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interference or a real  
atmospheric  
phenomenon?**

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**High concentrations of N<sub>2</sub>O<sub>5</sub> and NO<sub>3</sub>  
observed in daytime with a TD-CIMS:  
chemical interference or a real  
atmospheric phenomenon?**

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## Abstract

Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) and the nitrate radical ( $\text{NO}_3$ ) play important roles in atmospheric chemistry, yet accurate measurements of their concentrations remain challenging. A thermal dissociation chemical ionization mass spectrometer (TD-CIMS) was deployed to an urban site in Hong Kong to measure the sum of  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  in autumn 2010. To our surprise, very high concentrations of  $\text{N}_2\text{O}_5 + \text{NO}_3$  were frequently observed in daytime, with mixing ratios in the range of 200–1000 pptv. To investigate this unusual phenomenon, various interference tests and measurements with different instrument configuration were conducted. It was found that peroxy acetyl nitrate (PAN) contributed to measurable signals at 62 amu, and more importantly, this interference increased significantly with co-existence of  $\text{NO}_2$ . Nitric acid ( $\text{HNO}_3$ ), on the other hand, had little interference to the detection of  $\text{N}_2\text{O}_5/\text{NO}_3$  via the  $\text{NO}_3^-$  ion in our TD-CIMS. According to the test results, the interference from PAN and  $\text{NO}_2$  could have contributed to 30–50 % of the average daytime (12:00–16:00 LT)  $\text{N}_2\text{O}_5 + \text{NO}_3$  signal at our site. However, evidence exists for the presence of elevated daytime  $\text{N}_2\text{O}_5$ , in addition to the daytime signal at 62 amu. This includes: (1) daytime  $\text{N}_2\text{O}_5$  measured via the  $\text{I}(\text{N}_2\text{O}_5)^-$  cluster ion with an unheated inlet, which subjects to minimum interferences, and (2) observation of elevated daytime  $\text{ClNO}_2$  (a product of  $\text{N}_2\text{O}_5$  hydrolysis) during a follow-up study. In view of the difficulty in accurately quantifying the contribution from the interferences of PAN and  $\text{NO}_2$  and un-tested potential interfering chemicals in the real atmosphere, we caution the use of 62 amu in the TD-CIMS for measuring ambient  $\text{N}_2\text{O}_5$  in a high  $\text{NO}_x$  environment like Hong Kong. Additional studies are needed to re-examine the daytime issue using other measurement techniques.

## 1 Introduction

The nitrate radical ( $\text{NO}_3$ ) and dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) play important roles in the nocturnal tropospheric chemistry.  $\text{NO}_3$  is among the most important oxidants in the

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(Slusher et al., 2004; Huey et al., 2007) indicating the capability of this method in measuring  $\text{N}_2\text{O}_5$  in the atmosphere. Although non-negligible and varying background signals at 62 amu have been observed during field studies (Chang et al., 2011), there have been no reports of detailed assessment of these potential interferences under different atmospheric conditions and for different configurations of CIMS. Kercher et al. (2009) developed a method to detect  $\text{N}_2\text{O}_5$  via the  $\text{I}(\text{N}_2\text{O}_5)^-$  cluster ion at 235 amu with an unheated inlet to address the interference at 62 amu in their CIMS, however this method has its own limitation including a lower sensitivity and larger impact of water vapor than that at 62 amu.

In autumn 2010, a TD-CIMS (thermal dissociation-CIMS), which is the same type used by Slusher et al. (2004) and Huey et al. (2007), was deployed to an urban site in Hong Kong which is characterized by large quantities of  $\text{NO}_x$ , ozone and particulate matters. Unexpectedly, concentration peaks of  $\text{N}_2\text{O}_5 + \text{NO}_3$  were frequently observed in daytime in our study. To investigate this unusual observation, we have conducted a series of laboratory and field tests, including testing interferences individually and in combination from PAN,  $\text{NO}_2$ ,  $\text{O}_3$ ,  $\text{HNO}_3$ , detection of  $\text{N}_2\text{O}_5$  by using a cold inlet via the detection of  $\text{I}(\text{N}_2\text{O}_5)^-$  cluster ion at 235 amu, and examination of daytime  $\text{ClNO}_2$  which is a product of  $\text{N}_2\text{O}_5$ . In this paper, we will first present the ambient observations, and then the detailed test results on interferences and other evidence for daytime  $\text{N}_2\text{O}_5$ . A surprising result from the tests is that PAN +  $\text{NO}_2$  can have large interference to the TD-CIMS at 62 amu, which has not been reported in previous studies. Despite large chemical interference, we show that the observed daytime  $\text{N}_2\text{O}_5$  signal may be in part due to real contribution from  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ .

## 2 Experiment and methodology

### 2.1 Measurement site

The field study was conducted in the urban center of Hong Kong (22°18' N, 114°11' E, ~ 15 m a.s.l.). The sampling site was located on the rooftop of a seven-story teaching building (about 20 m above the ground) on the campus of the Hong Kong Polytechnic University (HKPU). To the southeast of the campus, there is a cross-harbor tunnel in the north-south direction with a large flow of vehicles, especially during rush hours (see Fig. 1). Victoria Harbor is located about 1 km south of the measurement site. Thus emissions from vehicles and marine vessels are the most important local anthropogenic sources. The sampling site is surrounded by business districts, tourism and residential areas, with no large industrial sources nearby. The field measurements were carried out from 15 October to 4 December 2010, which is the season with the most severe photochemical pollution in Hong Kong (Wang et al., 2009).

### 2.2 The CIMS apparatus

A TD-CIMS was deployed to measure the sum of  $N_2O_5$  and  $NO_3$  in this study. The system was developed at the *Georgia Institute of Technology* and is based on a soft and selective ionization process resulting from the reaction between a reagent ion and the target compounds, with the generated ions detected by a mass spectrometer. In the present study, the measurement method and operating parameters of TD-CIMS were the same as those described by Slusher et al. (2004) which was configured to simultaneously measure ambient  $N_2O_5$  and PANs. The schematic diagram of our TD-CIMS is shown in Fig. 2.  $I^-$ , which was produced from passing a flow of 2 sccm of 0.3%  $CH_3I/N_2$  through an alpha ion source (Po-210), served as the reagent ion. Ambient air samples were drawn through a PFA-Teflon tube (I.D., 9.5 mm; O.D., 12.7 mm; length, 2 m) to the CIMS at a flow rate of 1.5 standard liters per minute (SLPM). To reduce the residence time of air samples in the sampling tube, an extra bypass flow of 7.7 SLPM

