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Observation of Nitrate Radical in the Nocturnal Boundary Layer During a Summer Field Campaign in Pearl River Delta, China

Suwen Li[1, 2, *], Wenqing Liu[2], Pinhua Xie[2], Min Qin[2], and Yijun Yang[1]

[1] *Huaibei Normal University, Huaibei, China*
[2] *Key Laboratory of Environmental Optical & Technology, Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, China*

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ABSTRACT

From July 4 to 11, 2006 at Back Garden site (23°28'86"N; 113°02'91"E), nighttime nitrate radical (NO_3) was measured with a long path differential optical absorption spectroscopy (DOAS) during an intensive field campaign in the Pearl River Delta of China. The NO_3 concentration in polluted air masses varied from 3.6 to 82.5 ppt with an average level of 21.8 ± 1.8 ppt. NO_3 at these levels can play a significant role in oxidation of volatile organic compounds (VOCs). The calculated production rate of nitrate radical ranged from 8×10^5 to 2.98×10^7 cm^{-3} s^{-1}, while its lifetimes spanned from between just several seconds to 650 seconds, with an average of 89 seconds. N_2O_5 levels were calculated with the average of 620 ± 93 ppt during this campaign. The possible scavenging processes for the nitrate radical were obtained by using a statistical analysis of the correlation between NO_3 and NO levels, NO_3 concentration and its production rate, and the NO_3 lifetime and NO_2 levels, respectively. Results showed that the direct losses were of importance at Back Garden in summer Pearl River Delta, China.

Key words: Nitrate radical, Differential optical absorption spectroscopy, Production rate, Lifetime, Loss process

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1. INTRODUCTION

Nocturnal chemistry and physics play a crucial role in the conversion and removal of air pollutants such as nitrogen oxides and volatile organic compounds (VOCs), which determines the initial conditions for photochemistry during the following day (Platt et al. 1980; Wayne et al. 1991; Heintz et al. 1996; Geyer et al. 2001; Vrekoussis et al. 2004; Wood et al. 2005; Brown et al. 2006a). This is particularly true for the nitrate radical (NO_3). Following its first detection in the troposphere (Noxon et al. 1980; Platt et al. 1980), NO_3 has been measured in polluted and clean background air under both continental and marine conditions (Platt et al. 1980; Wayne et al. 1991; Heintz et al. 1996; Geyer et al. 2001; Vrekoussis et al. 2004; Wood et al. 2005; Brown et al. 2006b). The nitrate radical has been identified as a key oxidant in the nighttime, which is responsible for the removal of many VOCs, especially monoterpenes. In addition, it has been surmised that the nitrate radical plays an important role in the non-photochemical conversion of nitrogen oxides to HNO_3 (Platt et al. 1990; Bey et al. 2001; Geyer et al. 2001; Wood et al. 2005; Brown et al. 2006a).

The Pearl River Delta (PRD) is one of the areas which have experienced the fastest economic development in China. Urbanization in the PRD is characterized by city clusters with three mega-cities (Guangzhou, Hong Kong and Macao) and many medium-small cities (such as Zhuhai, Dongguan and Zhaoqing) linked by dense highway networks. Fueled by higher demands for energy, mobility and communications, the economy has increased at an impressive speed for decades. In consequence, coal smog and traffic exhaust together cause serious photochemical smog and particulate pollution problems on a large scale both in urban and regional areas (http://www.info.gov.hk/info/gprd/).

In this paper, we present the measurements of NO_3 by long path differential optical absorption spectroscopy

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* *Corresponding author*
E-mail: suwen_li2007@163.com

(DOAS) and an examination of other gases (NO_2, O_3 and NO), which were carried out from July 4 to 11, 2006 at Back Garden (23°28'86"N; 113°02'91"E) in Guangzhou during an intensive field campaign in PRD, China. Our main purpose was to determine the concentrations, production rates, lifetimes, and possible loss processes of the nitrate radical during this field campaign in the PRD, China.

2. THE EXPERIMENT

2.1 Location

The concentrations of nitrate radical were monitored using a long path DOAS instrument (Li et al. 2007) from July 4 to 11, 2006 at Back Garden located in the northwest quadrant of the Pearl River Delta, which was included as a part of the PRD-2006 summer field campaign. The DOAS setup was deployed on the third floor of a 4-floor building and an array of retro-reflectors was placed in another building, 10 m above the ground, resulting in a total atmospheric optical path of 3.1 km on average. A lake with dense foliage was beneath the optical path located around the measurement site. Figure 1 shows the map of monitoring site during PRD summer field campaign. Analysis of the NO, NO_2, and O_3 were carried out using Thermo-Fisher chemiluminescent detectors [Model 42C (NO_x) and 49C (O_3), respectively].

