Measurement report: Atmospheric nitrate radical chemistry in the South China Sea influenced by the urban outflow of the Pearl River Delta

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Abstract. Nitrate radical (NO_3) is a critical nocturnal atmospheric oxidant in the troposphere, which widely affects the fate of air pollutants and regulates air quality. Many previous works have reported the chemistry of NO_3 in inland regions of China, while ~~less study targets~~fewer studies target marine regions. Here, we present a field measurement of the NO_3 reservoir, dinitrogen pentoxide (N_2O_5), and related species at a typical marine site (Da Wan Shan Island) located in the South China Sea in the winter of 2021. Two patterns of air masses were captured during the campaign, including the dominant airmass from inland China (IAM) with a percentage of ~84%, and the airmass from eastern coastal areas (CAM) with ~16%. During the IAM period, the NO_3 production rate reached 1.6 ± 0.9 ppbv h^{-1} due to the transportation of the polluted urban plume with high NO_x and O_3. While the average nocturnal N_2O_5 and the calculated NO_3 mixing ratio were 119.5 ± 128.6 pptv and 9.9 ± 12.5 pptv, respectively, and the steady state lifetime of NO_3 was 0.5 ± 0.7 min on average, indicating intensive nighttime chemistry and rapid NO_3 loss at this site. By examining the reaction of NO_3 with volatile organic compounds (VOCs) and N_2O_5 heterogeneous hydrolysis, we revealed that these two reaction pathways were not responsible for the NO_3 loss (<20%), since the NO_3 reactivity ($k(NO_3)$) towards VOCs was

small (5.2×10^{-3} s^{-1}) and the aerosol loading was low. Instead, NO was proposed to significantly contribute to nocturnal NO_3 loss at this site, despite the nocturnal NO concentration always at sub-ppbv level and near the instrument detection limit. It might be from the local soil emission or others. We infer that the nocturnal chemical NO_3 reactions would be largely enhanced once without NO emission in the open ocean after the air mass passes through this site, thus highlighting the strong influences of the urban outflow to the ~~downward~~downwind marine areas in terms of nighttime chemistry. During the CAM period, nocturnal ozone was higher, while NO_x was much lower. The NO_3 production was still very fast, with a rate of 1.2 ppbv h^{-1}. With the absence of N_2O_5 measurement in this period, the NO_3 reactivity towards VOCs and N_2O_5 uptake were calculated to assess NO_3 loss processes. We showed that the average $k(NO_3)$ from VOCs (56.5%, $2.6 \pm 0.9 \times 10^{-3}$ s^{-1}) was higher than that from N_2O_5 uptake (43.5%, $2.0 \pm 1.5 \times 10^{-3}$ s^{-1}) during the CAM period, indicating a longer NO_3/N_2O_5 lifetime than that during IAM period. This study improves the understanding of the nocturnal NO_3 budget and environmental impacts with the interaction of anthropogenic and natural activities in marine regions.

1. Introduction

Reactive nitrogen compounds, especially the nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) play an essential role in nocturnal atmospheric chemistry (Wayne et al., 1991; Brown and Stutz, 2012). NO_3 is mainly generated via the oxidation of NO_2 by O_3 (R1), and then NO_3 further reacts with NO_2 to produce N_2O_5 (R2) with a thermal equilibrium. The temperature-dependent equilibrium constant, K_{eq}, regulates the equilibrium favoring NO_3 and NO_2 at higher temperatures (Osthoff et al., 2007; Chen et al., 2022). During daytime, the NO_3 mixing ratio is generally low as its lifetime is very short (< 5 s) due to the fast photolysis (R3) and rapid reaction with NO (R4) (a rate constant of 2.6×10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 298 K~~;~~, Atkinson et al., 2004). While at night, NO_3 accumulates and can reach tens to hundreds of parts per trillion by volume (pptv), making it the major nocturnal oxidizing agent (Wang et al., 2015).

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

$$NO_2 + NO_3 \rightleftharpoons N_2O_5 \quad \text{(R2)}$$

$$NO_3 + h\nu \rightarrow NO_2 + NO \quad \text{(R3)}$$

$$NO + NO_3 \rightarrow 2NO_2 \quad \text{(R4)}$$

During nighttime, NO_3 is the most important oxidant for alkenes (Mogensen et al., 2015; Edwards et al., 2017), particularly in rural, remote, or forested environments, where it predominantly reacts with unsaturated biogenic volatile organic compounds (VOCs), especially isoprene and monoterpene (Ng et al., 2017; Liebmann et al., 2018b; Liebmann et al., 2018a), to form alkyl nitrates ($RONO_2$), that ultimately lead to secondary organic aerosols (SOAs) (Brown and Stutz, 2012). The observations and model simulations showed that the measured particulate organic nitrates were largely attributed to the nocturnal NO_3 oxidation across Europe (Kiendler-Scharr et al., 2016). The NO_3 oxidation was also reported to play an important role in aerosol formation in the Southeastern United States with high isoprene and monoterpene emissions (Xu et al., 2015). These studies highlighted the critical role of the reaction of NO_3 with VOCs in NO_3 budget and organic aerosol pollution. In addition, NO_3 also reacts with dimethyl sulfide (DMS) over the ocean, affecting the marine sulfur cycle and thus cloud formation and global climate (Aldener et al., 2006; Brown and Stutz, 2012; Ian Barnes et al., 2006; Rosati et al., 2022). While in high aerosol loading regimes, the N_2O_5 heterogeneous uptake becomes a significant indirect NO_3 loss pathway. The hydrolysis reaction produces nitrate (NO_3^-) and nitryl chloride ($ClNO_2$) on chloride-containing ~~aerosols~~aerosol surfaces (Osthoff et al., 2008; Thornton et al., 2010), in which $ClNO_2$ activates the Cl radical and further enhances the photochemistry and ozone pollution in the following day (Riedel et al., 2012; Riedel et al., 2014; Behnke et al., 1993).

Different NO_3 loss pathways produce different air pollutants~~ and cause different environmental impacts~~, thus characterization of NO_3 budget is essential to clarify the NO_3 chemistry in air pollution under various environments. Observations of N_2O_5 and NO_3 in different regions and evaluation of their loss processes have been reported in numerous studies (Crowley et al., 2011; Geyer et al., 2001; Brown et al., 2011; Dewald et al., 2022; Niu et al., 2022; Brown et al., 2016; Wang et al., 2020a; Tham et al., 2016; Aldener et al., 2006; Lin et al., 2022). In general, the NO_3 loss process shows significant regional differences. In urban areas featuring intensive anthropogenic NO_x emissions and moderate (or high) aerosol loading, N_2O_5 uptake is comparable or even dominates the NO_3 loss (Wang et al., 2013). While in rural and forested areas with abundant biogenic ~~VOCs~~VOC (BVOC) emissions, the NO_3 loss processes were usually dominated by BVOCs (Dewald et al., 2022; Geyer et al., 2001; Brown et al., 2011). As for the coastal areas, which were jointly affected by the polluted air mass from the inland and the relatively clean air mass from the ocean, the dominant NO_3 loss process varies greatly depending on the air mass origin (Aldener et al., 2006; Niu et al., 2022; Brown et al., 2016; Crowley et al., 2011). For instance, Crowley et al. (2011) found in the Atlantic coast of Southern Spain (forested area) that when the air mass mainly originated from the Atlantic, NO_3 was mainly consumed by BVOCs (mainly monoterpenes) emitted from nearby forests, while when the air mass came

from the continent, NO_3 loss was mainly due to reactions with anthropogenic VOCs (AVOCs).

China has been recently proven to be a hot spot of nocturnal chemistry with a high NO_3 production rate (Wang et al., 2023). Many studies have reported the mechanisms, budget, or impacts of NO_3-N_2O_5 chemistry in different regions, while most of them were conducted in urban regions (Wang et al., 2013; Yan et al., 2021; Wang et al., 2020a; Wang et al., 2017c; Wang et al., 2017d). For example, Wang et al. (2017b) showed a significant contribution of N_2O_5 uptake to nitrate pollution in summer and winter, and they also highlighted the fast organic nitrate production rate observed in Beijing rural region in summer (Wang et al., 2018b). Only several studies focused on nighttime oxidation in coastal cities like Shanghai, Shenzhen, and Hong Kong (Zhu et al., 2022; Niu et al., 2022; Yan et al., 2019), which showed different patterns of NO_3 chemistry compared with urban regions. Even fewer field studies were conducted on the island which is far away from the coastal cities where the interactions of the oceanic atmosphere and urban plumes can significantly affect the NO_3 budget and impacts. Given the diversity of air masses in inland and coastal areas, studies are needed to gain a comprehensive understanding of NO_3 losses in different atmospheric environments, particularly in coastal and marine areas.

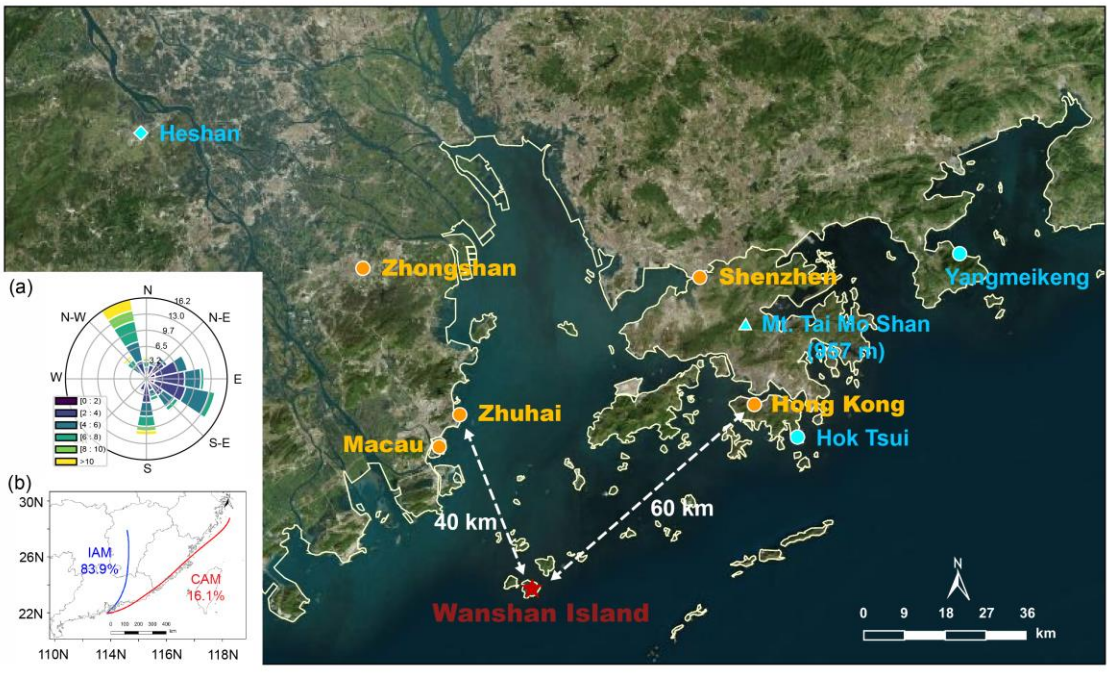
Therefore, we conducted an intensive field observation on Da Wan Shan Island (DWS) in the winter of 2021, which is a typical island site in the north of the South China Sea, and ~~downward~~downwind of the city clusters in the Pearl River Delta, China during the winter monsoon periods. The island features a subtropical oceanic monsoon climate, and the north and northeast synoptic winds from inland PRD and eastern China coast are generally predominant in winter (Liu et al., 2019; Wang et al., 2018a). This allows us to further investigate the interactions between anthropogenic emissions and marine emissions from the perspective of nighttime chemistry. In this study, the measurements of N_2O_5 and the related species ~~observed~~ during the DWS winter campaign are reported. We have identified two types of air masses from both mainland China and coastal areas. Finally, the NO_3 budget and loss processes in different air masses are characterized.