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was directed to the exhaust. Immediately before the flow tube, the last 14.8 cm of inlet was heated to 180 °C. The temperature of the air on the axis of the heated inlet was estimated at ~ 117 °C (Slusher et al., 2004), under which condition more than 99 % of the N<sub>2</sub>O<sub>5</sub> would decompose into NO<sub>3</sub> with an ambient NO<sub>2</sub> level of 40 ppbv. The produced and the original NO<sub>3</sub> then reacted with I<sup>-</sup> to produce NO<sub>3</sub><sup>-</sup> ions in the flow tube, which were subsequently detected and quantified by a quadruple mass spectrometer at 62 amu with a time resolution of 6 s. The NO<sub>3</sub><sup>-</sup> signal is proportional to the concentration of total NO<sub>3</sub>, the I<sup>-</sup> signal, the effective reaction rate constant between them, and the effective reaction time (Huey, 2007). Figure 3 depicts the mass spectrums of ambient air in urban Hong Kong obtained both at day and at night, which clearly shows the I<sup>-</sup> signal at 127 amu, NO<sub>3</sub><sup>-</sup> (N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub>) signal at 62 amu, and CH<sub>3</sub>C(O)O<sup>-</sup> (PAN) signal at 59 amu, etc.

In the present study, the TD-CIMS instrument was calibrated once a week using the on-line N<sub>2</sub>O<sub>5</sub> synthesis method (Bertram et al., 2009). The calibration source was generated from the reactions of NO<sub>2</sub> with O<sub>3</sub> and subsequently NO<sub>3</sub> with NO<sub>2</sub>. The concentrations of the prepared N<sub>2</sub>O<sub>5</sub> were determined via the change in NO<sub>2</sub> concentrations after adding ozone, and conversely verified by the change in ozone after adding NO<sub>2</sub>. Zero air that was free from moisture and aerosols served as the diluent so as to prevent the hydrolysis of N<sub>2</sub>O<sub>5</sub> during the calibrations (see Fig. 2). NO<sub>2</sub> was monitored with a chemiluminescence analyzer equipped with a photolytic converter, which ensured measurements of the true NO<sub>2</sub> (Xu et al., 2012). Based on the relative standard deviation of the sample signal, the precision of our TD-CIMS was 3 % for 1000 pptv N<sub>2</sub>O<sub>5</sub>. The sensitivity of N<sub>2</sub>O<sub>5</sub> during the campaign was 2.8 ± 0.2 (mean ± SD) Hz pptv<sup>-1</sup>. The instrument background was automatically measured for 2 min once an hour by adding a small flow (5 mL min<sup>-1</sup>) of NO (1000 ppm) to the sample flow (diluted to 9.2 SLPM), titrating NO<sub>3</sub> and thus N<sub>2</sub>O<sub>5</sub>. The background signal of the NO<sub>3</sub><sup>-</sup> ion during this field study was 71.7 ± 36.0 (mean ± SD) Hz. Figure 4 shows the raw signals of N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> (NO<sub>3</sub><sup>-</sup>, at 62 amu) with hourly automatic background determination on 30 November, when the maximum concentration of N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> was observed. Clearly, the signals

exhibited relatively low background compared to ambient  $\text{N}_2\text{O}_5 + \text{NO}_3$  during both day and night. According to three times the standard deviation of the background signal, the typical detection limit of  $\text{N}_2\text{O}_5$  for 6 s average time was estimated to be 13 pptv for our TD-CIMS.

### 2.3 Other instruments

In addition to the TD-CIMS, a large number of other instruments were deployed concurrently. Here, we briefly describe those that were used to aid the presentation of the  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  data.  $\text{O}_3$  was measured by a commercial UV photometric analyzer (*Model 49i*, *Thermo Environmental Instruments (TEI), USA*).  $\text{NO}$  and  $\text{NO}_2$  were analyzed with a chemiluminescence instrument (*Model 42i*, *TEI*) equipped with a photolytic  $\text{NO}_2$ -converter (*Air Quality Design, USA*) (Xu et al., 2012). Solar radiation was measured using a LI-200 Pyranometer Sensor (*LI-COR, USA*). The ambient RH and temperature were monitored with a RH/temperature probe (*Model 41382VC/VF, M.R. YOUNG, USA*). During the field measurements, the minute-average data of trace gases and meteorological parameters were collected in real time by a data logger (*Model 8816, Environmental Systems Corporation, USA*).

### 3 Observation results

The time series of hourly mixing ratios of  $\text{N}_2\text{O}_5 + \text{NO}_3$  measured in urban Hong Kong from 15 October to 4 December 2010 is shown in Fig. 3. Similar to the measurement results obtained in other locations, several night-time concentration peaks of  $\text{N}_2\text{O}_5 + \text{NO}_3$  were noticed in our study (e.g., 31 October, 1 and 10 November). However, very high mixing ratios of  $\text{N}_2\text{O}_5 + \text{NO}_3$  were frequently observed during the daytime (e.g., 23 and 24 October, 19, 22 and 30 November, and 2 December). During the 50 day measurement period (excluding 11 November due to a lack of data), the average hourly concentration of  $\text{N}_2\text{O}_5 + \text{NO}_3$  was 86.9 ( $\pm 85.6$ ) pptv with the maximum value of 1033 pptv

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recorded at 15:00 LT on 30 November. The mean daytime mixing ratio of  $N_2O_5 + NO_3$  was 102.5 pptv (06:00–17:59 LT), even higher than the value of 71.3 pptv at nighttime (18:00–05:59 LT).

To learn more about the atmospheric conditions associated with the elevated daytime  $N_2O_5$  and  $NO_3$  signals at 62 amu, we present six cases during which the hourly  $N_2O_5 + NO_3$  values exceeded 400 pptv. Figure 4 presents the 5 min data of  $N_2O_5 + NO_3$ ,  $O_3$ ,  $O_x$  ( $O_3 + NO_2$ ), NO,  $NO_2$ , RH, and solar radiation for these episodes. The ratio of  $NO_3/N_2O_5$ , calculated based on the temperature dependent equilibrium among  $N_2O_5$ ,  $NO_3$  and  $NO_2$ , is also given. Inspection of the figure reveals that the daytime  $N_2O_5 + NO_3$  peaks appeared when both ozone and  $NO_2$  were in high levels together with low levels of NO. However, daytime  $N_2O_5 + NO_3$  concentrations calculated using both steady state (Osthoff et al., 2006) and non-steady state approaches (McLaren et al., 2010) were much lower (by a factor of 1–100) than observations. The daytime concentrations in our study are also much higher than those of previous studies which reported daytime  $N_2O_5$  and  $NO_3$  concentrations of only a few to over ten pptv (Geyer et al., 2003; Brown et al., 2005; Osthoff et al., 2006).