2.2 Measurement System for Nitrate Radical

The DOAS system during PRD field campaign has been used in a past field campaign. The details of its operation have been presented elsewhere (Li et al. 2007); here, only a short description is given. Figure 2 shows the important parts of the DOAS system for measuring the nitrate radical. A Cassegrain telescope was used to transmit and receive light, which was reflected by an array of 13 retro-reflectors. The light was transmitted to the spectrograph and then to the detector via a 7 × 0.1 mm diameter fiber bundle, which was regulated by a mode mixer to reduce the interference fringe produced by the total reflections inside the fiber of the light leaving the fiber. The spectrograph was an Andor Shamrock SR-303i with a focal length of 303 mm, a linear dispersion of 2.6 nm mm^{-1}, and diffraction grating with 600 groves mm^{-1}. In order to reduce dark current, the Andor iDUS CCD detector was cooled down to -45°C by a Peltier cascade. A 610 nm long pass red filter, to reduce stray light effects below 610 nm, was placed in the fiber optic coupler. Finally, the spectral signal was stored and analyzed in a computer. The integration time of the measurement spectra was adjusted automatically to the incoming light intensity, so the nitrate radical could be retrieved every 2 - 15 minutes while evaluating the spectral range between 647 and 677nm.

3. NITRATE RADICAL CHEMISTRY IN THE BOUNDARY

The nitrate radical is formed by the reaction of NO_2 with O_3 in the boundary layer (Noxon 1980; Wayne et al. 1991; Geyer et al. 2001; Brown et al. 2003a; Platt et al. 2002; Vrekoussis et al. 2004):

Fig. 1. Map monitoring the site during PRD summer field campaign.

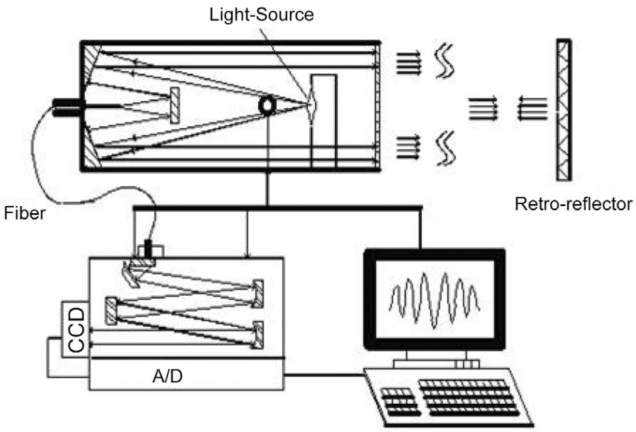

Fig. 2. Schematic view of a LP-DOAS experimental setup for NO_3 measurement.

$$NO_2 + O_3 \rightarrow NO_3 + O_2 \quad (1)$$

with the reaction rate: $k_1 = 1.4 \times 10^{-13} \exp(-2470/T)$ cm^3 s^{-1}, k_1 (298 K) = 3.55×10^{-17} cm^3 s^{-1} (http://www.iupac-kinetic.ch.cam.ac.uk).

The nitrate radical reacts further with NO_2 to produce N_2O_5, some of which thermally decomposes to produce NO_3 and NO_2 again:

$$NO_3 + NO_2 + M \Leftrightarrow N_2O_5 + M \quad (2)$$

The strongly temperature dependent equilibrium rate is $K_{eg}(T) = 9.7 \times 10^{14} (T/300)^{0.01} \exp(-11080/T)$ cm^3 s^{-1}.

During the daytime, NO_3 has a very short lifetime of about 5 s (Heintz et al. 1996; Geyer et al. 2001; McLaren et al. 2004) due to its rapid photolysis. The photolysis frequency for solar zenith angles below 70° is about 0.2 s^{-1} (Geyer et al. 2001; Platt et al. 2002; Vrekoussis et al. 2004):

$$NO_3 + h\upsilon \rightarrow NO_2 + O(^3P) \quad (3)$$

$$NO_3 + h\upsilon \rightarrow NO + O_2 \quad (4)$$

A rapid loss mechanism is the gas phase reaction with NO in the polluted boundary (Geyer et al. 2001; Platt et al. 2002):

$$NO_3 + NO \rightarrow NO_2 + NO_2 \quad (5)$$

The reaction rate is $k_5 = 1.8 \times 10^{-11} \exp(110/T)$ cm^3 s^{-1}, k_5 (298 K) = 2.6×10^{-11} cm^3 s^{-1}. Reaction (5) is a daytime sink for NO_3 that can be much more important than photolysis under polluted conditions. For instance, lifetime of NO_3 is about 0.1 - 0.5 s^{-1} at NO levels of 2.5 - 0.5 ppb. However, if the NO is recently injected into the air mass sampled, then a decomposing N_2O_5 source could support some level of steady state NO_3 before it is quenched by NO (Brown et al. 2003b).

In addition, NO is rapidly oxidized by the reaction with ozone:

$$O_3 + NO \rightarrow NO_2 + O_2 \quad (6)$$

Rate constant is k_6 (298 K) = 1.8×10^{-14} cm^3 s^{-1}, resulting in typical lifetime of NO of the order 1 minute at 30 ppb ozone.

In a marine atmosphere, the reaction of NO_3 with dimethylsulfide (DMS) is of importance (Carslaw et al. 1997; Allan et al. 1999; Vrekoussis et al. 2004). However, the discussion will be restricted to the nitrate radical in the continental boundary layer, which reacts with VOCs, in particular alkenes (e.g., monoterpenes) (Mihelcic et al. 1993; Smith et al. 1995; Carslaw et al. 1997; Geyer et al. 2001). Nitrate radicals can noticeably contribute to the degradation of several hydrocarbons in the nighttime atmosphere. Some rate constants for the reactions with NO_3 are even comparable to that with OH (e.g., Atkinson et al. 1990; Heintz et al. 1996; Geyer et al. 2001).