2. Methods

2.1 Site description

The field campaign was conducted at Da Wan Shan Island (21~~.93°~~°55′57″ N, 113~~.72°~~°43′15″ E) from Nov. 9th to Dec. 16th, 2021. Fig. 1 shows the location of the study site, which is approximately 60 km southwest of Hong Kong; 40 km southeast of Zhuhai; and about 100 km and 80 km away from the megacities Guangzhou and Shenzhen,

respectively. This island is dominated by mountainous terrain with an area of 8.1 km^2 and has a small population of about ~~3000~~3,000. Anthropogenic emissions are sparse and no industrial pollution sources were identified, though numerous ships engaging in local fishing activities were observed, potentially affecting the local atmosphere. During the measurement, local airflow was ~~consistent~~consistently from either the northwest ~~to~~or southeast (Fig. 1a) due to the winter monsoon, with wind speeds most frequently ranging from 1.8 to 7.9 m s^{-1} (10^{th} - 90^{th} percentiles) and an average of 4.5 ± 2.6 m s^{-1}. This wind direction is indicative of the mixing of air masses from both continental and coastal areas. The HYbrid Single-Particle Lagrangian Integrated Trajectory model (HYSPLIT) was adopted to investigate the historical trajectory. The HYSPLIT model was run for 48 hours backward in time at local times of 20:00, 24:00, and 04:00, and at a height of 70 m above sea level. It confirmed that the airmass during nighttime mostly came from ~~continental~~inland China (~~defined as inland air mass~~fresh urban emissions, IAM, 84%) and the coastal areas (~~defined as coastal air mass~~aged urban emissions, CAM, 16%). IAM featured the outflow from inland China, such as Guangzhou and Changsha, while CAM featured the outflow of coastal cities like Hong Kong and Shenzhen. No air masses free of pollution from the South China Sea were observed during the measurement period. All measurement instruments were placed in the DWS Atmospheric-Marine Research Station, located on the rooftop with inlets approximately 10 m above ground level and about 72 m above sea level. All times were given in CNST (Chinese National Standard Time = UTC + 8 h), with sunrise around 06:40 CNST and sunset at 17:40 CNST.



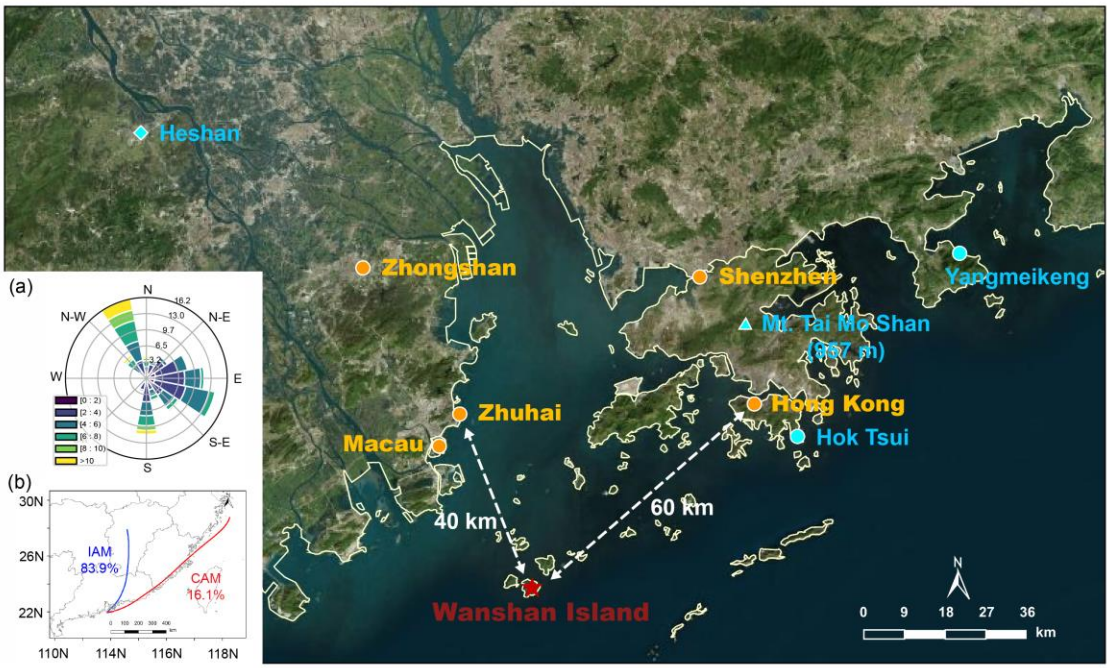


Figure 1. A map of the field measurement site of Wanshan Island (red star) and the surrounding environment (extracted from BingSatelliteMap). Two coastal sites Hok Tsui (Yan et al., 2019) and Yangmeikeng (Niu et al., 2022), and an urban site Heshan (Wang et al., 2022; Yun et al., 2018b) are denoted as blue circle and diamond, respectively. The blue triangle denoted Mt. Tai Mo Shan (957 m), a mountainous site that studied the nighttime chemistry in the nocturnal residual layer (Brown et al., 2016). The inset plot (a) provides the wind rose for the sampling site during the campaign. Panel (b) shows the clustering result of the 48-hrs backward trajectory calculations at nighttime using the HYSPLIT model throughout the campaign.

2.2 Instrument setup

Various parameters were measured in this study, including N_2O_5, NO, NO_2, O_3, VOCs, particle number size distribution (PNSD), and meteorological parameters with different instruments. The detail information about these instruments is listed in Table 1. The N_2O_5 measurements were performed using a cavity-enhanced absorption spectrometer (CEAS) which has been deployed in several field campaigns (Wang et al., 2017a; Wang et al., 2017b; Wang et al., 2018b; Wang et al., 2020b). In brief, ambient N_2O_5 was thermally decomposed to NO_3 in a perfluoro alkoxy alkane (PFA) tube (length: 35 cm, I.D.: 4.35 mm) heated to 130 °C, and NO_3 was detected within a 110 °C PFA resonator cavity. NO was injected to destroy NO_3 from N_2O_5 thermal decomposition every 5 min cycle, and the result was used as the reference spectrum to avoid the influence of ambient water vapor. A pair of high-

reflectivity (HR) mirrors (Layertec GmbH, Mellingen, Germany) with a diameter of 25.0 mm (C0.00/-0.10 mm) was used to enhance the effective optical pathlength. Mirror reflectivity (R(λ)) was calibrated with high purity He and N_2 in the current experimental setup during the field measurements. R(λ) was calibrated to be 0.99997, and the effective pathlength of the optical resonator was 13.96 km. A Teflon polytetrafluoroethylene (PTFE) filter was used to remove ambient aerosol particles, and the inlet flow rate was 1.0 $L \cdot min^{-1}$. The loss of N_2O_5 in the sampling line and filter was considered in the data correction~~.~~ according to previous work (Wang et al., 2017a). Here the CEAS measurement encompasses the combined concentration of ambient [N_2O_5 + NO_3] and effectively represents N_2O_5 under high NOx (or low temperature) conditions when the NO_3-to-N_2O_5 ratio is likely to be low. Accounting for the instrument's transmission efficiency and the thermal transformation between NO_3 and N_2O_5, the contribution of NO_3 is sufficiently negligible in comparison to N_2O_5. Nevertheless, we have taken it into account during the N_2O_5 data correction. The limit of detection (LOD) was 2.7 pptv (1σ), and the measurement uncertainty was ± 19%.

Table 1. The information of observation instruments used during the DWS campaign.

Species	Techniques	Detection limit	Accuracy	Time resolution
N_2O_5	CEAS	2.7 pptv (1σ)	±19%	10 s
NO	Chemiluminescence	0.4 ppbv	±5%	1 min
NO_2	Chemiluminescence	0.4 ppbv	±5%	1 min
O_3	UV photometry	0.4 ppbv	±5%	1 min
VOCs	PTR-TOF-MS	0.01 ppbv	±10%	10 s
PNSD	SMPS	5–300 nm	±10%	5 min

NO_x and O_3 were measured by commercial instruments (model T200U and model T400U, Teledyne API Inc., respectively) calibrated with zero air before the measurement. The nitrogen oxide analyzer uses the chemiluminescence detection method to measure the original NO and converted NO_2~~.~~, and the LOD was 0.4 ppbv for each species. Aerosol surface area density (S_a, μm^2 cm^{-3}) was calculated based on the particle numbers and geometric diameter, which was ~~measured by a laboratory-assembled scanning-mobility particle sizer (SMPS).~~calculated through the results measured by a laboratory-assembled scanning-mobility particle sizer (SMPS) according to Mcmurry et al. (2000). This SMPS system consists of two differential mobility analyzers (DMA, "nano-DMA" mode 3081A, and "regular-DMA" mode 3085A, TSI Inc.) in parallel, and a condensed particle counter (mode 3787, TSI Inc.) as the detector. The combination of nano DMA and conventional mode 3085A DMA enables the SMPS to have better detection performance for particles below 50 nm. In this measurement, SMPS measured the particle size distribution in 5-300 nm with a time resolution of 5 minutes, and Sa can be regarded as the lower limit value. A growth factor $f(RH) = 1 + 8.8 \times (RH/100)^{9.7}$ (Liu et al., 2013) was used here to correct dry state S_a to wet state S_a.

VOCs were measured by proton transfer reaction time of flight mass spectrometry (PTR-TOF-MS, Ionicon Analytik GmbH, Innsbruck, Austria) with a time resolution of 10 s. ~~Meanwhile, VOCs were also sampled every 2 h using 2 L canisters on the selected days when the hourly O_3 mixing ratio exceeded 70 ppbv, and the canister samples were~~At the end of this campaign, background measurements and instrument calibration were conducted with high-purity nitrogen and multi-component VOC gas standards, respectively. The instrument calibration results yielded strong linear relationships ($R^2 = 0.98$) between the proton transfer reaction rate constants and the sensitivities of ten calibrants, including acetaldehyde, acetone, dimethyl sulfide, isoprene, methyl ethyl ketone, benzene, toluene, styrene, o-xylene, and trimethylbenzene. The sensitivities of the uncalibrated species were determined through the rate constants of the proton transfer reactions and their correlation coefficients with sensitivity. Meanwhile, the VOCs were also sampled by canister and analyzed by a gas chromatograph equipped with a mass spectrometer or flame ionization

detector (GC-MS~~).~~) for some ozone polluted days. For the absence of nocturnal data from canister samples, the following analysis was based on the PTR-TOF-MS measurement~~.~~ except the weight of α-pinene and β-pinene detected by GC-MS. Since monoterpene species cannot be distinguished by PRT-TOF-MS, the reaction rate constant of the sum monoterpene reaction with NO_3 was weighted by the campaign-averaged ~~percentage~~weight of α-pinene and β-pinene detected by GC-MS. Meteorological parameters (i.e., temperature (T), relative humidity (RH), wind speed, and wind direction) were routinely monitored with a time resolution of 5 min.