## 4 Chemical interferences

A major drawback of the TD-CIMS technique is that there could be potential interferences to the selected  $NO_3^-$  ion that can give rise to significant background noise at 62 amu (Chang et al., 2011). Previous laboratory studies have proposed many possible ion-molecule reactions yielding the  $NO_3^-$  ion, as summarized in Table 1. As stated earlier, the detailed results of these interferences in the real atmospheres have not been reported to date. To examine the influences of these potential interferences to our  $N_2O_5 + NO_3$  measurements, a series of tests were conducted in various atmospheric conditions and in laboratory during and after the measurement campaign.

The background determination by adding excess NO provided a first examination of the interferences. Such determined background reflects the interferences from

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compounds that are unreactive to NO, including most potential ones other than PAN and HO<sub>2</sub>NO<sub>2</sub>. As stated above, the background was periodically measured once an hour throughout the campaign. Considerable amount of background signals at 62 amu in our CIMS was indeed seen during the present study with a mean counts (±SD) of 71.7 (±36.0) Hz, and they also exhibited a diurnal pattern with higher values in the late afternoon (see Fig. 5). This indicated that the N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> measurements via the 62 amu channel in our TD-CIMS were subject to some interference during the present study. However, the background signals were much lower than the ambient signals. For the six cases with daytime N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> concentrations exceeding 400 pptv, the instrument background only accounted for on average 10 % of the ambient values. This background signal due to most of the gases shown in Table 1 and has been accounted for (i.e., subtracted from the total signals at 62 amu) in our final data. The interference from PAN and HO<sub>2</sub>NO<sub>2</sub> could not be determined because they also reacted with NO during zeroing. Their interferences are addressed below.

#### 4.1 Interference of PAN

PAN is the most possible compound to interfere the TD-CIMS measurements in this study, not only due to its relatively high ambient abundances but also because it can escape from background determination by adding NO. In the previous studies, higher N<sub>2</sub>O<sub>5</sub> signals than the steady-state predictions were usually observed with elevated mixing ratios of PAN (Brown et al., 2005; Osthoff et al., 2006). The interference from PAN to the NO<sub>3</sub><sup>-</sup> signals in our TD-CIMS was evaluated post the field campaign by adding synthetic PAN to zero air and in the ambient air samples. The PAN was generated from a PAN calibrator (*Meteorologie Consult GmbH*), which is based on the reaction sequence of NO and acetone in ultrapure air with a Penray lamp. The concentrations of PAN that were added to the CIMS were quantified simultaneously by a NO<sub>y</sub> analyzer (*TEI 42CY*). We also generated PAN using a conventional wet chemistry method by reacting peracetic acid with HNO<sub>3</sub> (Gaffney et al., 1984). The test

results from the two PAN sources are consistent, thus this study only shows the result which used the PAN generated from the photolytic source.

For tests of PAN in zero air and in relatively clean ambient air at a coastal site (Hok Tsui), measurable interference from PAN was observed at 62 amu. The result in zero air indicates 17 ~ 25 ( $22.8 \pm 4.1$ ) pptv from  $\text{NO}_3 + \text{N}_2\text{O}_5$  for every ppbv of PAN (see intercepts in Fig. 7). Adding PAN to ambient air at the coastal site yielded similar results. Table 2 shows the results from four tests conducted with varying ambient pollution levels and meteorological conditions. Introducing 5.6–6.3 ppb of PAN to the ambient air resulted in an increase in the  $\text{NO}_3^-$  signal of 42–75 pptv of  $\text{NO}_3 + \text{N}_2\text{O}_5$  in our TD-CIMS, again indicating interference from PAN to the field  $\text{NO}_3/\text{N}_2\text{O}_5$  measurements via the  $\text{NO}_3^-$  by TD-CIMS. The mechanism how PAN interferes the  $\text{NO}_3^-$  detection is unclear. Some researchers proposed that the  $\text{CH}_3\text{C}(\text{O})\text{O}^-$  ion (produced from the reaction of  $\text{I}^-$  with  $\text{CH}_3\text{C}(\text{O})\text{O}_2$  – the product of PAN thermo-dissociation) likely reacts with  $\text{HNO}_3$  to produce  $\text{NO}_3^-$  (Veres et al., 2008; Roberts et al., 2010). This appeared not to be the case in our CIMS as additions of both PAN and  $\text{HNO}_3$  didn't lead to any increase at 62 amu compared to the addition of PAN alone (see Fig. 6).

A surprising finding was much large interferences at 62 amu when the same spike tests were conducted at the PolyU site, which has very high  $\text{NO}_x$  concentrations, and the interference appeared to increase with ambient  $\text{NO}_2$  suggesting that reaction between PAN and  $\text{NO}_2$  leads to significant interference at 62 amu. To confirm this, a series of tests were conducted. Figure 7 shows the signal at 62 amu as a function of PAN and  $\text{NO}_2$  concentrations in zero, which clearly shows that the interference increases with both PAN and  $\text{NO}_2$ . For example, at 5 ppbv of PAN, adding 60 ppbv of  $\text{NO}_2$  produces 400 ppt equivalent  $\text{NO}_3$  signal, compared to 150 pptv without  $\text{NO}_2$ , indicating an amplifying effect of  $\text{NO}_2$  on the previously reported PAN interference. The exact chemical reaction that leads to the interference is not clear. We believe that interference of PAN +  $\text{NO}_2$  is related to the thermal dissociation of PAN followed by radical reactions with  $\text{NO}_2$  in the heated inlet. The radical reactions might serve as a source of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$ , or the products could react with  $\text{I}^-$  to produce  $\text{NO}_3^-$  ions which is detected at

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62 amu. We will evaluate the possible contribution of PAN + NO<sub>2</sub> to the observed high daytime N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> for the 2010 autumn study later.

## 4.2 Interference of HNO<sub>3</sub>

Another possible source of interference to the NO<sub>3</sub><sup>-</sup> ion is the HNO<sub>3</sub> since it has a NO<sub>3</sub> group. Several studies have proposed the production of NO<sub>3</sub><sup>-</sup> from ion-molecule reactions involving HNO<sub>3</sub>, with somewhat inconsistent results. Huey and co-workers showed that the reaction of I<sup>-</sup> with HNO<sub>3</sub> (producing NO<sub>3</sub><sup>-</sup>) was rather inefficient. Thornton and coworkers on the other hand found a significant background signal (10–50 Hz) at the NO<sub>3</sub><sup>-</sup> mass in a cold iodide CIMS under conditions of long ion-molecule reaction time, and attributed this to the reaction of HNO<sub>3</sub> with I<sup>-</sup> (Thornton et al., 2003; Thornton and Abbatt, 2005). Roberts and coworkers reported that the HNO<sub>3</sub> was sensitive to the acetate ions and react to produce NO<sub>3</sub><sup>-</sup> ions at the 62 amu (Veres et al., 2008; Roberts et al., 2010).