Since NO_3 is in equilibrium with N_2O_5, the sink process for N_2O_5 will affect the NO_3 concentration and its lifetime. The homogeneous reaction with water vapor is a possible sink of N_2O_5, producing gaseous HNO_3, and rate constant is about 3 ~ 9 × 10^{-22} cm^3 s^{-1} (Carslaw et al. 1997; Allan et al. 1999; Vrekoussis et al. 2004):

$$N_2O_5 + H_2O \rightarrow 2HNO_3 \quad (7)$$

On the other hand a heterogeneous reaction on wet particulate surfaces form particulate nitrate:

$$N_2O_5 + H_2O_{(p)} \rightarrow 2HNO_{3(p)} \quad (8)$$

The reaction of N_2O_5 on aerosol surfaces is another possible sink of N_2O_5. N_2O_5 can also be removed by dry deposition to the ground (Geyer et al. 1999, 2001; Stutz et al. 2004).

4. RESULTS AND DISCUSSION

4.1 Meteorological Data

Figure 3 gives an overview of the meteorological data at Back Garden. A multitude of meteorological parameters including temperature, relative humidity, wind speed and wind direction were monitored at the measurement site. The temperature and relative humidity were a typical diurnal variation with mean values of 303 K and 79%, respectively.

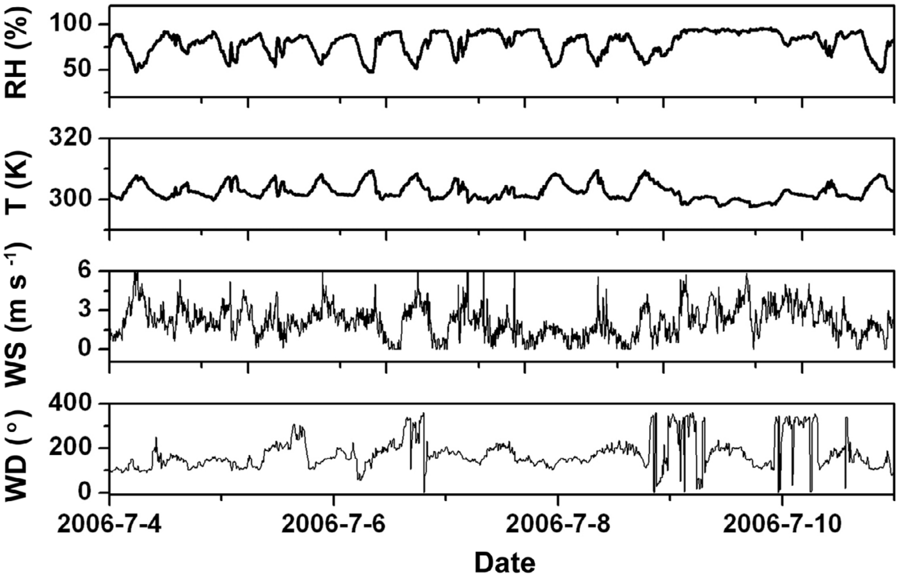

Fig. 3. Time series of the meteorological parameters.

Usually, wind speed was below 6 m s^{-1} at an average of 2.1 m s^{-1}. The frequency distribution of the wind direction was shown in Fig. 4. The prevailing wind direction was characterized by southeast during this campaign. The measurement site (seen in Fig. 1) was located in the northwest of the Pearl River Delta, and measurement was sampling outflow from the PRD mega-cities.

4.2 The Concentrations of NO_3, O_3, NO, and NO_2

The nitrate radical was measured from July 4 to 11, 2006 at Back Garden during an intensive field campaign in PRD region. Figure 5a shows the time series of NO_3 concentrations. Its nighttime average was about 21.8 ± 1.8 ppt with the detection limits of about 3.6 ppt. NO_3 at this level can play a significant role in oxidation of volatile organic compounds (VOCs). The level was slightly higher than those shown in several previous studies that also used the DOAS method (Heintz et al. 1996; Geyer et al. 2001; McLaren et al. 2004). Recently, Brown et al. (2003a, b, 2006b) using a cavity ring-down spectroscopy (CaRDS) instrument for in situ quantification have indicated NO_3 and N_2O_5 are significantly higher.

The data in Fig. 5 display several interesting features whose description and analysis will be discussed in the next section. These include the influence of NO concentrations on the NO_3 and N_2O_5 levels, the equilibrium between NO_2, NO_3 and N_2O_5.

Figures 5b and c show the concentrations of O_3 and NO, respectively. The concentration of O_3 showed a typical diurnal variation with maximum mixing ratios of 118 ppb and an average of 38 ppb. As for NO, its average was at 8 ppb during this campaign. The time series of the NO_2 concentration were showed in Fig. 5d, whose average was 18 ppb in the nighttime.