2.3 The calculation of NO_3 budget and lifetime

With the observation of N_2O_5, NO_3 can be calculated according to their temperature-dependent equilibrium relationship (Eq. 1) (Brown and Stutz, 2012). Lifetimes are commonly expressed as the ratio of their concentrations to the NO_3 production rate as determined by Eq. 2 and Eq. 3, assuming the production and loss are in dynamic balance at night (Brown et al., 2003; Brown and Stutz, 2012). The production rate of nitrate radical, $P(NO_3)$, is commonly expressed by Eq. ~~2~~4, where $k_{NO_2+O_3}$ represents the temperature-dependent reaction rate constant of NO_2 and O_3 (Atkinson et al., 2004). In general, the nocturnal NO_3 losses typically include three main pathways~~:~~ (Eq. 5): (1) the reaction with NO, (2) the reactions with VOCs, and (3) N_2O_5 uptake.

$$[NO_3] = [N_2O_5]/\mathrm{Keq}(T)[NO_2] \quad \text{(Eq. 1)}$$

$$\mathrm{Keq} = 5.50 \times 10^{-27} \times \exp(10724/T)$$

$$\tau_{N_2O_5} = \frac{[N_2O_5]}{P(NO_3)} = \frac{[N_2O_5]}{k_{NO_2+O_3}[NO_2][O_3]} \quad \text{(Eq. 2)}$$

$$\tau_{NO_3} = \frac{[NO_3]}{P(NO_3)} = \frac{[NO_3]}{k_{NO_2+O_3}[NO_2][O_3]} \quad \text{(Eq. 3)}$$

~~$P(NO_3) = k_{NO_2+O_3}[O_3][NO_2]$ (Eq. 23)~~

$$P(NO_3) = k_{NO_2+O_3}[O_3][NO_2] \quad \text{(Eq. 4)}$$

$$L(NO_3) = \sum k_i[VOC_i][NO_3] + k_{NO+NO_3}[NO][NO_3] + k_{het}[N_2O_5] \quad \text{(Eq. 3~~5~~)}$$

The NO_3 reactivity towards VOCs, ~~k(NO_3),~~k(NO_3), is the first-order loss rate coefficient calculated from the products of the bimolecular rate coefficients k_i and the VOC concentrations as shown in Eq. 4~~6~~.

$$k(NO_3) = \sum k_i[VOC_i] \quad \text{(Eq. 46)}$$

The k_{het} is the first-order loss rate coefficient of N_2O_5 uptake on the aerosol surface. It depends on the uptake coefficient $\gamma(N_2O_5)$, the aerosol surface area density Sa ($\mu m^2\ cm^{-3}$), and the mean molecular speed c (Eq. 57). The $\gamma(N_2O_5)$ is influenced by chemical composition, physical properties of aerosol, as well as ambient conditions including related humidity and temperature (Yu et al., 2020; Wagner et al., 2013; Wang et al., 2018b; Bertram and Thornton, 2009; Tang et al., 2014; Kane et al., 2001). ~~Here $\gamma(N_2O_5)$ is parameterized based on RH and temperature (Eq. 6~~There are several kinds of methods proposed to quantify or estimate $\gamma(N_2O_5)$ by using observed parameters. Given that some essential parameters were not directly measured during this campaign, only two approaches were employed to estimate the N_2O_5 uptake coefficient. The first method is the pseudo steady state method by assuming that N_2O_5 and NO_3 have achieved a steady state (Brown et al., 2009). $\gamma(N_2O_5)$ and k_{NO_3} can be determined from the slope and intercept of linear regression of $K_{eq}[NO_2]\ \tau(N_2O_5)^{-1}$ versus $0.25cSaK_{eq}[NO_2]$ respectively as shown in Eq. 8. The second is the parameterization method. As the aerosol compositions used to estimate the N_2O_5 uptake coefficients were not measured, only a simplified parameterization is available that based on relative humidity (RH) and temperature (Eq. 9) (Hallquist et al., 2003; Kane et al., 2001; Evans and Jacob, 2005). Although simple, it had an overall reasonable performance in China (Wang et al., 2022; Tham et al., 2018; Wang et al., 2020a).

$$k_{het} = \frac{1}{4}cS_a\gamma(N_2O_5) \quad \text{(Eq. 57)}$$

$$K_{eq}[NO_2]\tau(N_2O_5)^{-1} = \frac{1}{4}cS_a\gamma(N_2O_5)K_{eq}[NO_2] + k_{NO_3} \quad \text{(Eq. 8)}$$

$$\gamma(N_2O_5) = \alpha \times 10^{\beta}$$

$$\alpha = 2.79 \times 10^{-4} + 1.3 \times 10^{-4} \times RH - 3.43 \times 10^{-6} \times RH^2 + 7.52 \times 10^{-8} \times RH^3$$

$$\beta = 4 \times 10^{-2} \times (T - 294) \quad (T > 282K)$$

$$\beta = -0.48 \quad (T < 282K) \quad \text{(Eq. 6)}$$

~~Lifetimes are commonly expressed as the ratio of their concentrations to the NO_3 production rate as determined by Eq. (7) and Eq. (8), assuming the production and loss are in dynamic balance at night (Brown et al., 2003; Brown and Stutz, 2012).~~

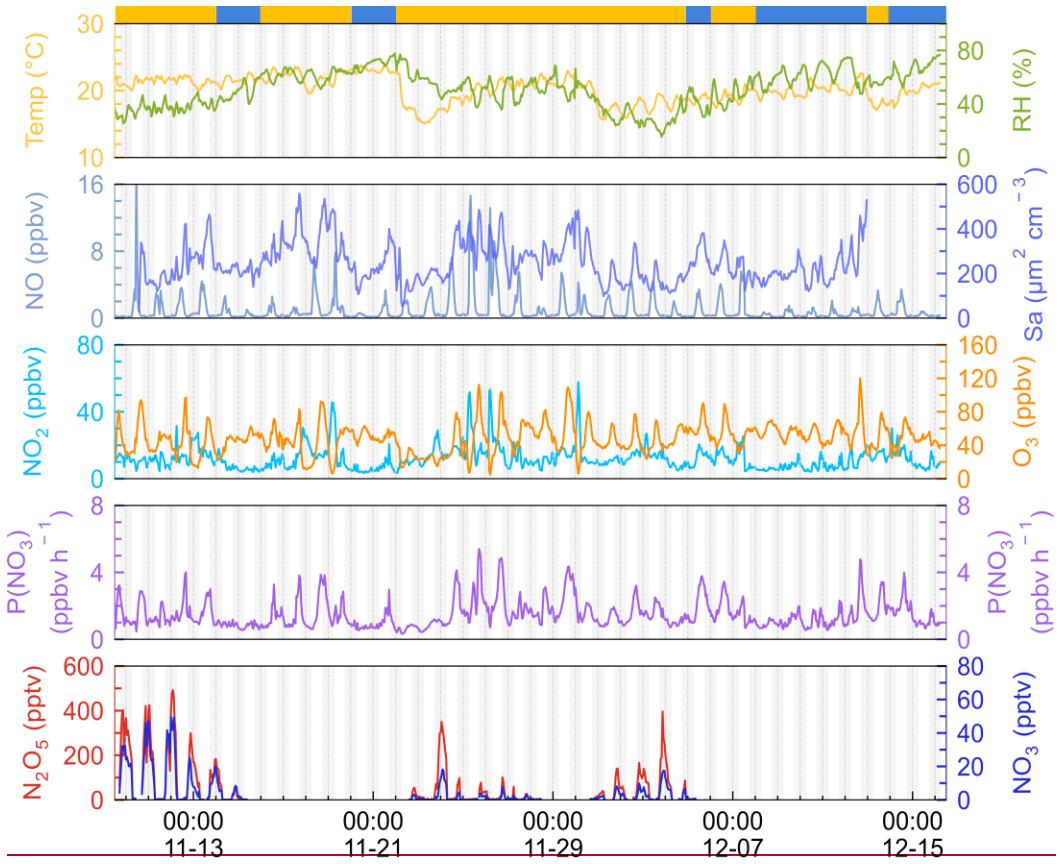
$$9\tau_{N_2O_5} = \frac{[N_2O_5]}{P(NO_3)} = \frac{[N_2O_5]}{k_{NO_2+O_3}[NO_2][O_3]} \quad \text{(Eq. 7)}$$

$$\tau_{NO_3} = \frac{[NO_3]}{P(NO_3)} = \frac{[NO_3]}{k_{NO_2+O_3}[NO_2][O_3]} \quad \text{(Eq. 8)}$$

3. Results and discussion

3.1 Measurement overview

The time series of N_2O_5, related trace gases, and selected meteorological parameters for the study period are depicted in Fig. 2. The air masses are categorized into IAM and CAM according to the backward trajectories at 20:00, 00:00, and 04:00 each day as illustrated in Fig. 1. The detailed information of two kinds of air masses is listed in Table 2. Data gaps for N_2O_5 were caused by technical problems, mirror reflectivity calibration, or instrumental maintenance, which usually took place in the daytime. In this campaign, meteorological conditions featured a typical subtropical winter climate with average temperature and RH values of 20.1 ± 1.9 ℃ and 52.0% ± 13.6%, respectively.



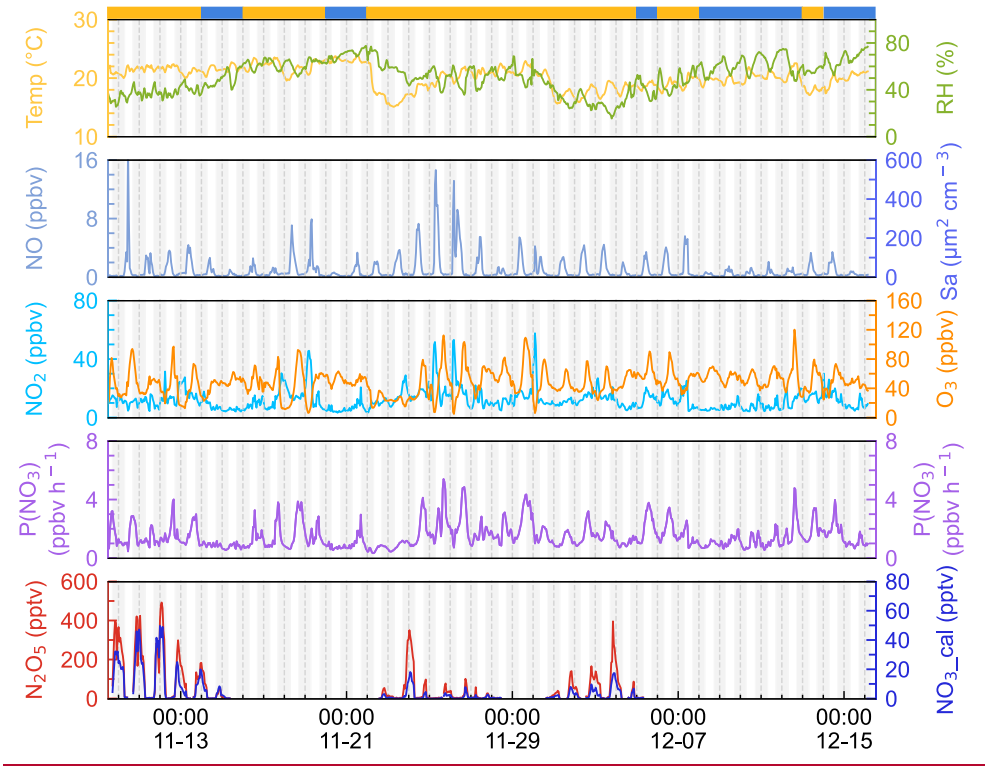


Figure 2. Time series of N_2O_5, NO_3, $P(NO_3)$, NO, NO_2, Sa, temperature, and relative humidity in 1-hour average. NO_3 was calculated by measured N_2O_5 according to the thermal equilibrium. The light gray shadow indicates the nighttime period. The ribbon at the top separates the air masses into two categories, yellow for ~~inland air masses (~~IAM~~)~~ and blue for ~~coastal air masses (~~CAM~~).~~.