The relatively low background signals by adding NO in our study suggest insignificant interference from HNO<sub>3</sub> to our CIMS, which has been corrected during data reduction. This was further confirmed by the addition of HNO<sub>3</sub>. The test was carried out three times for varying ambient conditions to check the repeatability of the results, which are listed in Table 2 with an example being shown in Fig. 6. It can be seen that after introducing a trace amount of HNO<sub>3</sub> to the inlet tube of our TD-CIMS, there was no significant increase in the NO<sub>3</sub><sup>-</sup> signal compared to the ambient air. Additionally, adding HNO<sub>3</sub> to a trace level of PAN which resulted in an acetate ion signal of ~0.9 × 10<sup>4</sup> Hz, the NO<sub>3</sub><sup>-</sup> signal showed no apparent change compared to that for only adding PAN. These results suggest that the HNO<sub>3</sub> itself and its mixture with acetate ions have no significant interference to the detection of N<sub>2</sub>O<sub>5</sub> + NO<sub>3</sub> via the NO<sub>3</sub><sup>-</sup> ion in our TD-CIMS. It should be noted that the result of non-reactivity of HNO<sub>3</sub> to the acetate ion in our TD-CIMS is different from that obtained by Roberts and coworkers using a NI-PT-CIMS

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(negative-ion proton-transfer CIMS) (Veres et al., 2008; Roberts et al., 2010), possibly due to different configurations and operation conditions.

### 4.3 Interference of other possible compounds

5 CIONO<sub>2</sub>, BrONO<sub>2</sub> and HO<sub>2</sub>NO<sub>2</sub> also react efficiently with I<sup>-</sup> to produce NO<sub>3</sub><sup>-</sup> (Huey et al., 1995; Hanson et al., 1996; Zhang et al., 1997; Amelynck et al., 2001). Again, the relatively low instrument background indicated small interference from CIONO<sub>2</sub> and BrONO<sub>2</sub> and any interference from them would have been corrected in our measurements because they cannot be removed by adding NO. The zeroing would not work for HO<sub>2</sub>NO<sub>2</sub>. However, it is impossible for HO<sub>2</sub>NO<sub>2</sub> to pass through the heated inlet tube  
10 in our TD-CIMS considering its thermally unstable nature.

In addition, the NO<sub>3</sub><sup>-</sup> ion may also come from the ion-molecule reactions involving Cl<sup>-</sup> (35 amu), C<sub>2</sub>H<sub>2</sub>N<sup>-</sup> (40 amu), NO<sub>2</sub><sup>-</sup> (46 amu), O<sub>3</sub><sup>-</sup> (48 amu), CO<sub>3</sub><sup>-</sup> (60 amu), and CO<sub>4</sub><sup>-</sup> (76 amu) (listed in Table 1). These reagent ions were observed in quite low levels (i.e., < 20 Hz for 40 and 48 amu, and 10–500 Hz for 35, 46, 60 and 76 amu) in our TD-CIMS  
15 during the field measurements (see Fig. 3). Therefore, the ion-molecule reactions induced by Cl<sup>-</sup>, C<sub>2</sub>H<sub>2</sub>N<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, O<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>-</sup> and CO<sub>4</sub><sup>-</sup> are also believed to have no significant influence to the NO<sub>3</sub><sup>-</sup> detection based on the relationship between the product ion and reactants.

In summary, according to the above tests and discussions, reactions between PAN  
20 and NO<sub>2</sub> in the heated inlet are found to have significant interference to signal at 62 amu in our TD-CIMS, while HNO<sub>3</sub> and other compounds are not believed to have contributed to signal at 62 amu, although our tests are not exhaustive for including all other chemicals.

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not re-scaled according to the  $I(\text{H}_2\text{O})^-/I^-$  ratio as described by Kercher et al. (2009), because the  $I^-$  ion at 127 amu was not detected in real-time in our study. The re-scaled  $\text{N}_2\text{O}_5$  concentrations during the daytime would be even higher, because the daytime  $I(\text{H}_2\text{O})^-$  signals were generally lower than (by a factor of 0.4–1.0) those during the calibrations. Despite the above uncertainty in determining the absolute value, the general variation pattern of  $\text{N}_2\text{O}_5$  should be trustworthy. Consistent with the setup with the heated inlet and the detection at 62 amu, signal at 235 amu with the cold CIMS also showed a daytime peak. Figure 9 gives an example of the ambient results taken on 20 December 2010.

Another independent piece of evidence for the daytime  $\text{N}_2\text{O}_5 + \text{NO}_3$  in Hong Kong is concurrent increase in the mixing ratios of  $\text{ClNO}_2$  (a product of  $\text{N}_2\text{O}_5$  hydrolysis) observed in a follow-up study in western Hong Kong (Tung Chung; see SI for the experiment information). At this site, elevated  $\text{N}_2\text{O}_5 + \text{NO}_3$  concentrations were also found at daytime during photochemical episodes, with the  $\text{ClNO}_2$  signals (208 amu) showing concurrent increases. Figure 10 shows an example for 28 August 2011. On that day,  $\text{N}_2\text{O}_5 + \text{NO}_3$  from 62 amu exhibited an afternoon peak of 670 pptv (5 min average, at 14:00 LT), and  $\text{ClNO}_2$  had a concurrent enhancement to 120 pptv. To estimate the levels of  $\text{N}_2\text{O}_5$  that would be needed to sustain such amount of  $\text{ClNO}_2$ , we assumed a photostationary steady state for  $\text{ClNO}_2$  in the afternoon with an uptake coefficient of 0.03 for  $\text{N}_2\text{O}_5$  hydrolysis on aerosol surfaces and a  $\text{ClNO}_2$  yield of 10%. The photolysis rate of  $\text{ClNO}_2$  was estimated as  $7.8 \times 10^{-4} \text{ s}^{-1}$  using the method by Simon et al. (2009), and the aerosol surface area was  $979 \text{ mm}^2 \text{ m}^{-3}$  from concurrent measurements of aerosol size distribution. The calculation showed that to produce the observed 120 pptv of  $\text{ClNO}_2$ , at least 518 pptv of  $\text{N}_2\text{O}_5$  would be required. This result provides additional corroboration of the possible elevated daytime concentrations of  $\text{N}_2\text{O}_5 + \text{NO}_3$  in Hong Kong.