Figure 6 shows the rose plots of NO_3, NO, NO_2 and O_3 concentrations with wind direction. For NO_3 is a kind of highly reactive radical species with short atmospheric lifetime, NO_3 remained at a low level and showed no obvious relationship with regard to a wind direction. The distributions of NO and NO_2 were a consistent tendency when the southeast wind was popular during the field campaign. As a secondary pollutant, O_3 was manly distributed when the wind direction was southeast. Its sources were transportation and the local photochemical formation. Figure 7 shows the average diurnal patterns of NO, NO_2 and the NO_2-to-NO_x ratio, respectively. The diurnal trend of NO and NO_2

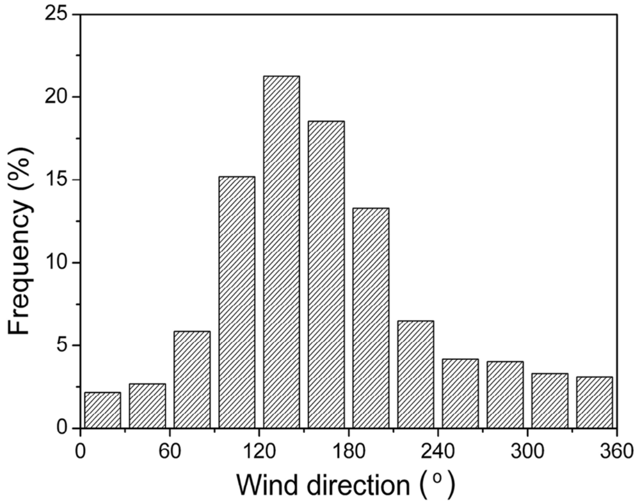

Fig. 4. A frequency distribution of wind direction.

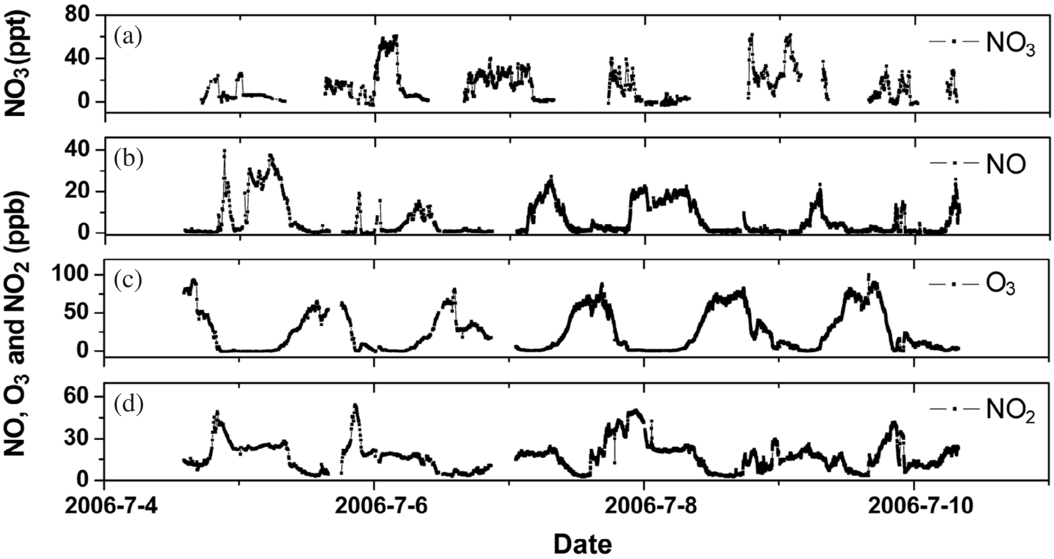

Fig. 5. Time series of the concentrations of (a) NO_3 in ppt, (b) NO in ppb, (c) O_3 in ppb and (d) NO_2 in ppb during this campaign.