Ozone exhibited the characteristic of afternoon photochemical peaks especially when the airmass comes from the inland. The average and maximum concentrations of ozone were 48.2 ± 18.2 ppbv and 120.1 ppbv, respectively~~, among which~~. Once the ~~hourly~~ maximum hourly average O_3 exceeded the Chinese national air quality standard (200 μg m^{-3}, equivalent to 93 ppbv~~) for~~), we marked this day as an O_3 pollution day. There are 6 O_3 polluted days out of 37 days ~~of measurements. All these O_3 pollution episode days~~during the campaign and all occurred during ~~the~~ IAM ~~period~~periods. Meanwhile, the mixing ratio of NO, NO_2, and Sa usually increased during these days, indicating that this site was strongly affected by regional transport from ~~inland China, i.e.,~~ the PRD ~~region~~city clusters. Previous observations by Wang et al. (2018a) also found high O_3 levels in autumn on the same island due to the weak NO titration and high O_3 production rate. ~~Detailed analysis of ozone and VOCs will be subjected to another manuscript (Fang et al., 2023).~~

Nitrogen oxides (NO_x = NO + NO_2) were at a moderate level with an average value of 13.1 ± 8.2 ppbv, which is much lower than the values in PRD regions (usually > 20 ppbv, (Wang et al., 2022; Yang et al., 2022; Yun et al., 2018b) and higher than those on the remote islands

in South China Sea (< 5 ppbv, Chuang et al., 2013). The mixing ratio of NO at nighttime was low and showed small peaks during daytime. With the O_3 accumulating throughout the day, NO decreased to below the instrument detection limit in the first half of the night, while it began to increase as the O_3 concentration decreased in the second half of the night. Given that the lifetime of NO is only a few minutes in the presence of several tens of ppbv of O_3 (Dewald et al., 2022), we inferred that NO is likely ~~to come~~originated from a local source such as soil emission, boats, cooking, and so on.

Table 2. Summary of ~~detailed information~~parameters on the two air mass types (mean ± standard deviation).

Species	IAM		CAM	
	All day [b]	Nighttime [b]	All day	Nighttime
O_3 (ppbv)	45.8 ± 20.2	42.9 ± 18.4	53.1 ± 11.9	51.4 ± 9.6
NO_x (ppbv)	15.1 ± 8.7	14.5 ± 9	9.2 ± 5.1	8.8 ± 4.8
NO_2 (ppbv)	13.9 ± 7.6	14.1 ± 8.3	8.6 ± 4.8	8.6 ± 4.8
NO (ppbv)	1.2 ± 2.3	0.4 ± 1.1	0.5 ± 0.6	0.2 ± 0.1
Temp (°C)	19.9 ± 2	19.9 ± 1.9	20.8 ± 1.5	20.6 ± 1.5
RH (%)	46.7 ± 12.5	47.7 ± 13.2	61.2 ± 10	64.1 ± 9.6
$P(NO_3)$ (ppbv h^{-1})	1.6 ± 0.9	1.5 ± 0.8	1.3 ± 0.8	1.2 ± 0.6
N_2O_5 (pptv)	- [c]	119.5 ± 128.6	- [c]	-
NO_3 (pptv)[a]	-	9.9 ± 12.5	-	-
$\tau_{N_2O_5}$ (min)	-	6.5 ± 6.5	-	-
τ_{NO_3} (min)	-	0.5 ± 0.7	-	-

Note: [a] NO_3 is calculated by the thermal equilibrium between NO_2, NO_3, and N_2O_5.
[b] "All day" means the 24-hour average and the "Nighttime" means the time between 18:00-06:00 local time.
[c] Without N_2O_5 measurement in the daytime and limited N_2O_5 data during the CAM period, N_2O_5, NO_3, and their lifetimes were not valid here.

N_2O_5 was at a moderate level on most days with a nocturnal average of 119.5 ± 128.6 pptv, with high concentrations (>400 pptv in 1-hour average) ~~only lasting for~~in the first three days during this campaign. During the nights from November 9th to 12th, the N_2O_5 concentrations were significantly higher than those ~~at~~on other nights, with a maximum of 657.3 pptv at midnight of November 12th. The NO_3 concentration (calculated based on the thermal equilibrium with N_2O_5) was also moderate with an average mixing ratio of 9.9 ± 12.5 pptv, which was higher than that reported on a nearby coastal site of Hong Kong Island (Yan et al., 2019). Table 3 compares the N_2O_5, NO_3, and $P(NO_3)$ found in other coastal (or island) and continental regions from Europe, the United States, and China. In our study,

N_2O_5 and NO_3 were at a moderate level compared to other coastal regions when they were affected by emission plumes from continental regions, such as Northwestern Europe (Morgan et al., 2015), the East coast of the USA (Brown et al., 2004), and Shenzhen, China (Niu et al., 2022), and were comparable with urban regions (Wang et al., 2017b; Wang et al., 2018b). The concentrations of NO_3 precursors (NO_2 and O_3) at this site were much similar to some rural areas, leading to a high NO_3 production rate with a daily average of 1.5 ± 0.9 ppbv h^{-1} and a maximum of 5.9 ppbv h^{-1}. The average value is much higher than that reported in Beijing in winter (0.4 ppbv h^{-1},~~(~~ Wang et al., 2021), comparable to autumn (1.4 ± 1.7 ppbv h^{-1}, ~~(~~Wang et al., 2017b) and even higher than that in summer Taizhou (1.01 ± 0.47 ppbv h^{-1}, ~~(~~Wang et al., 2020a). The nocturnal average $P(NO_3)$ during this campaign was 1.4 ± 0.7 ppbv h^{-1}, ~~even~~which is higher than the average value in the warm season of China with 1.07 ± 0.38 ppbv h^{-1} (Wang et al., 2023). ~~Besides the high NO_2 and O_3, the~~The high reaction rate constant for NO_2 and O_3 due to the high temperature at this site is a potential explanation for the high $P(NO_3)$ values observed in this study~~.~~ (i.e., at same NO_2 and O_3 level, if temperature increased from 10 ℃ to 20 ℃, the reaction rate constant would increase from 2.27×10^{-17} to 3.05×10^{-17}, which means the $P(NO_3)$ would be 1.34 times faster). The high $P(NO_3)$ and the low concentrations of N_2O_5 and NO_3 indicate intensive atmospheric oxidation capacity and fast NO_3 and N_2O_5 removal over the Pearl River Estuary.

~~The difference of trace gases in IAM and CAM periods, and the~~The mean diurnal profiles of N_2O_5, together with relevant species are shown in Fig. 3. Daytime N_2O_5 and NO_3 in the IAM period were shown as ~~zero~~NaN due to the absence of observation. Because of limited N_2O_5 data for the CAM period, neither N_2O_5 nor NO_3 is shown in Fig. 3. NO exhibited similar diurnal variation in both periods and the mixing ratio was higher in the IAM period. The wind rose plot (Fig. S1) showed high concentrations of NO originating from the north characterized by the outflow from PRD regions. However, NO_2 differed in the two periods, showing ~~highly~~high anti-correlation with O_3 only in the IAM period and little diurnal variation in the CAM period. ~~A fit of nocturnal O_3 against NO_2 (Fig. S2) yields a slope of -1.1 in IAM, implying that the major emission of NO_x was NO and almost no nocturnal NO_2 production occurred (Brown et al., 2016).~~

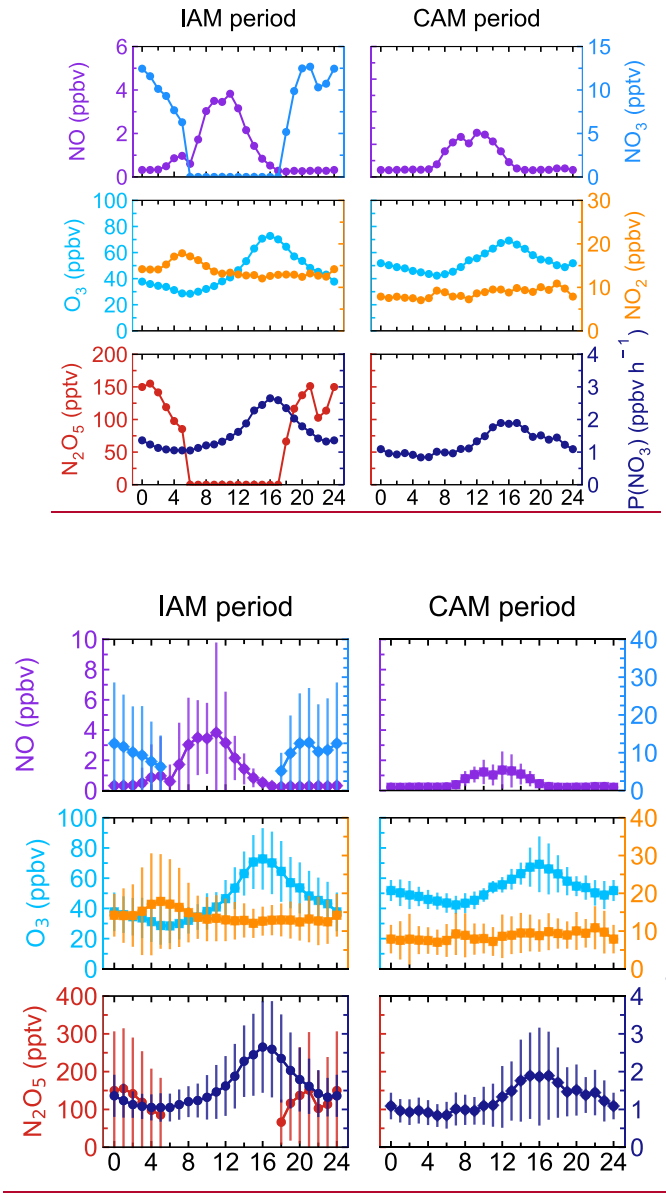


Figure 3. Mean diurnal profiles of N_2O_5, NO_3, $P(NO_3)$, and relevant parameters in the two types of air masses. NO_3 was calculated from N_2O_5. Neither N_2O_5 nor NO_3 was shown during CAM period because of limited N_2O_5 measurement.