## 7 Conclusions

A TD-CIMS technique, which has been previously applied to field measurements in the US, was deployed to measure ambient  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  in urban Hong Kong in a photochemical season. Surprisingly, concentration peaks of  $\text{NO}_3 + \text{N}_2\text{O}_5$  were frequently observed in daytime at 62 amu channel in the TD-CIMS, which is in contrast to our current understanding of reactive nitrogen chemistry. Our subsequent laboratory and field tests provide new insights into chemical interferences in the TD-CIMS. In particular, we have discovered that reaction between  $\text{NO}_2$  and PAN can amplify the interference from PAN at 62 amu. This interference could have contributed 30–50 % to the average daytime  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  at our site. Despite the large interference, evidence exists to suggest that the elevated  $\text{N}_2\text{O}_5$  in daytime may be in part due to real contribution from  $\text{NO}_3$  or  $\text{N}_2\text{O}_5$ . In viewing of the large and variable interferences at 62 amu and difficulty in correcting them, we conclude that it is not suitable to use the TD-CIMS to measure  $\text{NO}_3$  or  $\text{N}_2\text{O}_5$  at 62 amu in a high  $\text{NO}_x$  environment like the present study site. Adoption of either 235 amu with a cold inlet or an optics-based technique is recommended. We also suggest more studies to examine the abundance of daytime  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  in similar urban areas with co-existence of high ozone and  $\text{NO}_2$ .

**Supplementary material related to this article is available online at <http://www.atmos-meas-tech-discuss.net/6/7473/2013/amtd-6-7473-2013-supplement.pdf>.**

*Acknowledgements.* We thank Steven Poon and K.S. Lam for their help in the field study and setting up the instruments. This research was supported by the Environment and Conservation Fund of Hong Kong (Project No. 2009-07), Niche Area Development Scheme of the Hong Kong Polytechnic University (1-BB94), and the Research Grants Council of Hong Kong (PolyU 5015/12P).

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**Table 1.** Ion-molecule reactions with product of  $\text{NO}_3^-$  and the rate constants.

Reaction	Rate constant ( $\text{molecule}^{-1}\text{cm}^3\text{s}^{-1}$ )	Comments	Reference
$\text{I}^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HI}$	$< 5 \times 10^{-11}$ No reaction		Fehsenfeld et al. (1975) Huey et al. (1995)
$\text{I}^- + \text{ClONO}_2 \rightarrow \text{NO}_3^- + \text{ICl}$	$9 \times 10^{-10}$	$\pm 40\%$	Huey et al. (1995)
$\text{I}^- + \text{BrONO}_2 \rightarrow \text{NO}_3^- + \text{IBr}$	Unknown		Hanson et al. (1996)
$\text{I}^- + \text{HO}_2\text{NO}_2 \rightarrow \text{NO}_3^- + \text{HIO}$	Unknown		Zhang et al. (1997)
$\text{CO}_3^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{products}$	$8 \times 10^{-10}$		Fehsenfeld et al. (1975)
$\text{CO}_3^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{CO}_2$	$2 \times 10^{-10}$	$\pm 50\%$	Ikezoe and Viggiano (1987)
$\text{CO}_4^- + \text{NO} \rightarrow \text{NO}_3^- + \text{CO}_2$	$4.8 \times 10^{-11}$	$\pm 30\%$	Ikezoe and Viggiano (1987)
$\text{C}_2\text{H}_2\text{N}^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{CH}_3\text{CN}$	$1.4 \times 10^{-9}$	297 K	Ikezoe and Viggiano (1987)
$\text{C}_2\text{H}_3\text{O}_2^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{C}_2\text{H}_4\text{O}_2$	Unknown		Roberts et al. (2010)
$\text{Cl}^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HCl}$	$1.6 \times 10^{-9}$	$\pm 40\%$	Ikezoe and Viggiano (1987)
$\text{NO}_2^- + \text{HNO}_3 \rightarrow \text{NO}_3^- + \text{HONO}$	$1.6 \times 10^{-9}$	$\pm 40\%$	Ikezoe and Viggiano (1987)
$\text{NO}_2^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{NO}$	$< 2 \times 10^{-13}$		Ikezoe and Viggiano (1987)
$\text{NO}_2^- + \text{N}_2\text{O} \rightarrow \text{NO}_3^- + \text{N}_2$	$< 1 \times 10^{-12}$		Ikezoe and Viggiano (1987)
$\text{NO}_2^- + \text{O}_3 \rightarrow \text{NO}_3^- + \text{O}_2$	$1.2 \times 10^{-10}$	$\pm 40\%$	Ikezoe and Viggiano (1987)
$\text{O}_3^- + \text{NO}_2 \rightarrow \text{NO}_3^- + \text{O}_2$	$2.8 \times 10^{-10}$	$\pm 30\%$ , 280 K	Ikezoe and Viggiano (1987)

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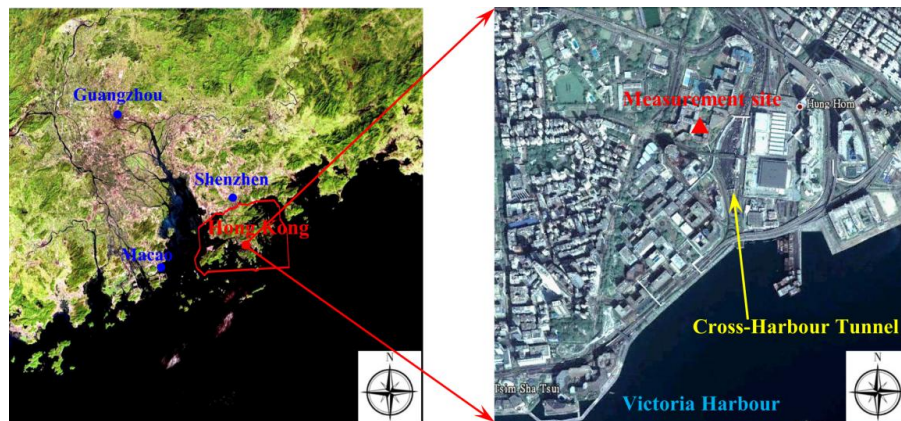
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**Table 2.** Summary of the interference tests for the TD-CIMS.