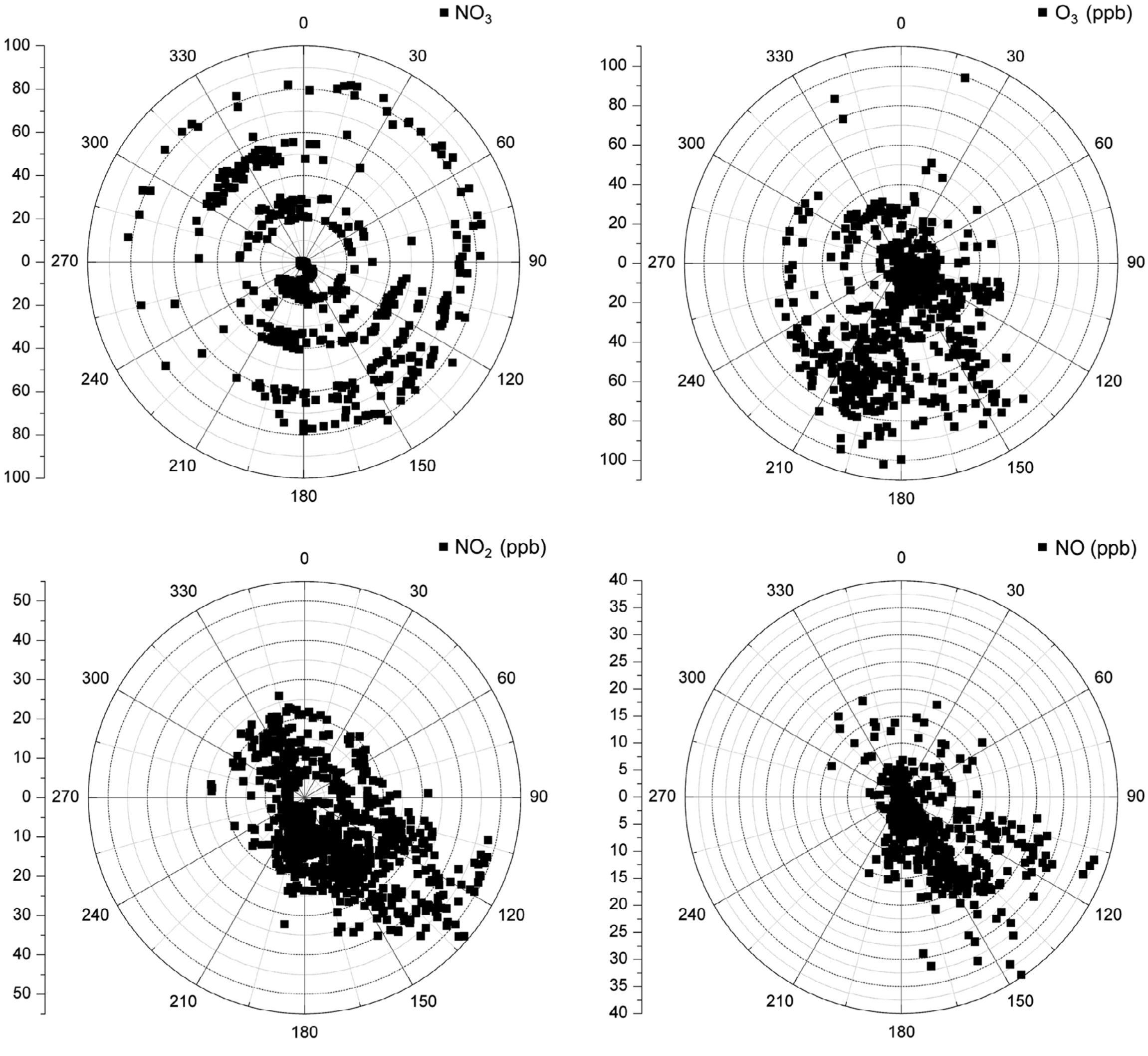

Fig. 6. Rose plots of NO_3, O_3, NO_2 and NO concentrations with wind direction.

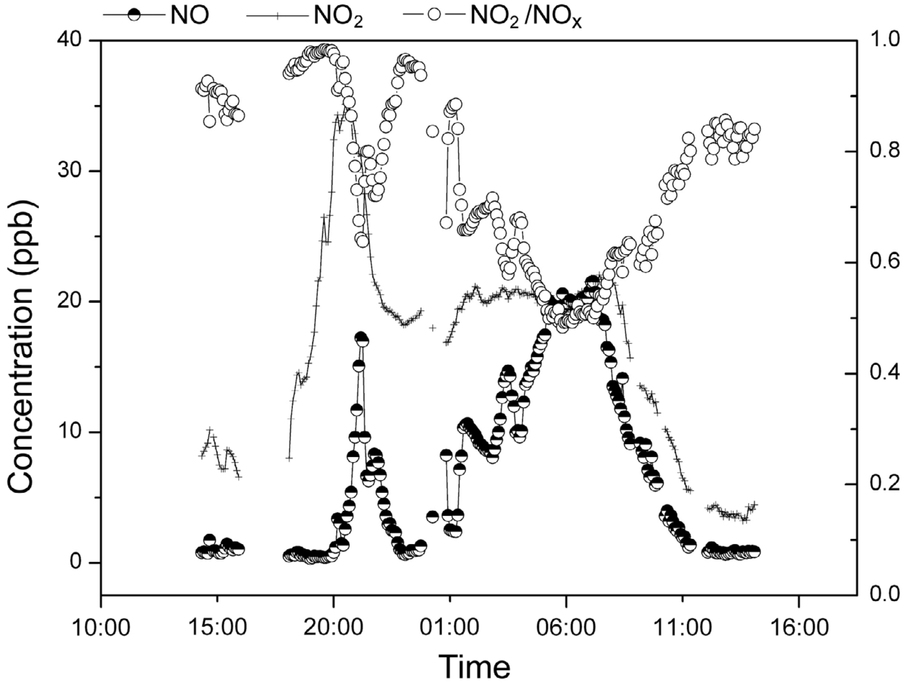

Fig. 7. Average diurnal patterns of NO, NO_2 and the NO_2-to-NO_x ratio.

was similar, and the NO_2-to-NO_x ratio was bigger than 0.5 (Jenkin 2004). Therefore, these results further indicated that NO and NO_2 came from the PRD.