Ozone exhibited a typical diurnal pattern for all ~~airmasses~~air masses, gradually increasing until its peak at 16:00 and then slowly decreasing throughout the night until its lowest mixing ratio was reached at about 06:00. Compared to the CAM period, the lower minimum hourly O_3 concentration and a small peak of NO_2 in the early morning indicated that NO titration effect was stronger in the IAM period, and the higher maximum of O_3 concentration in IAM indicated that photochemical formation of O_3 and/or transport was faster to completely offset the titration. In addition, the higher NO_x and VOC

concentrations (as shown in Table S1) in the IAM period facilitated O_3 formation. With the elevated precursor concentrations (NO_2 and O_3) in the IAM period, N_2O_5 and NO_3 accumulated rapidly after sunset, reaching their peak values (~~155.0~~492.1 pptv and 49.6 pptv for each~~) near 20:00.~~). $P(NO_3)$ was highly consistent with O_3 in diurnal variation and reached the peak at 16:00, with peak values of 2.7 ppbv h^{-1} (IAM) and 1.9 ppbv h^{-1} (CAM), as well as a nocturnal average value of 1.5 ± 0.8 ppbv h^{-1} (IAM) and 1.2 ± 0.6 ppbv h^{-1} (CAM), respectively. The $P(NO_3)$ of CAM was consistent with the observation ~~in~~when the air mass over eastern Shenzhen was transported from the clean area or sea surface (1.2 ± 0.3 ppbv h^{-1}~~),~~ ~~(~~Niu et al., 2022)~~ during which the air masses were transported from clean areas or the sea surface.~~

391 .

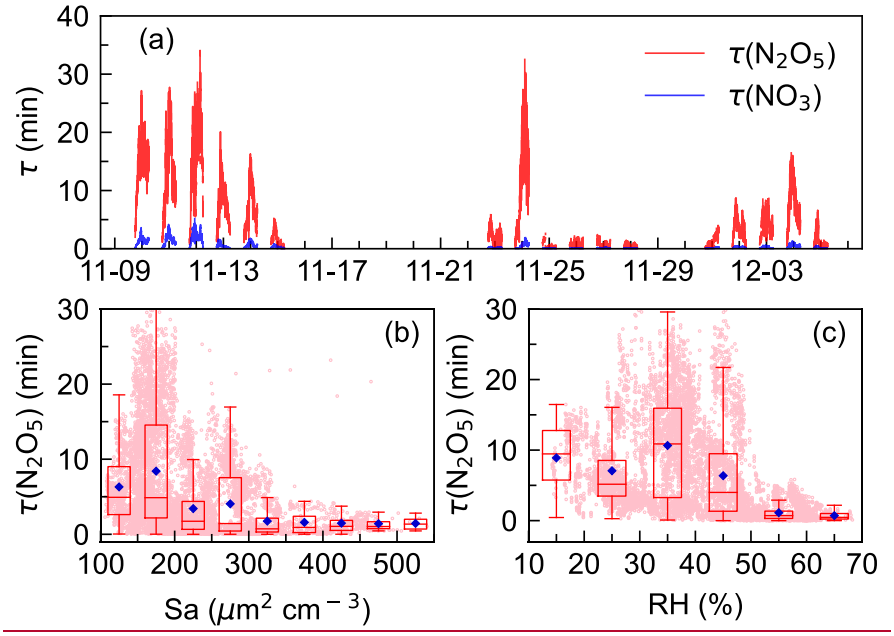
Table 3. Summary of field-observed N_2O_5, NO_2, O_3 concentrations, and NO_3 production rate.

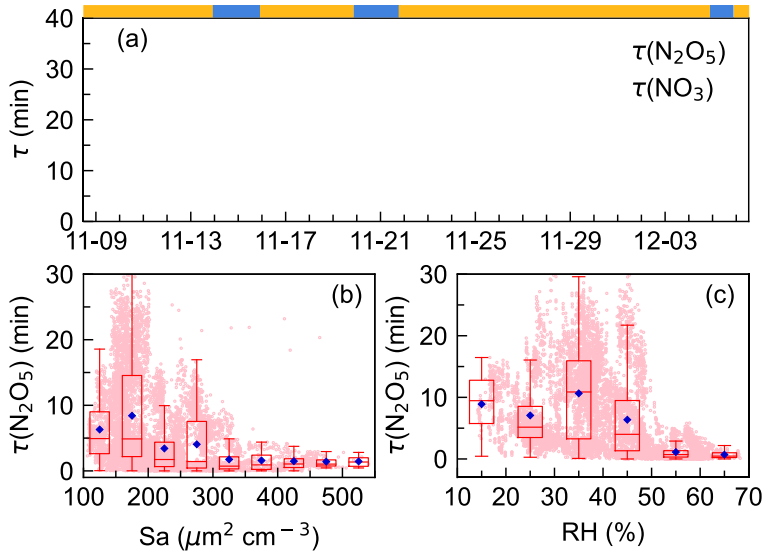
Region	Location	Time	N_2O_5 (pptv)	NO_3 (pptv)	NO_2 (ppbv)	O_3 (ppbv)	*P* (NO_3) (ppbv hr^{-1})	References
Urban	Jinan, China	Aug.-Sep.,2014	22 ± 13 (max 278)		74.6	55	/	(Wang et al., 2017c)
Urban	Shanghai, China	Aug.-Oct., 2011	310 ± 380	16±9 (max 95)	0-76	23 ± 8 (max 57)	1.10 ± 1.09	(Wang et al., 2013)
Urban	Beijing, China	May-Jul., 2016	100–500 (max 937)	27	/	/	1.2 ± 0.9	(Wang et al., 2018b)
Urban	Mt. Tai, China	Jul.-Aug., 2014	6.8±7.7	/	16.4 (±6.1)	88.6 (±16.6)	0.45±0.40	(Wang et al., 2017d)
Urban	Heshan, China	Sep.-Nov., 2019	64 ± 145 (night)	max 90	21.0±10.4	75.2±20.9 (max 152.8)	2.5 ± 2.1 (day)	(Wang et al., 2022)
			(max 1180)				1.8 ±1.5 (night)	
Urban	Beijing, China	Sep.-Oct., 2019	68.0 ±136.7	/	35.1 ±16.6	27.7 ±25.2	2.25 ±2.02	(Wang et al., 2017b)
Suburban	Changzhou, China	May-Jul., 2019	53.4 ± 66.1 (max 304.7)	4.7 ± 3.5 (max 17.7)	13.7 ± 8.9	48.4 ± 27.8	1.7 ± 1.2 (max 7.7)	(Lin et al., 2022)
Rural	Wangdu, China	Jun.-Jul., 2014	<200 (max 430)	/	10-80	(max 146)	1.7 ±0.6	(Tham et al., 2016)
Rural	Taizhou, China	May-Jul., 2018	26.0 ± 35.7 (max 492)	4.4 ± 2.2 (max 150)	28.28 ± 18.57	48.2 ± 32.5	1.01 ± 0.47 (night)	(Wang et al., 2020a)
Coastal	Tai Mo Shan, HK	Nov.-Dec., 2013	0.5-11.8 ppbv	-	7.88	68.5	0.01-2	(Brown et al., 2016)
Coastal	East coast of USA	Jun.-Aug., 2002	85	17	6	35	/	(Brown et al., 2004)
Coastal	California, USA	Jan.,2004	0-200	/	0-15	15–35	/	(Wood et al., 2005)
Coastal	Southern Spanish	Nov.-Dec., 2018	~500 (max)	/	1-15	15-40	/	(Crowley et al., 2011)
Coastal	Shenzhen, China	Sep.-Oct., 2019	55.6 ± 89 (max 1420)	/	6.2	88.9±24.6	2.9 ± 0.5 (UAM)	(Niu et al., 2022)
			45.4 ± 55.2 (BAM)				1.2 ± 0.3 (BAM)	
Coastal	Northwestern Europe	Jul., 2010	670	/	0.5–2	30– 40	/	(Morgan et al., 2015)
Island	Hok Tsui, HK	Aug.-Sep., 2012	17±33 (max 336)	7 ± 12	6 ± 7	33 ± 24	/	(Yan et al., 2019)
Island	Wanshan, China	Nov.-Dec., 2021	107.22 ± 125.17	7.56 ± 10.95	13.14 ± 8.68	43.75 ± 18.49	1.38 ± 0.83	This work

Notes: UAM means air masses coming from continental areas, and BAM means air masses coming from background marine areas. Mean values are in the form of mean ± standard deviation or single data. The maximum was noted in the table.

3.2 The lifetimes of N_2O_5 and NO_3

Steady-state lifetime is one of the most common and useful diagnostics for NO_3 and N_2O_5 analysis in the atmosphere (Brown et al., 2003; Wang et al., 2018b; Wang et al., 2020a; Brown et al., 2016). As shown in Fig. 4, τ_{NO_3} was low during the whole campaign with an average of 0.5 ± 0.7 min. $\tau_{N_2O_5}$ showed a similar pattern to τ_{NO_3} but had a much higher value, ranging from 0 to 34.1 min with an average of 6.1 ± 6.5 min. The N_2O_5 lifetime was higher in the first half of the campaign (11.5 min, November 9th to 14th) than in the second half (3.5 min, November 22th to 28th). The difference was mainly due to the N_2O_5 mixing ratio rather than $P(NO_3)$, as $P(NO_3)$ shows no significant difference during the whole observation (Fig. 2).





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407 **Figure 4.** Time series of N_2O_5 and NO_3 lifetimes (a) and variations of nocturnal N_2O_5
408 lifetime as a function of aerosol surface area density, Sa (b), and relative humidity, RH (c).
409 The blue diamond represents the average $\tau_{N_2O_5}$ and pink dots represent the scatter data
410 point in 1 min. The ribbon at the top separates the air masses into two categories, yellow
411 for IAM and blue for CAM.

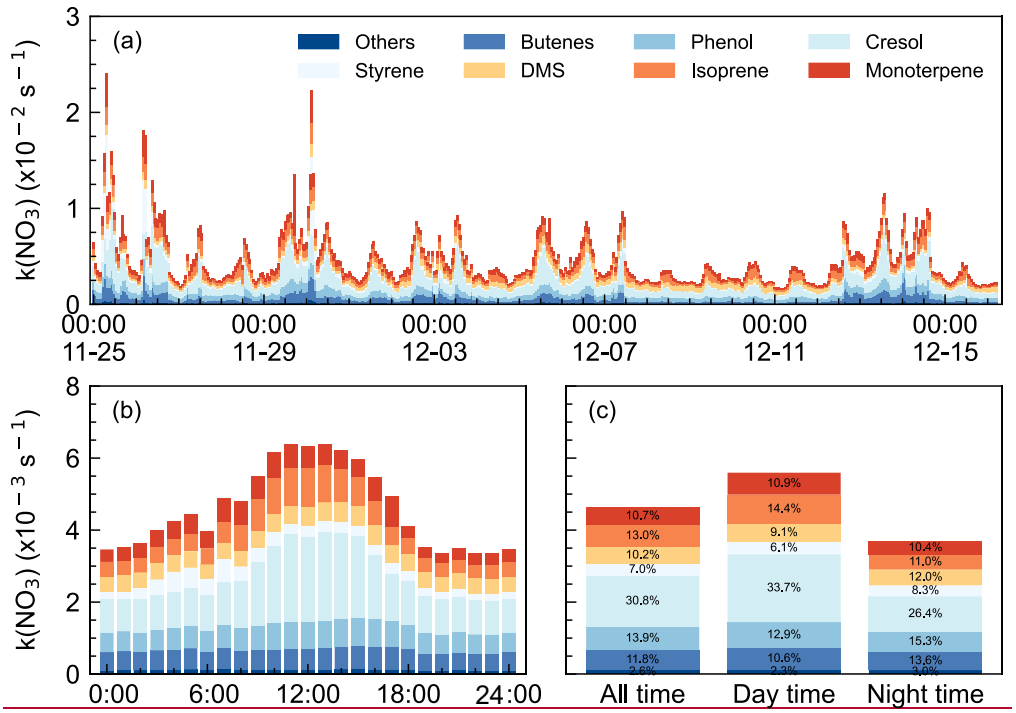
412 $\tau_{N_2O_5}$ values were comparable to those measured on the coastline of Finokalia, Greece for
413 a median of 5 min (Vrekoussis et al., 2004; Vrekoussis et al., 2007), but much lower than
414 those previously reported in the residual layer in Hong Kong for 1-5 h (Brown et al., 2016).
415 In comparison, the lifetimes were much longer than in inland urban areas, for example,
416 0.93 ± 1.13 min in Taizhou (Li et al., 2020), 1.6 ± 1.5 min in Changzhou (Lin et al., 2022)
417 for YRD regions, 1.1-10.7 min (Zhou et al., 2018) and 4.5 ± 4.0 min (Wang et al., 2018b)
418 in Beijing. Typically, high aerosol loading, more intensive VOC, and NO emissions in these
419 areas led to enhanced N_2O_5 uptake and reactions of NO_3 with VOC. ~~But at this site, the~~
420 ~~atmosphere was relatively clean since the maximum S_a value was less than 600 μm^2 cm^{-3},~~
421 ~~making N_2O_5 uptake slow.~~While in this site, measurement indicated that the peak diameter
422 in the particle number distribution was small during the whole campaign and indicated no
423 significant difference between two air masses with respect to the aerosol diameters (Fig.
424 S2). S_a value ranged from 29 μm^2 cm^{-3} to 557 μm^2 cm^{-3}. All of these indicated the
425 atmosphere was relatively clean (Wang et al., 2017b), making N_2O_5 uptake slow. Fig. 4b
426 shows N_2O_5 lifetime decreased rapidly from 8.3 min to 1.7 min when S_a increased up to
427 300 μm^2 cm^{-3} and then remained at relatively low constant levels though S_a still increased.
428 Such a trend of $\tau_{N_2O_5}$-S_a dependence was consistent with previous observations and varied
429 in exact values (Zhou et al., 2018; Wang et al., 2018b; Li et al., 2020). Fig. 4c. showed that