Test	Ambient conditions				Standard addition*		CIMS response	
	NO <sub>y</sub> (ppb)	O <sub>3</sub> (ppb)	T (°)	RH (%)	ΔPAN (ppb)	ΔHNO <sub>3</sub> (ppb)	ΔN <sub>2</sub> O <sub>5</sub> (ppt)	ΔS <sub>62</sub> /ΔS <sub>59</sub> (cps/cps)
1	3.5	69	25	83	6.3	0	75	0.014
2	4.8	71	25	87	5.8	0	42	0.009
3	4.5	60	23	83	5.9	0	69	0.014
4	14.0	35	22	69	5.6	0	62	0.013
5	7.2	70	24	81	0	1.4	1	n.a.
6	6.2	76	24	64	0	9.1	1	n.a.
7	15.2	38	22	69	0	8.9	2	n.a.
8	12.8	41	21	68	5.3	8.9	62	n.a.

\* The concentrations of PAN and HNO<sub>3</sub> that were added to the ambient air were determined by a NO<sub>y</sub> analyzer.



**Fig. 1.** Location of the measurement site and surrounding layout.

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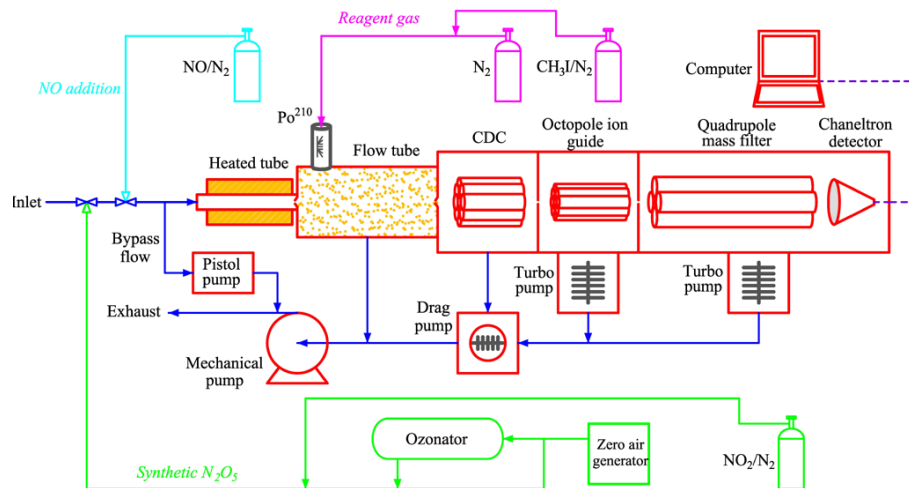


Fig. 2. Schematic diagram of the TD-CIMS deployed in this study.

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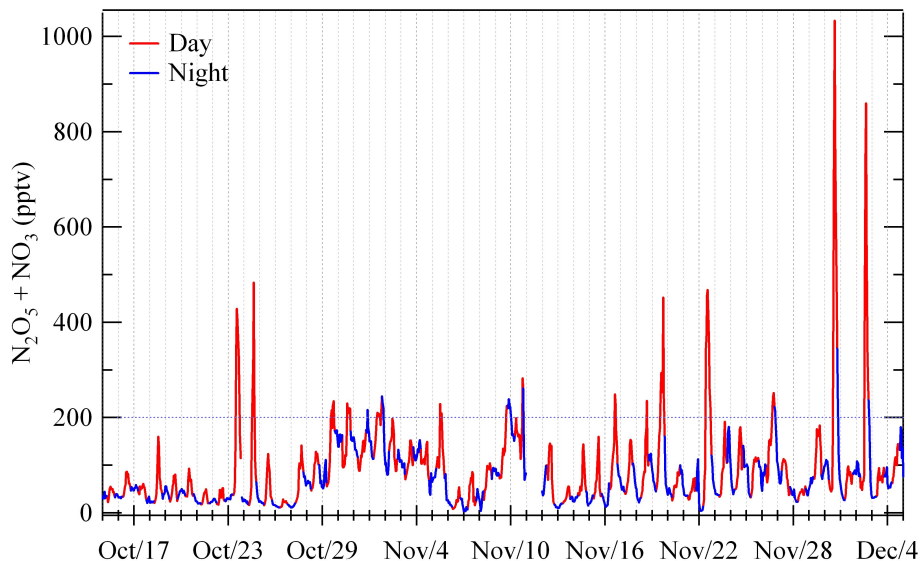
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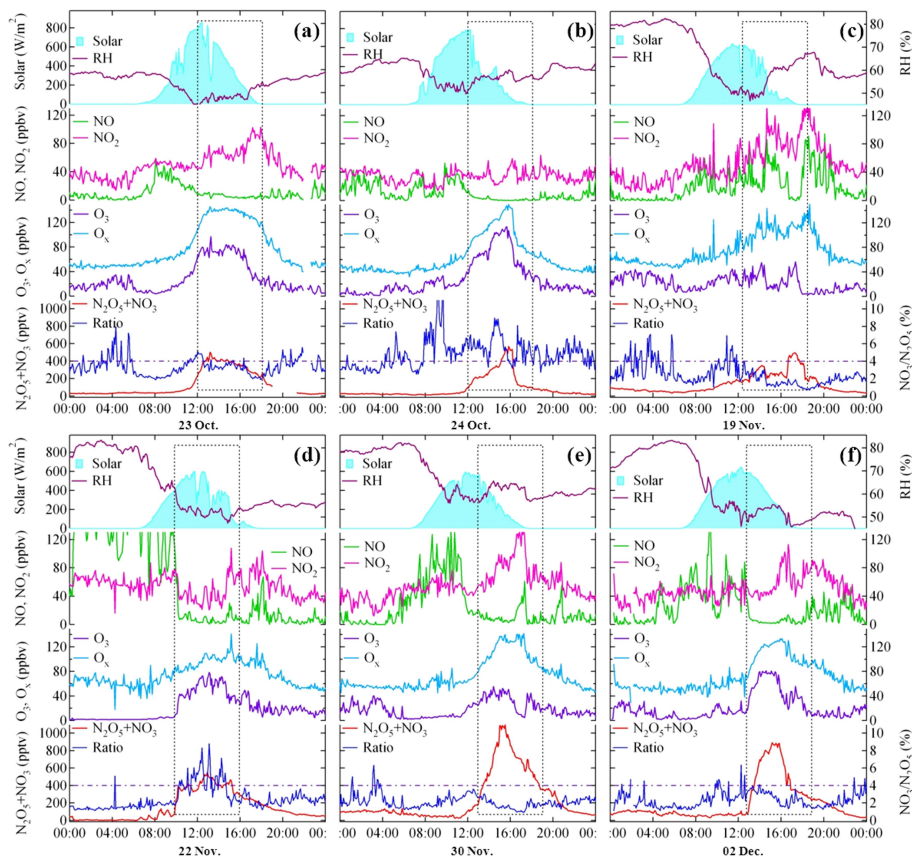
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**Fig. 3.** Time series of hourly average concentrations of  $\text{N}_2\text{O}_5 + \text{NO}_3$  measured in Hong Kong.[Title Page](#)[Abstract](#)[Introduction](#)[Conclusions](#)[References](#)[Tables](#)[Figures](#)[◀](#)[▶](#)[◀](#)[▶](#)[Back](#)[Close](#)[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)

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**Fig. 4.** Time series of  $\text{N}_2\text{O}_5 + \text{NO}_3$ ,  $\text{NO}_3/\text{N}_2\text{O}_5$  ratio, trace gases and meteorological parameters for six pollution episodes on **(a)** 23 October, **(b)** 24 October, **(c)** 19 November, **(d)** 22 November, **(e)** 30 November, and **(f)** 2 December 2010. The pollution episodes with daytime concentration peaks of  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$  are shown in the panes.

