5 from the $I(N_2O_5)^-$ cluster ion was determined at 0.55±0.003 Hz/pptv, which is smaller than the value of 0.93 Hz/pptv obtained by Kercher et al. (2009), possibly due to a smaller sample flow and stronger electric field in the collisional dissociation chamber (CDC) in our CIMS. Because of strong CDC electric field and the fast reaction rate, the NO_3^- ion acted as the major product of the reaction of N_2O_5 with I^- instead of the $I(N_2O_5)^-$ ion. It should be noted that the $I(N_2O_5)^-$ signals in this study were not re-scaled according to the $I(H_2O)^-/I^-$ ratio, because the I^- ion at

127 *amu* was not detected in real-time. Because of this uncertainty, we only show the raw signals in Hz for the general variation pattern of N_2O_5..

4 Measurements of $ClNO_2$ in western Hong Kong

Another field application of CIMS is to detect the nitryl chloride ($ClNO_2$), a product of N_2O_5 hydrolysis on surfaces of chlorine-containing aerosols. $ClNO_2$ can react with iodides to produce ICl^- ions and $I(ClNO_2)^-$ cluster ions, the latter of which can be used to quantify the concentrations of $ClNO_2$ (Kercher et al. 2009). As $ClNO_2$ is relatively stable to heating, it can be detected by the TD-CIMS with the inlet tube heated to around 180°C (Mielke et al., 2011). A follow-up field study was conducted at a suburban site (Tung Chung) in western Hong Kong during 2011-2012. The same TD-CIMS was deployed with the same configuration as that at the HKPU site. During that study, $ClNO_2$ was concurrently measured from the $I(ClNO_2)^-$ cluster ion (at 208 *amu*) with the apparent N_2O_5+NO_3 (at 62 *amu*). The sensitivity for $ClNO_2$ was determined, after the field campaign, using the most common calibration method by passing a known concentration of N_2O_5 through NaCl slurry (Behnke et al., 1997; Roberts et al., 2009). Figure S3 illustrates the experimental setup for the $ClNO_2$ calibration. A small flow (150 sccm) of N_2O_5 was introduced through a Teflon chamber (length = 5 cm; OD = 4.2 cm; volume = 69 cm^3) quarter-filled with NaCl slurry and then mixed into 5 SLPM stream of humidified zero air. The loss of N_2O_5 concentration after reacting with NaCl slurry was assumed to be converted into $ClNO_2$ (Kercher et al., 2009). The average response factor of $ClNO_2$ via the $I(ClNO_2)^-$ cluster ion at 208 *amu* was 0.43 ± 0.03 (mean ± SD) Hz/pptv for the campaign. Prior to the $ClNO_2$ calibration, we worried that there may be a shift in the equilibrium between N_2O_5, NO_2, and O_3 in the calibration system as the N_2O_5 being used up to synthesize $ClNO_2$ and contribute to new formation of N_2O_5 from the excess NO_2 and O_3 through the sampling inlet. So we also monitored changes of NO_2 during the whole calibration process, but no indication of such phenomenon occurred in our calibrations.

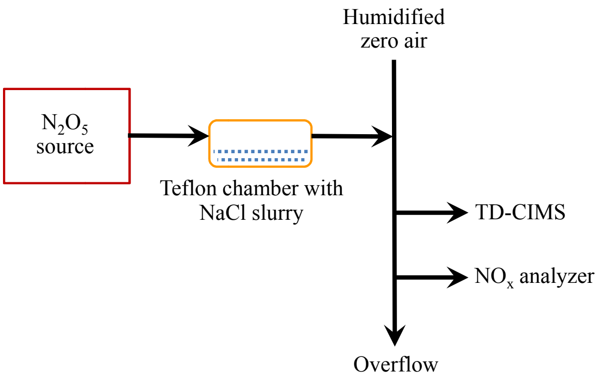

Fig. S3. Experimental setup for $ClNO_2$ calibration.

To further confirm our measurement of $ClNO_2$, we also measured the ambient isotopic ions of $I(^{37}ClNO_2)^-$ at 210 *amu*. The signal of 210 *amu* for ambient air well correlated with that of $I(^{35}ClNO_2)$ at 208 *amu* during periods of both daytime and night-time and the slope between them was quite close to the ratio of the isotopes in natural abundance (as shown in Fig. S4).

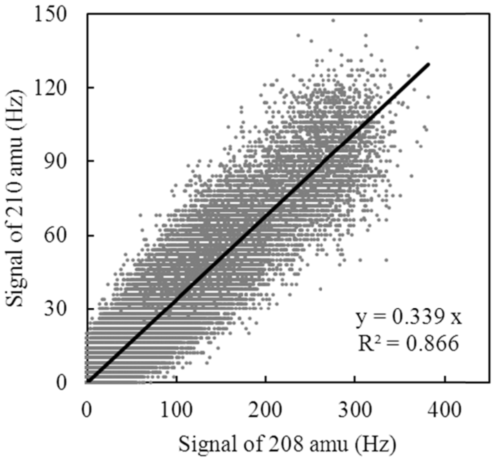

Fig. S4. Scatter plot between the signal of 210 *amu* and that of 208 *amu* for ambient air.

References

Aldener, M., Brown, S., Stark, H., Williams, E., Lerner, B., Kuster, W., Goldan, P., Quinn, P., Bates, T., and Fehsenfeld, F.: Reactivity and loss mechanisms of NO_3 and N_2O_5 in a polluted marine environment: Results from in situ measurements during New England Air Quality Study 2002, J. Geophys. Res., 111, D23S73, doi:

10.1029/2006JD007252, 2006.