$\tau_{N_2O_5}$ decreased as RH increased (> 40%) possibly due to the hygroscopic aerosol growth and the dependence of the N_2O_5 uptake coefficient on the RH (Brown and Stutz, 2012). Overall, the trend is consistent with previous works, while the large discrepancy of the dependence implied that N_2O_5 uptake was not the dominant NO_3 loss process.

3.3 The NO_3 reactivity and N_2O_5 uptake coefficients

The concurrent high $P(NO_3)$ and low NO_3 lifetime imply high NO_3 reactivity as well as a large nocturnal NO_3 loss process at DWS. The NO_3 reactivity ~~($k(NO_3)$)~~ towards VOCs was calculated by Eq. 4, towards which were categorized into anthropogenic VOC and biogenic VOC~~.~~ (Gu et al., 2021). Throughout the campaign, $k(NO_3)$ varied considerably (Fig. 5a), showing relatively high and fluctuated values when the airmasses featured IAM. The $k(NO_3)$ ranged from 1.6×10^{-3} s^{-1} to 2.4×10^{-2} s^{-1} with the daily average of $4.6 \pm 2.8 \times 10^{-3}$ s^{-1}. Low values of $k(NO_3)$ were observed from December 9th to 12th when the air masses originate from coastal or offshore from the east and southeast, which features the outflow of coastal cities like Hong Kong and Shenzhen.

Fig. 5b shows the mean diurnal profile of $k(NO_3)$, where a trend of high values in the daytime and low values at nighttime are observed. Anthropogenic VOC, especially cresol, dominated the daily trend of $k(NO_3)$, while biogenic VOC-$k(NO_3)$ showed no significant diurnal variation. Except cresol, other highly reactive VOC showed little change throughout the day. Regarding the biogenic VOC-$k(NO_3)$, the concentrations of monoterpene, isoprene, and DMS changed smoothly although their emissions would increase with elevated temperature and sunlight during daytime (Fuentes. et al., 2000). The detailed contributions of VOC categories to $k(NO_3)$ were shown in Fig. 5c. The $k(NO_3)$ was $5.6 \pm 2.8 \times 10^{-3}$ s^{-1} and $3.7 \pm 2.5 \times 10^{-3}$ s^{-1} on average for daytime and nighttime, respectively. The daytime distribution of $k(NO_3)$ differed from that at the mountaintop of Tai Mo Shan in Hong Kong (Brown et al., 2016). During the nighttime, anthropogenic VOC-$k(NO_3)$ tripled the biogenic VOC-$k(NO_3)$ and was dominated by cresol (26.4%). The nighttime $k(NO_3)$ corresponded to a NO_3 lifetime of 4.5 min, which was about 10 times the lifetime derived from steady-state analysis, indicating that the reaction of NO_3 with VOC was not significant enough. The faster NO_3 loss rate also indicated the less aged air mass that was influenced by surface-level emissions.



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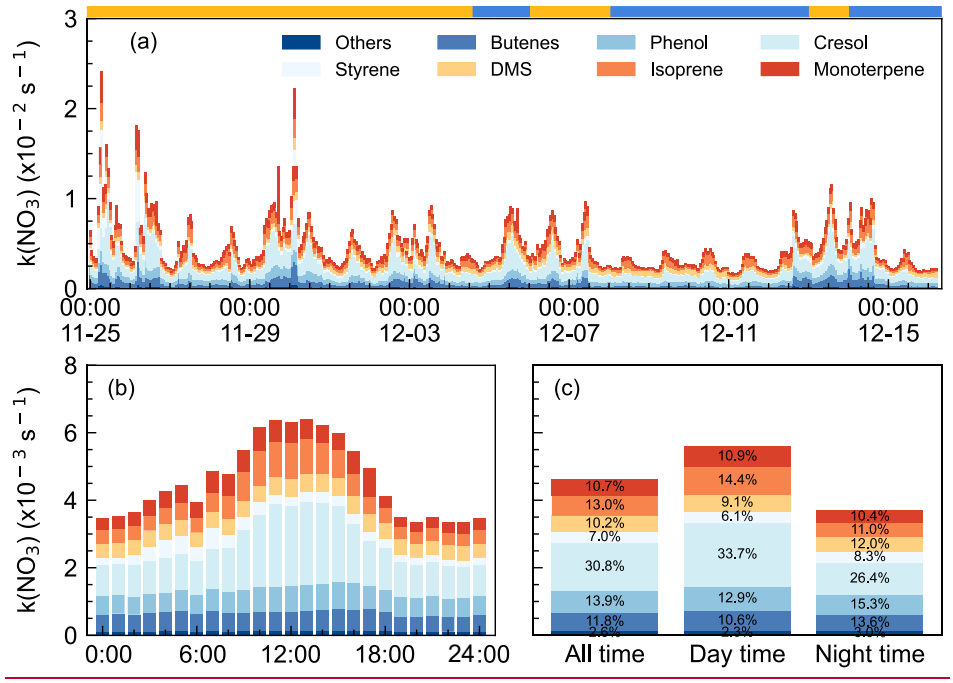

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462 **Figure 5.** NO_3 reactivity via VOCs during the campaign. (a) $k(NO_3)$ time series from Nov.
463 25th to Dec. 15th; (b) mean diurnal profiles; and (c) the relative contribution in different
464 categories. The ribbon at the top separates the air masses into two air masses types, yellow

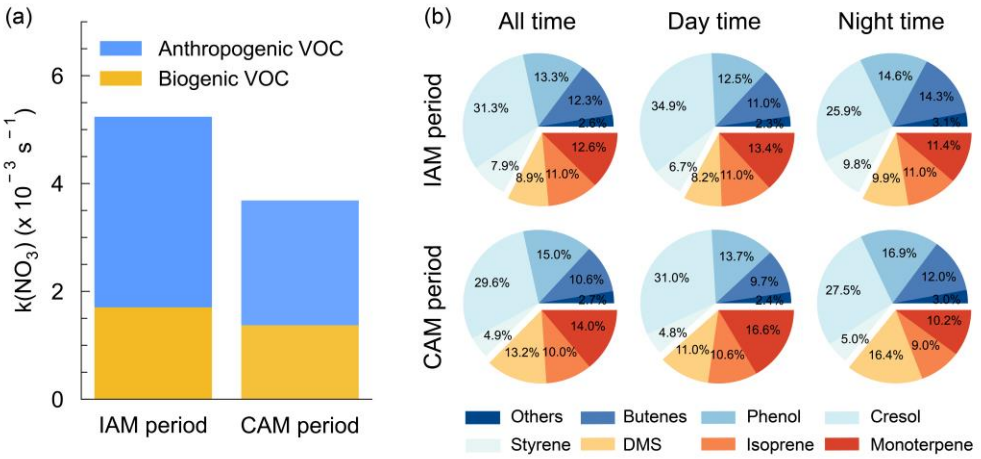
for IAM and blue for CAM.

We showed that NO_3 reactivity and its composition in this study exhibited significant differences compared to other urban or forested regions (Wang et al., 2017d; Ayres et al., 2015; Brown et al., 2016; Lin et al., 2022). Although anthropogenic VOCs played a dominant role, accounting for 66.1%, the major contributors were not low-carbon alkenes but phenol (13.9%, 0.64 ± 0.28 $\times10^{-3}$ s^{-1}) and cresol~~,~~ (30.8%, 1.4 ± 1.0 $\times10^{-3}$ s^{-1}), which have received little attention in previous studies. Despite their relatively low concentrations, averaging 7 ± 3 pptv and 4 ± 3 pptv respectively, their substantial contribution to $k(NO_3)$ is notable due to their fast rate constants (3.8×10^{-12} cm^3 $molecule^{-1}$ s^{-2} and 1.4×10^{-11} cm^3 $molecule^{-1}$ s^{-2} at 298 K, respectively) for reaction with NO_3. ~~These substances are mainly secondary species from aromatic compounds and significantly higher concentrations have also been observed in urban areas (Delhomme et al., 2010; Zhu et al., 2005; Belloli et al., 1999).~~Considering that the measured phenol and cresol concentration is low and near the instrumental detection limit, we note this may bring some uncertainties in quantifying the contribution to the total NO_3 reactivity and NO_3 loss rate. These substances are mainly secondary species from aromatic compounds and higher concentrations have also been observed, such as in the Strasbourg area, France (14 pptv, Delhomme et al., 2010) and in Great Dun Fell, UK (16 pptv, Lüttke et al., 1997). Hence, these phenolic compounds were potentially important but often overlooked for their contributions to NO_3 reactivity in urban areas, and their reactions with NO_3 may also contribute to the formation of nitrophenol. These reactions warrant further attention in future research. Regarding biogenic VOCs, besides the contributors commonly observed in forest regions such as monoterpenes and isoprene, the marine emissions indicator, dimethyl sulfide (DMS), contributed 10.2% to NO_3 reactivity (daily average). Previous studies have suggested that DMS may serve as a major direct sink for NO_3 in clean marine regions (Allan et al., 1999; Aldener et al., 2006; Brown et al., 2007). However, this study reveals that anthropogenic VOC emissions significantly enhanced the NO_3 reactivity in marine areas, highlighting the crucial influence of anthropogenic activities on marine atmospheric chemistry.