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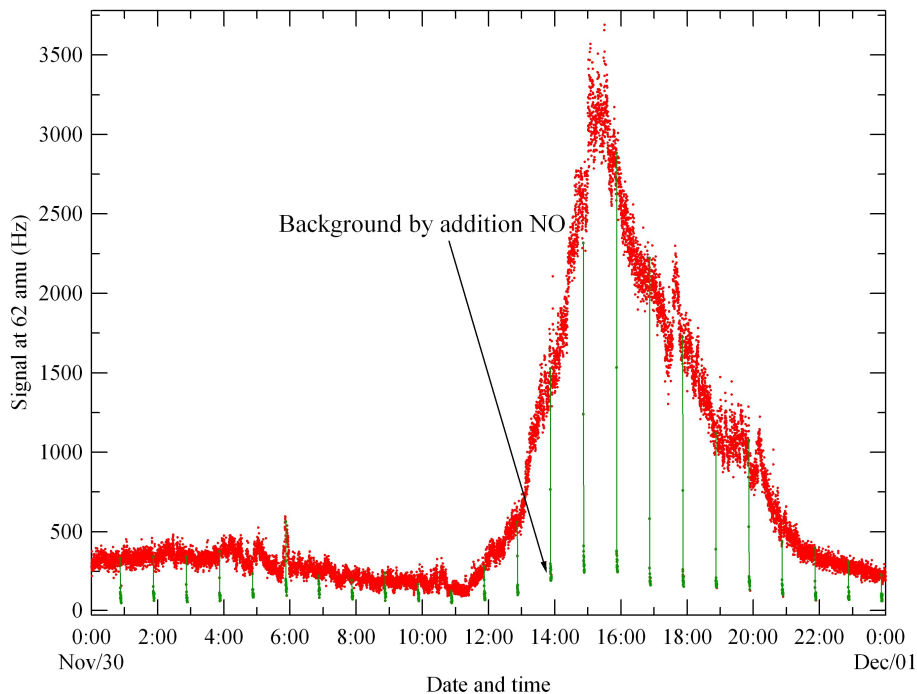
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**Fig. 5.** Raw  $\text{NO}_3^-$  (62 amu) signal with hourly automatic background detection by adding excess NO, 30 November 2010.

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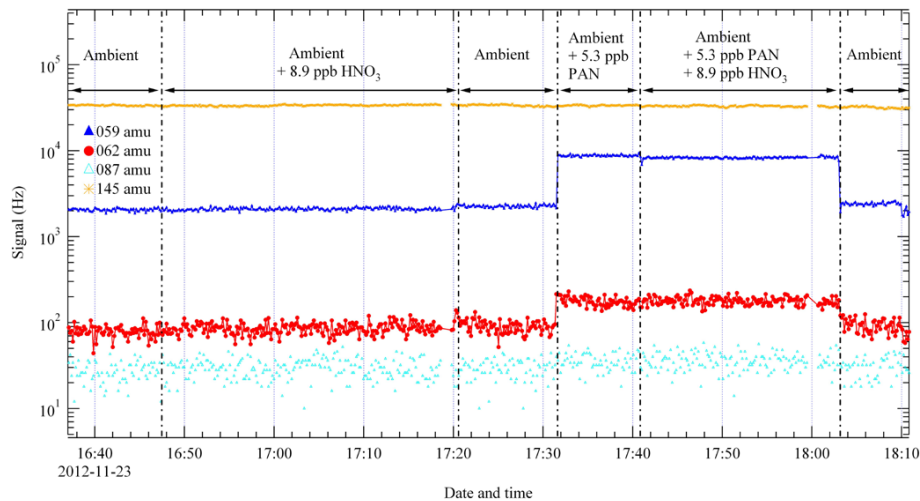
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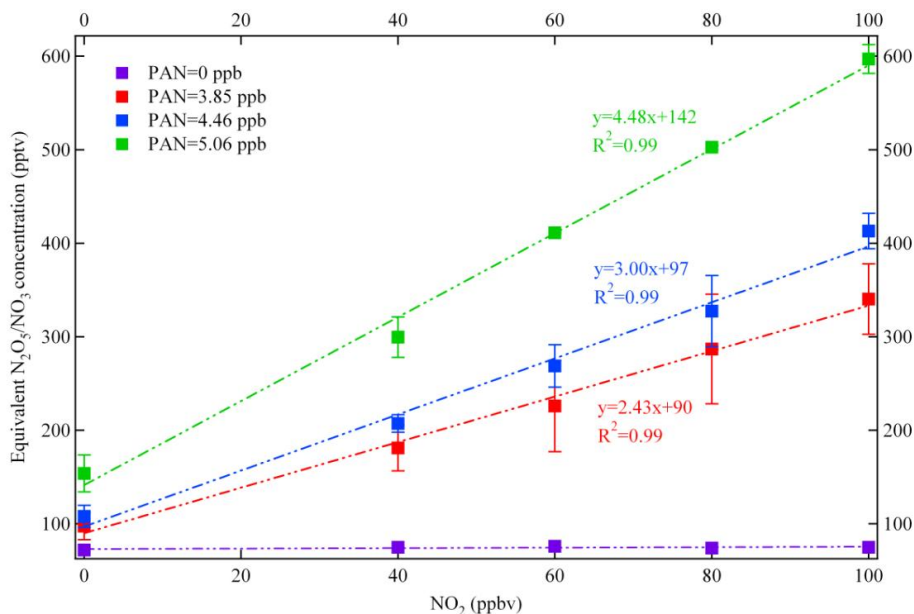
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**Fig. 6.** Changes of raw signals of  $\text{CH}_3\text{C}(\text{O})\text{O}^-$ ,  $\text{NO}_3^-$ ,  $\text{C}_3\text{H}_7\text{C}(\text{O})\text{O}^-$ ,  $\text{I}(\text{H}_2\text{O})^-$  detected by  $\text{I}^-$  TD-CIMS when adding trace amounts of PAN,  $\text{HNO}_3$ , or their mix to the ambient air.