4.3 Production Rate and Lifetime of Nitrate Radical

Since the only significant source of NO_3 is reaction (1), the production rate of nitrate radical, $P(NO_3)$, could be calculated:

$$P(NO_3) = [NO_2][O_3]k_1 \tag{9}$$

Figure 8 was the calculated production rate of NO_3 when the data were available. The production rate generally varied from 1×10^5 cm^{-3} s^{-1} to 3.7×10^7 cm^{-3} s^{-1} with an average value of 5.1×10^6 cm^{-3} s^{-1}.

A steady state occurred considerably more rapidly at a warmer temperature, for example 300 K (Brown et al. 2003a, b). Therefore, we assumed that it was in a steady state; lifetimes were given by (Heintz et al. 1996; Geyer et al. 2001; Brown et al. 2006a):

$$\tau(NO_3) = \frac{[NO_3]}{[NO_2][O_3]k_2} = \frac{[NO_3]}{P(NO_3)} \tag{10}$$

The calculated lifetimes of NO_3 were in the range several to 650 seconds with an average value of 89 seconds (seen Fig. 9).

4.4 Time Series of N_2O_5

Although N_2O_5 could not directly be measured with DOAS, its equilibrium concentration can be calculated from the measured levels of NO_2, NO_3, and temperature:

$$[N_2O_5] = K_{eq}(T)[NO_2][NO_3] \tag{11}$$

Field studies of this equilibrium in which all three components were measured showed that it was in agreement with the calculated equilibrium to within 30% (Brown et al. 2003a); therefore, this was a reasonable estimate for the uncertainty of the calculated N_2O_5. The calculated peak mixing ratio of N_2O_5 was 2054 ppt with the average of 298 ± 89 ppt (seen in Fig. 10).

4.5 Possible Loss Process

Because of the lack of ancillary measurement (e.g., VOCs), it is not possible to quantitatively identify the nature of the sinks for NO_3. Several possibilities can be obtained by analyzing the correlation between NO_3 and its production rate $[P(NO_3)]$, NO_3 lifetime $[\tau(NO_3)]$ and NO_2, NO_3 and NO, respectively (Allan et al. 1999; Geyer et al. 2001).

As a first step, the correlation between NO_3 and its productive rate was studied to estimate the impact of direct sinks at Bark Garden in Guangzhou. Figure 11 showed NO_3 concentration as a function of its production rate separated in the intervals of $P(NO_3)$ of length 5×10^6 cm^{-3} s^{-1}. The data was in good agreement with a regression coefficient R = 0.8 between P(NO_3) and [NO_3], which indicated that the direct loss of the nitrate radical are much important under polluted air masses at the measurement site.

The reaction of NO_3 with NO can be a very rapid direct sink for NO_3 under a polluted air mass. Nocturnal concentrations of NO, however, are generally quite small because the reaction with ozone converts this compound into NO_2 within a few minutes. In the absence of photolytic conversion of NO_2 back to NO, the concentration of NO falls essentially to zero. But local sources can provide nonzero levels of NO, which in turn have a clear impact on observed NO_3 and N_2O_5 concentrations. A clear tendency of higher NO_3 levels at lower NO is found in Fig. 12. Sometimes both NO and NO_3 were high in the morning in several later peaks. Based on a technical characteristic between NO and NO_3 measurement, this may be caused by the difference in the measuring condition (different air mass etc.). NO_3 was measured along

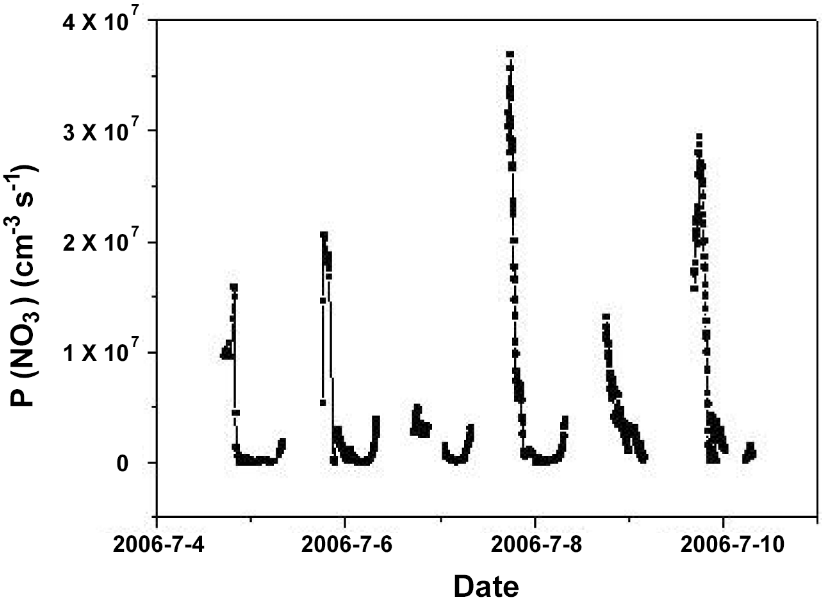

Fig. 8. Time series of the productive rate of NO_3.