As shown in Fig. 6a, $k(NO_3)$ differed significantly between the inland and coastal air masses, with 5.2 ± 3.1$\times10^{-3}$ s^{-1} and 3.7 ± 1.9$\times10^{-3}$ s^{-1} on average in IAM and CAM periods, respectively. Of which anthropogenic VOC-$k(NO_3)$ in IAM (3.5 ± 2.3$\times10^{-3}$ s^{-1}) was higher than in CAM (2.3 ± 1.4$\times10^{-3}$ s^{-1}) and dominant in both air masses, while biogenic VOC-$k(NO_3)$ was comparable~~.~~ (1.7 ± 0.9 $\times10^{-3}$ s^{-1} and 1.4 ± 0.6$\times10^{-3}$ s^{-1} for IAM and CAM, respectively). The difference indicated that this region was affected by long-range transport emissions to a certain extent. The pie charts in Fig. 6b showed different VOC categories that contributed to $k(NO_3)$ in two periods with AVOC dominant at any time. The change in the relative contribution of various VOCs to $k(NO_3)$ varied simultaneously throughout the

day, ~~reflecting as~~showing an increase in butene, phenol, and DMS~~ increased, while~~, and a decrease in cresol and monoterpene~~ decreased~~ from daytime to nighttime.

N_2O_5 heterogeneous uptake on aerosol is one of the vital loss processes of NO_3 and the uptake coefficient varied greatly under different environmental conditions. For instance, $\gamma(N_2O_5)$ can reach up to 0.072 in polluted urban regions (Wang et al., 2017b; Wang et al., 2018b; Lu et al., 2022; Li et al., 2020), while usually below 0.03 in coastal areas (Brown et al., 2016; Morgan et al., 2015; Niu et al., 2022). N_2O_5 uptake coefficient can be gotten from the pseudo steady state method by assuming that N_2O_5 and NO_3 have achieved a steady state (Brown et al., 2009), in which the fitted slope represents $\gamma(N_2O_5)$ and the intercept represents the direct loss rate coefficient, $k(NO_3$~~).~~) (as shown in Eq. 8). However, this approach failed to generate valid results in our study since a negative slope or intercept was observed (Fig. ~~S3~~S4). These results indicated that a large NO_3 removal process existed at this site, making it unable to approach a stable state. ~~Based on relative humidity and temperature, we~~The $\gamma(N_2O_5)$ was also calculated ~~the uptake coefficient by Eq.6~~ from ~~November~~Nov. 9th to 16th by using the simplified parameterization, as shown in Eq. 9. The parameterized average $\gamma(N_2O_5)$ showed a large variation ranging from 0.0014 to 0.0299, with an average of 0.0095 ± 0.0059. This value is within the range from <0.0016 to 0.03 derived from the ambient observation around other coastal areas (Niu et al., 2022; Yun et al., 2018a; Brown et al., 2006; Brown et al., 2016; Morgan et al., 2015) and smaller than the polluted North China Plain (Wang et al., 2017c; Wang et al., 2017b; Wang et al., 2017d; Tham et al., 2018).



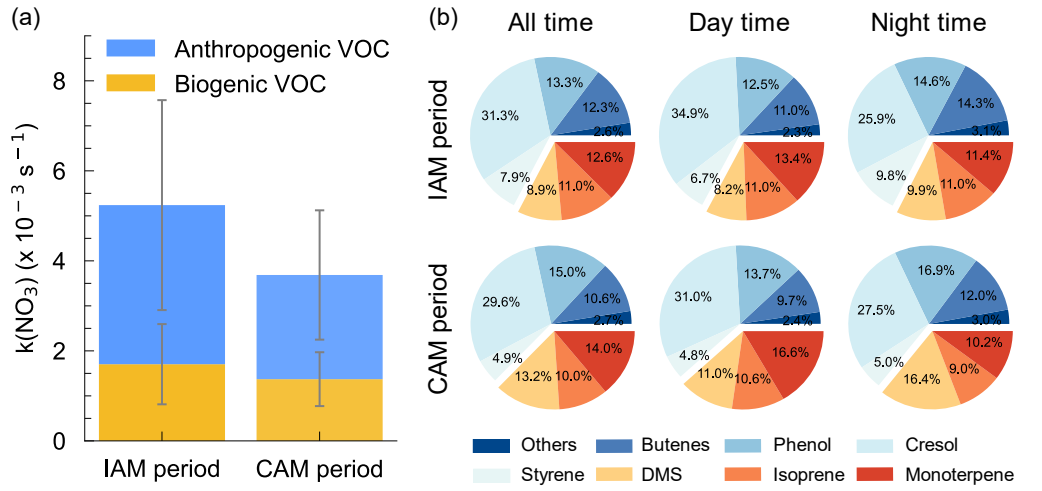


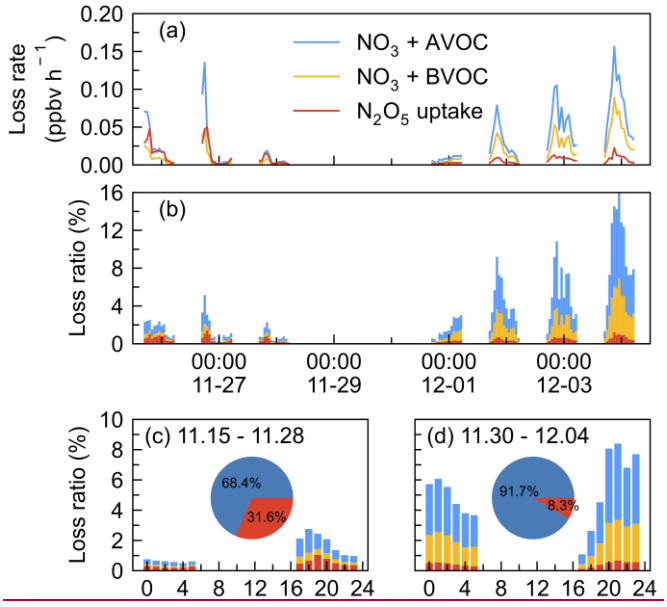
Figure 6. (a) Distributions of k(NO_3) ~~in continental~~from AVOC and ~~coastal air masses.~~BVOC for both IAM and CAM period. The error bar indicates the standard deviation. (b) The relative contribution of VOC categories to the k(NO_3).

3.4 The NO_3 loss budget

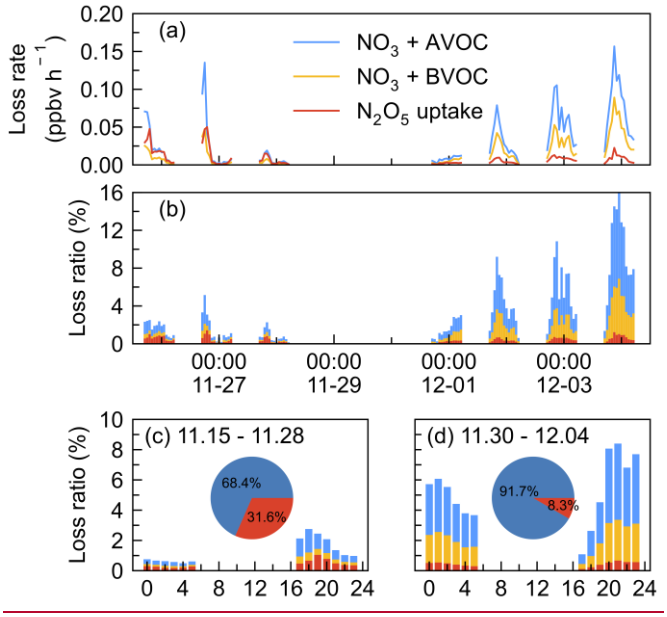
To assess the contribution of various loss processes to the total NO_3 removal, we calculated their loss rate and the loss ratio, *LR*(NO_3). ~~Considering~~The *LR*(NO_3) is defined as the ~~short lifetime~~sum of ~~NO_3~~the loss rate by process X (VOC or N_2O_5 uptake) to the total NO_3 loss rate, here the total NO_3 loss rate is represented by P(NO_3) ~~which characterizes the atmospheric oxidation capacity~~since we cannot quantify the total NO_3 loss rate due to the NO concentration below the limit of ~~NO_3 to its reactants~~instrument detection. Due to the data absence of measured VOCs or N_2O_5 during certain periods, the loss proportion of VOCs and N_2O_5 uptake in NO_3 loss only presented from Nov. 26th to Dec. 5th during which all air masses originated from continental China. As shown in Fig. 7, a closer examination revealed that the nights can be divided into two periods, period I: November 25th to 28th when the loss ratio of VOC and N_2O_5 uptake remained below 3%, and period II: November 30 to December 4 when the loss ratio was higher. Both periods had large nocturnal NO_3 production rates with an average of 2.1 ± 1.1 ppbv h^{-1} in period I and 1.4 ± 0.6 ppbv h^{-1} in period II, respectively.

N_2O_5 uptake rate was larger in period I (0.01 ± 0.01 ppbv h^{-1}) than that in period II (0.006 ± 0.004 ppbv h^{-1}), which can be explained by the increased RH, Sa, and N_2O_5 concentration as shown in Fig. 2. The loss ratio of these processes was shown in Fig. 7b, the total NO_3 loss through reactions with VOCs and N_2O_5 uptake accounted for less than 20%, with an

average of 1.2% (period I) and 5.3% (period II), respectively. This result shows that the nighttime NO_3 chemistry may be almost negligible~~,~~ to the NO*x* removal compared with the ~~NO_x removal capacity during the~~ day $OH + NO_2$ pathway according to previous works reported in urban regions (Wang et al., 2017b; Wang et al., 2020a). The diurnal variation of the NO_3 loss fraction of both periods was shown in Fig. 7c and 7d, revealing that NO_3 loss via N_2O_5 uptake and VOCs was slightly higher in the early evening and relatively stable in the late evening. The pie charts in the center were the relative contribution between VOCs and N_2O_5 uptake, showing that VOCs were overwhelming compared with N_2O_5 uptake during the two periods, with an average of 68.4% and 91.7% during the first and second periods, respectively.



To better understand the nocturnal oxidation of VOCs, we compared the nighttime oxidation of VOCs by NO_3 with O_3. Since OH was not measured and OH is often regarded as a vital daytime oxidant (Finlayson-Pitts, 2000; Lu et al., 2010), we did not consider OH oxidation in the nighttime. Figure S4 showed the diurnal pattern of VOC loss rate by NO_3 and O_3, NO_3 predominantly achieves its peak oxidation rates (0.07 ppbv h^{-1}) during the initial half of the night, accounting for 63.1% of the total VOC oxidation on nocturnal average. Meanwhile, O_3 also makes a contribution to VOC oxidation, mainly owing to its relatively high nighttime concentration levels (42.9 ± 18.4 ppbv).



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567 **Figure 7.** Time series of (a) the loss rate of NO_3 reactions with AVOC, BVOC, and N_2O_5
568 uptake, and (b) fractional contribution to the NO_3 loss during the nighttime by taking
569 $P(NO_3)$ as the total NO_3 loss in the IAM period. The mean diurnal profiles of NO_3 loss
570 ratio in two periods (c) November 25th - 28th, and (d) November 30th - December 4th. Pie
571 charts in the center showed the relative contribution of VOCs (blue) and N_2O_5 uptake (red)
572 in NO_3 loss.