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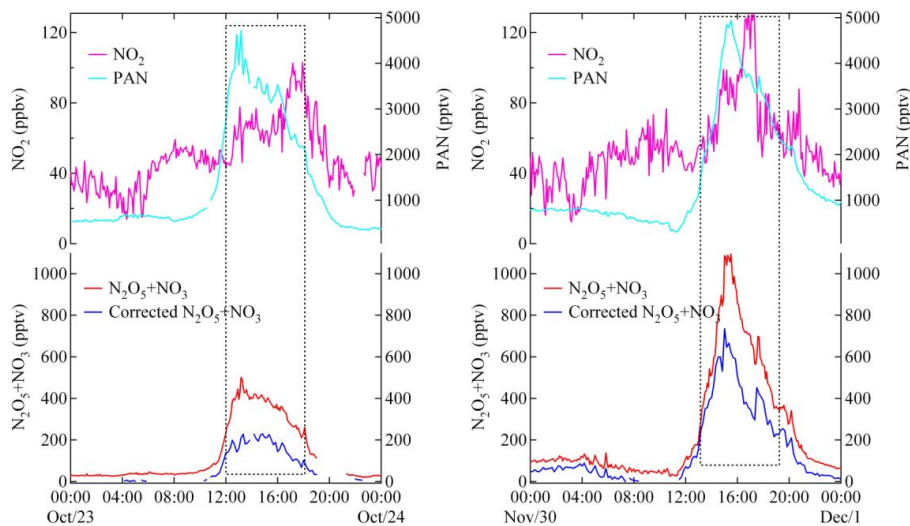
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**Fig. 7.** Interference of NO<sub>2</sub> to equivalent NO<sub>3</sub><sup>-</sup> concentration under different levels of PAN. Vertical bars are standard deviations of tests results.

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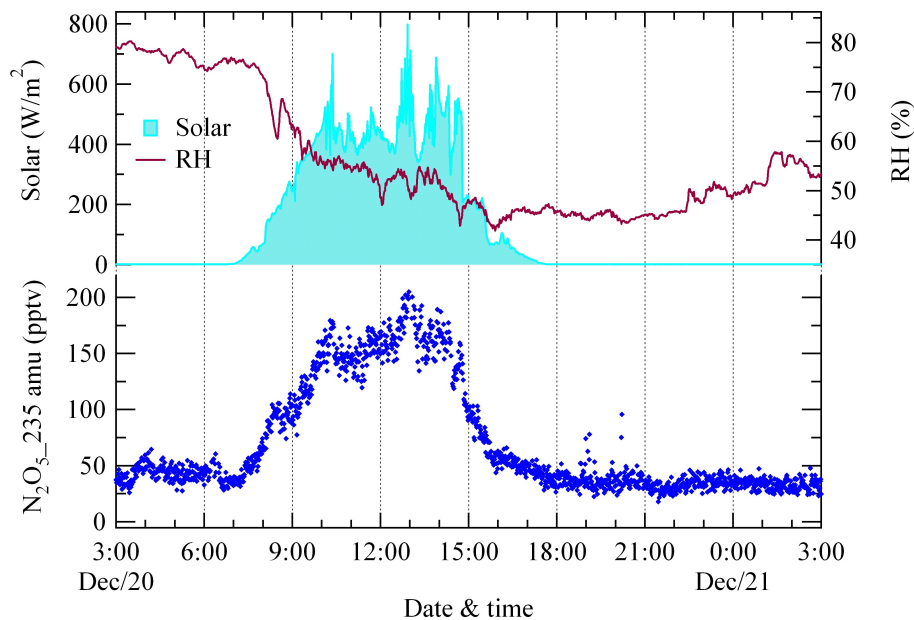
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**Fig. 8.** Time series of corrected and uncorrected  $\text{N}_2\text{O}_5 + \text{NO}_3$ , PAN,  $\text{NO}_2$  and NO on 23 October and 30 November 2010.

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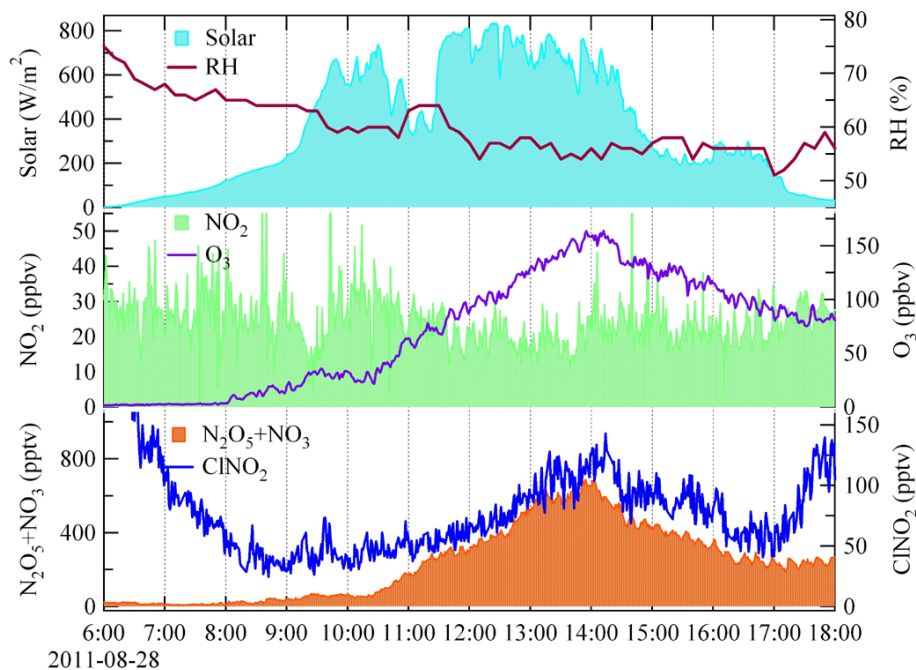
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**Fig. 9.** Time series of of N<sub>2</sub>O<sub>5</sub> from the I(N<sub>2</sub>O<sub>5</sub>)<sup>-</sup> ion, solar radiation and relative humidity in urban Hong Kong on 20 December 2010.

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**Fig. 10.** A case showing concurrent increase of ClNO<sub>2</sub> and N<sub>2</sub>O<sub>5</sub> at daytime during a photochemical episode at a suburban site (Tung Chung) in western Hong Kong.

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