Atkinson, R., and Arey, J.: Atmospheric degradation of volatile organic compounds, Chem. Rev., 103, 4605-4638, doi: 10.1021/cr0206420, 2003.

Atkinson, R., Baulch, D., Cox, R., Crowley, J., Hampson, R., Hynes, R., Jenkin, M., Rossi, M., and Troe, J.: Evaluated kinetic and photochemical data for atmospheric chemistry: Volume I-gas phase reactions of O_x, HO_x, NO_x and SO_x species, Atmos. Chem. Phys., 4, 1461-1738, doi: 10.5194/acp-4-1461-2004, 2004.

Behnke, W., George, C., Scheer, V., and Zetzsch, C.: Production and decay of $ClNO_2$ from the reaction of gaseous N_2O_5 with NaCl solution: Bulk and aerosol experiments, J. Geophys. Res., 102, 3795-3804, doi: 10.1029/96JD03057, 1997.

Bertram, T. H., and Thornton, J. A.: Toward a general parameterization of N_2O_5 reactivity on aqueous particles: the competing effects of particle liquid water, nitrate and chloride, Atmos. Chem. Phys., 9, 8351-8363, doi: 10.5194/acp-9-8351-2009, 2009.

Bertram, T., Thornton, J., Riedel, T., Middlebrook, A., Bahreini, R., Bates, T., Quinn, P., and Coffman, D.: Direct observations of N_2O_5 reactivity on ambient aerosol particles, Geophys. Res. Lett., 36, L19803, doi: 10.1029/2009GL040248, 2009.

Brown, S. S., Osthoff, H. D., Stark, H., Dubé, W. P., Ryerson, T. B., Warneke, C., de Gouw, J. A., Wollny, A. G., Parrish, D. D., and Fehsenfeld, F. C.: Aircraft observations of daytime NO_3 and N_2O_5 and their implications for tropospheric chemistry, J. Photoch. Photobio. A, 176, 270-278, doi: 10.1016/j.jphotochem.2005.10.004, 2005.

Evans, M., and Jacob, D. J.: Impact of new laboratory studies of N_2O_5 hydrolysis on global model budgets of tropospheric nitrogen oxides, ozone, and OH, Geophys. Res. Lett., 32, 1-4, doi: 10.1029/2005GL022469, 2005.

Geyer, A., Alicke, B., Ackermann, R., Martinez, M., Harder, H., Brune, W., di Carlo, P., Williams, E., Jobson, T., and Hall, S.: Direct observations of daytime NO_3: Implications for urban boundary layer chemistry, J. Geophys. Res., 108, 4368, doi: 10.1029/2002JD002967, 2003.

Kercher, J., Riedel, T., and Thornton, J.: Chlorine activation by N_2O_5: simultaneous, in situ detection of $ClNO_2$ and N_2O_5 by chemical ionization mass spectrometry, Atmos. Meas. Tech., 2, 193-204, doi: 10.5194/amt-2-193-2009, 2009.

Mielke, L. H., Furgeson, A., and Osthoff, H. D.: Observation of $ClNO_2$ in a mid-continental urban environment, Environ. Sci. Technol., 45 8889–8896, doi: 10.1021/es201955u, 2011.

Osthoff, H. D., Sommariva, R., Baynard, T., Pettersson, A., Williams, E. J., Lerner, B. M., Roberts, J. M., Stark, H., Goldan, P. D., and Kuster, W. C.: Observation of daytime N_2O_5 in the marine boundary layer during New England Air Quality Study–Intercontinental Transport and Chemical Transformation 2004, J. Geophys. Res., 111, D23S14, doi: 10.1029/2006JD007593, 2006.

Riedel, T. P., Bertram, T. H., Ryder, O. S., Liu, S., Day, D. A., Russell, L. M., Gaston, C. J., Prather, K. A., and Thornton, J. A.: Direct N_2O_5 reactivity measurements at a polluted coastal site, Atmos. Chem. Phys., 12, 2959-2968, doi: 10.5194/acp-12-2959-2012, 2012.

Roberts, J. M., Osthoff, H. D., Brown, S. S., Ravishankara, A., Coffman, D., Quinn, P., and Bates, T.: Laboratory studies of products of N2O5 uptake on Cl containing substrates, Geophys. Res. Lett., 36, L20808, doi: 10.1029/2009GL040448, 2009.

Sander, S. P., Golden, D., Kurylo, M., Moortgat, G., Wine, P., Ravishankara, A., Kolb, C., Molina, M., Finlayson-Pitts, B., and Huie, R.: Chemical kinetics and photochemical data for use in atmospheric studies evaluation number 15, Pasadena, CA: Jet Propulsion Laboratory, National Aeronautics and Space Administration, 2006, 2006.

Wahner, A., Mentel, T. F., and Sohn, M.: Gas phase reaction of N_2O_5 with water vapor: Importance of heterogeneous hydrolysis of N_2O_5 and surface desorption of HNO_3 in a large Teflon chamber, Geophys. Res. Lett., 25, 2169-2172, doi: 10.1029/98GL51596, 1998.

Yan, Y., Wang, Z., Bai, Y., XIE, S., and Shao, M.: Establishment of vegetation VOC emission inventory in China, China Environmental Science (in Chinese), 25, 110-114, doi: CNKI:SUN:ZGHJ.0.2005-01-00T, 2005.