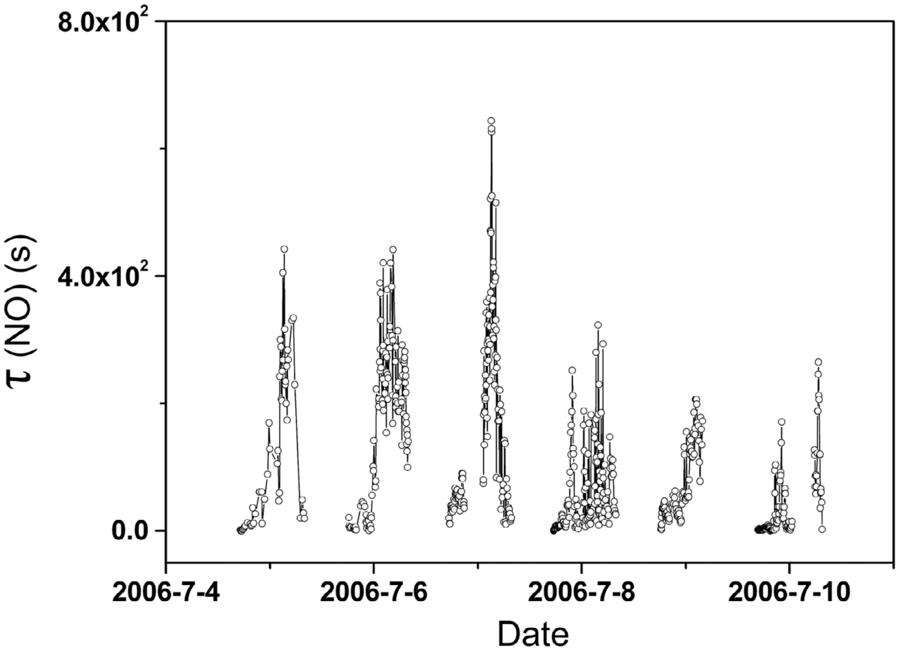

Fig. 9. Time series of the lifetimes of NO_3.

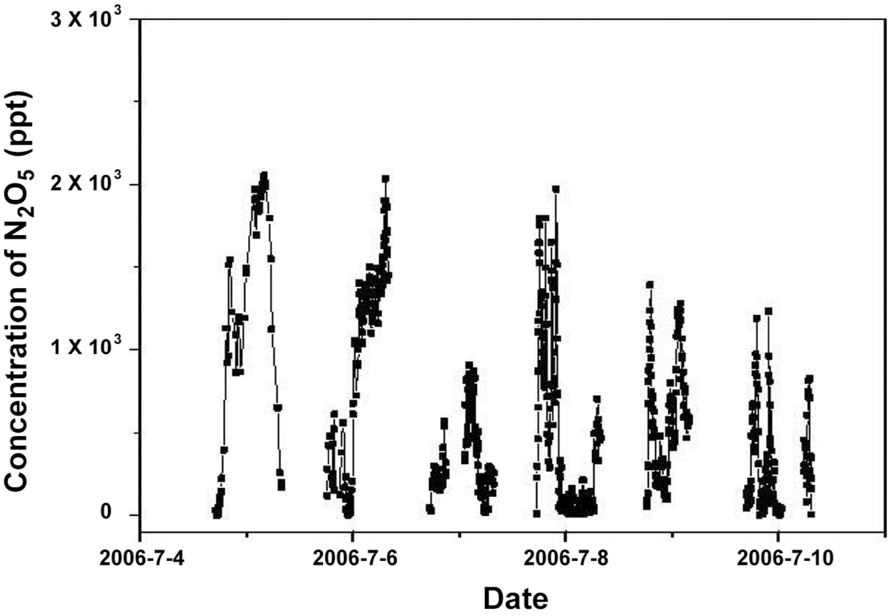

Fig. 10. The time series of calculated N_2O_5 concentrations.

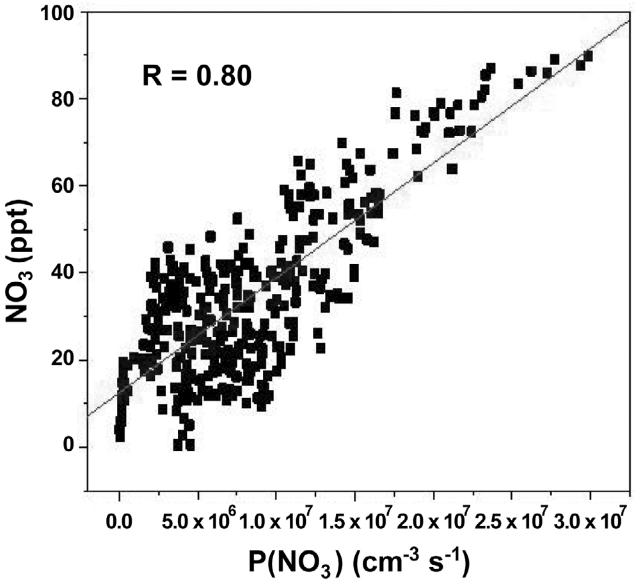

Fig. 11. The NO_3 concentration as a function of its production rate.

with optical path of 3.1 km on the average. Analysis of the NO was carried out using point-instrument.