573 Due to the difficulty in experimental quantifying $\gamma(N_2O_5)$, the estimation of N_2O_5 uptake
574 in NO_3 loss may include some uncertainty. Considering the uncertainty both in
575 parameterized $\gamma(N_2O_5)$ and the NO_3 reactivity calculation, three sensitivity tests were
576 conducted to assess the uncertainty in period II because of the relatively high loss ratio in
577 the above analysis (Fig. 8), and the three cases were used to represent the upper limit of
578 their contribution to NO_3 loss. Case 1 represents the overrated contribution of N_2O_5 uptake
579 by taking $\gamma(N_2O_5) = 0.08$, which was the high value reported in high N_2O_5 and $ClNO_2$
580 plume of Shenzhen (Niu et al., 2022) and approximately seven times the parameterized
581 value at this site. In this case, the fraction of NO_3+VOCs and N_2O_5 uptake was significantly
582 elevated to account for approximately 30% of NO_3 loss. Case 2 shows the total NO_3
583 reactivity reached an average of 5.0×10^{-3} s^{-1} by taking β-pinene as the total monoterpene
584 because of the higher reaction rate constant. The weak change in the loss ratio indicates the
585 reactions of NO_3 with VOC may not be sensitive to the weights of monoterpenes, since the
586 contribution of monoterpenes to the NO_3 reactivity is not dominant. Case 3 is the synthesis
587 of Case 1 and Case 2 by considering higher N_2O_5 uptake coefficient and higher $k(NO_3)$ to
588 represent the upper limit of N_2O_5 uptake and NO_3 reaction with VOCs to NO_3 loss, whose

result is slightly higher than the contribution of Case 1. Nevertheless, the quantified upper contribution was still less than half. Thus, we conclude that most of the NO_3 loss was not well accounted for even considering the uncertainties.

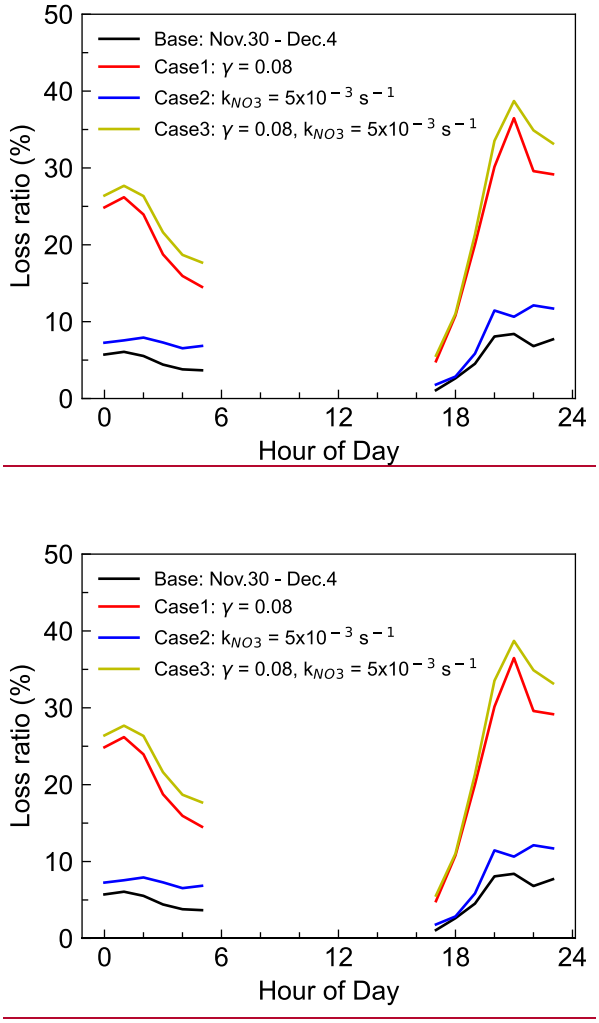

Figure 8. Three sensitivity tests for the contribution of VOCs and N_2O_5 uptake to the NO_3 loss during the nighttime of period II (November 30th - December 4th). Case 1 takes $\gamma(N_2O_5)$ = 0.08, which is the high value reported in the previous study. Case 2 takes β-pinene as the total monoterpene with a higher reaction rate constant, and Case 3 is the synthesis of the above two cases to represent the upper limit of the contribution.

The NO_3 reaction with NO was often considered to be one of the dominant loss processes during the daytime since at nighttime NO decreased to low levels, thus not considered in the above analysis. However, by taking NO into consideration although at low concentration levels below the detection limit of the instrument (0.4 ppbv), the contribution

of NO to the nighttime NO_3 loss exceeded 100% frequently as shown in Fig. ~~S4~~S5. Due to the rapid reaction between NO and NO_3, several pptv concentrations of NO could effectively account for most NO_3 loss in a relatively clean coastal environment (Crowley et al., 2011). Nevertheless, limited by NO precise measurement, we considered the following assessments to understand the total NO_3 loss processes (Fig. 9). By assuming NO at a constant value of 40-400 pptv, more than 80% of the total NO_3 loss can be well explained. Although some loss remained unidentified, these results underline that NO, often considered to be important during daytime, was the predominant NO_3 loss way during nighttime at this study site. This also suggests accurate measurement of low NO concentrations is crucial for identifying removal pathways of nocturnal NO_3 oxidants and has significant implications for nighttime atmospheric chemistry. We can infer that the nocturnal chemical NO_3 reactions would be largely enhanced once without NO emission in the open ocean after the air mass passes through this site, indicating the strong influences of the urban outflow to the ~~downward~~downwind marine areas with respect to nighttime chemistry.

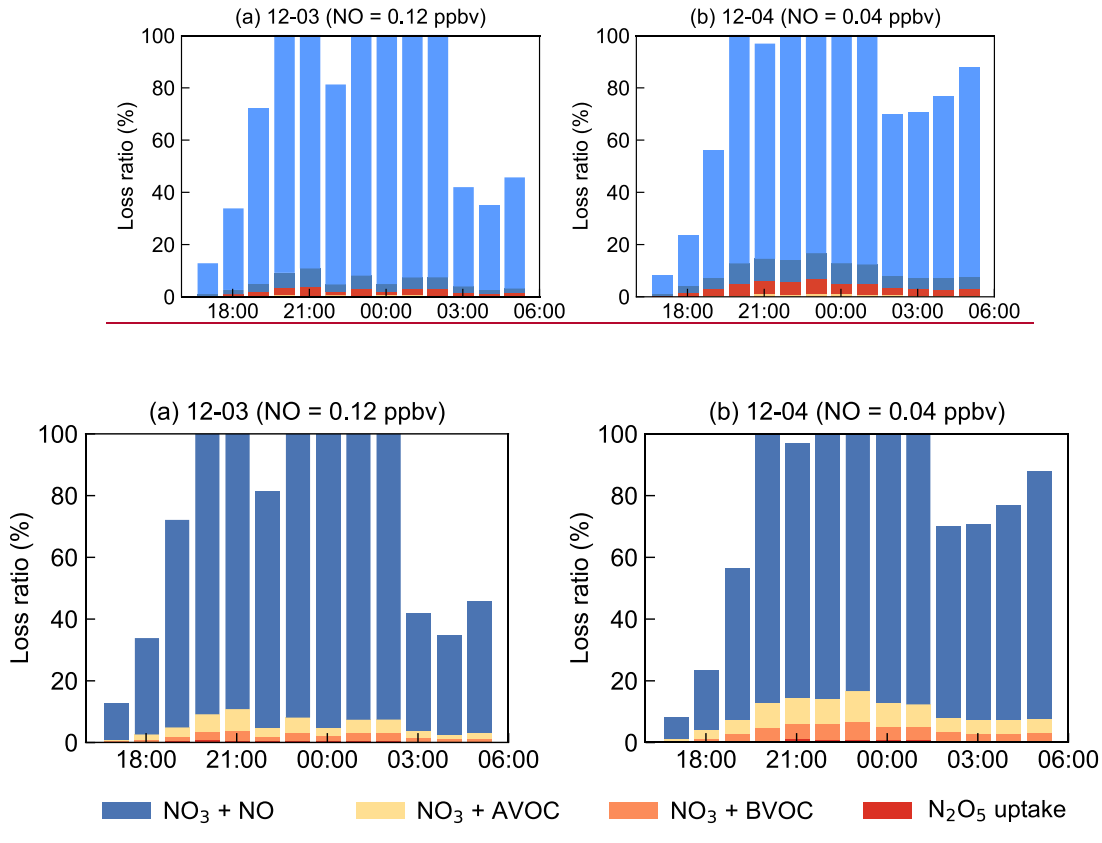

Figure 9. ~~Assessments~~Examples for the assessment of NO_3 loss process by assuming NO as constant values~~. Blue represents the contribution of NO and others are N_2O_5 uptake and~~

~~VOCs.~~ to approximately explain about 80% of the budget.

For the absence of measured N_2O_5 during the CAM period, we compared the k(NO_3) and the reactivity of N_2O_5 uptake ($k_{het}K_{eq}NO_2$) to indirectly reflect NO_3 removal process. Overall, the NO_3 reactivity values from VOCs and N_2O_5 uptake during nighttime was relatively comparable, for 56.5% and 43.5%, respectively. This indicates that VOCs still had a slightly larger contribution than N_2O_5 uptake during the CAM period, which is consistent with the findings in southern China (Brown et al., 2016) and on the east coast of the USA (Aldener et al., 2006).

4. Summary and Conclusion

This study presents the first observation of nocturnal nitrogen oxide species, N_2O_5, at a typical marine site (Da Wan Shan Island, Zhuhai) in the north of the South China Sea during the winter of 2021. Although Da Wan Shan Island was almost free of local anthropogenic emissions, the air pollutants from the megacities of the Pearl River Delta were transported to this area by northerly or northeasterly winds during the measurement period. The maximum ratio of N_2O_5 was 657.27 pptv (1 min average) and the nocturnal average was 119.5 ± 128.6 pptv. The NO_3 production rate was comparable to that in urban areas such as north China and the Yangtze River Delta, with an average value of 1.5 ± 0.9 ppbv h^{-1} and a maximum of up to 5.84 ppbv h^{-1}, indicating an active nighttime chemical process in that area.

Further analysis of N_2O_5 and NO_3 steady state lifetimes indicates that NO_3 had a very short average life of 0.5 ± 0.6 minutes, which was to some extent comparable to that in urban areas in summer. The combination of the high NO_3 production rate and short lifetime suggests a rapid NO_3 loss at night. While N_2O_5 uptake is inefficient in relatively clean air masses. The nighttime k(NO_3) corresponded to a NO_3 lifetime of 4.5 minutes, indicating that VOCs also contribute little to NO_3 loss. Both VOC and N_2O_5 uptake can only explain less than 20% of the total loss. The fast NO_3 loss rate also indicated the ~~less aged~~ air mass that was influenced by local surface-level emissions. We infer that the local weak NO emission may significantly change the near-surface chemical pattern of NO_3 chemistry, which may result in a huge difference between the observed results on the island and those on the sea surface. We suggested that future field measurements should be made on sea surfaces away from islands, such as ship-based cruise observation, to get a comprehensive understanding of the nocturnal NO_3 chemistry in the background marine regions.

Code/Data availability. The datasets used in this study are available at: https://doi.org/10.5281/zenodo.8089100 (Wang et al., 2023).

Author contributions. H.C.W. and Y. J.T. designed the study. J.W. and H.C.W. analyzed the data with input from H.J.H., Z.L.Z., G.Z.F., C.Z.S., Z.H.L., J.Z., S.J.F.. H.C.W., L.M. Y. J.T., Z.H.L., and J.Z. organized this field campaign and provided the field measurement dataset. J.W., H.C.W., and Y.J.T. wrote the paper. All authors commented on and edited the manuscript.

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Competing interests. The authors declare that they have no conflicts of interest.

Appendix A Supplementary data

Supplementary data associated with this article can be found in the online version at xxxxxx.

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