A negative correlation between the NO_3 lifetime and NO_2 concentration, which is usually presented as evidence of the predominance of N_2O_5 loss over NO_3 loss mechanisms (Geyer 2000), was only found to exist in relative humidity above 58% (Wood et al. 2005). The mean relative humidity was about 79% during this campaign, which is near the deliquescence relative humidity of many common aerosol systems suggesting that most aerosol particles were in a liquid phase. Uptake of N_2O_5 is, in general, much faster onto aqueous aerosols than onto solid aerosols. Therefore, in order to prove the existence and importance of indirect loss pathways the correlation between the lifetime of NO_3 and concentration of NO_2 was studied (Fig. 13). The analysis was restricted to data with NO_3 and NO_2 above the detection limits. The lifetime of NO_3 rapidly dropped at NO_2 higher than 40 ppb, for $\tau(NO_3)$ is inverse proportion to NO_2 from Eq. (10). A linear fit was performed for the statistical values of NO_2 and $\tau(NO_3)$ yielding a correlation coefficient R = -0.52 indicating indirect sinks play a role in determining NO_3 concentrations during this campaign.

Therefore, there was evidence from statistical analysis of correlations showing adirect loss process was much more significant at the Back Garden site during this campaign. Under polluted conditions, possible sinks for NO_3 were similar to those in Los Angeles and in Colorado (Platt et al. 1980; Brown et al. 2003b).

5. CONCLUSIONS

The nighttime nitrate radical was measured by using long path DOAS in the continental boundary layer in the Pearl River Delta (PRD). The mean value of the nitrate radical was 21.8 ± 1.8 ppt during this campaign. An assessment of NO_3 lifetimes using concentration of O_3 and NO_2 averaged 89 seconds. The calculated peak mixing ratio of N_2O_5 was 3424 ppt with the average of 620 ± 93 ppt. The possible loss processes of NO_3 were also discussed basing on statistical analysis of the correlation of nitrate radical and supporting parameters in this paper. The direct losses were important sinks for NO_3 at Back Garden in summer Pearl River Delta.

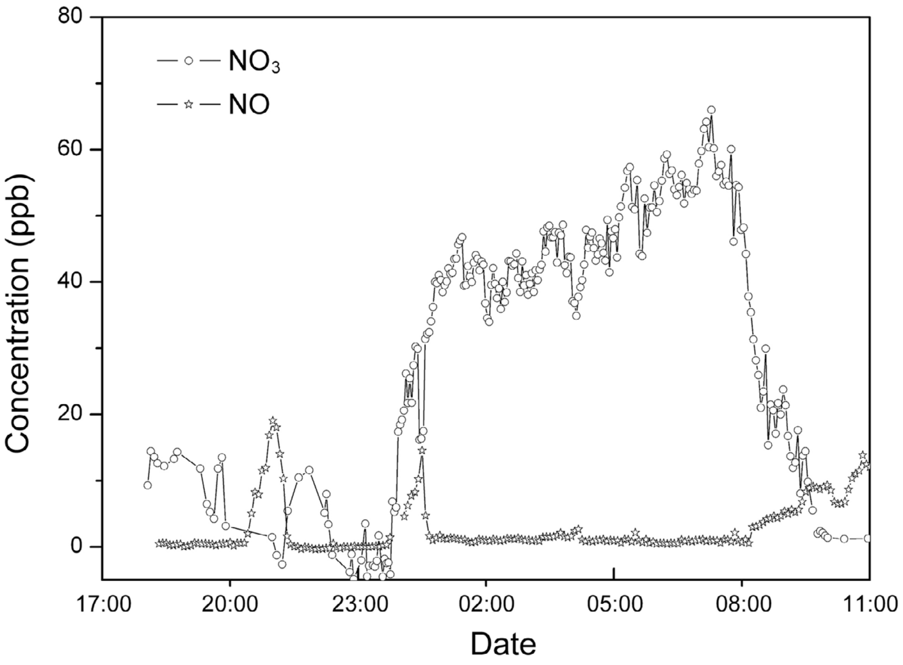

Fig. 12. Average diurnal patterns of NO, NO_3 concentrations and NO_2 concentration.

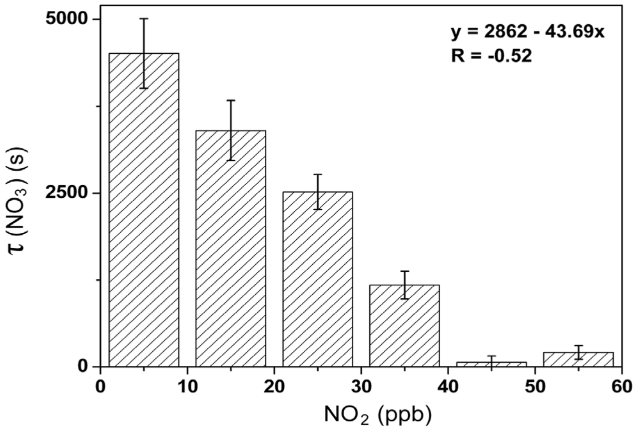

Fig. 13. The correlation of calculated NO_3 life times and NO_2 concentrations; the error bars for NO_3 life times represent the standard deviation.

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