Observation and modelling of atmospheric OH and HO_2 radicals at a subtropical rural site and implications for secondary pollutants

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Abstract

HO_X radicals (OH and HO_2) are crucial oxidants that determine atmospheric oxidation capacity and the production of secondary pollutants; however, their sources and sinks remain incompletely understood in certain rural, forest and maritime environments. This study measured HO_2 and OH concentrations using a chemical ionisation mass spectrometer at a subtropical rural site in southern China from 12 November to 19 December 2022. The average peak concentrations were $3.50 \pm 2.47 \times 10^6$ cm^{-3} for OH and $1.34 \pm 0.93 \times 10^8$ cm^{-3} for HO_2. Calculations based on an observation-constrained chemical model revealed an overestimation of HO_2 and OH concentrations during warm periods of the field study. Sensitivity tests suggest that adding HO_x sinks or a HO_2 recycle process to the model could improve the model performance. The over-simulation of HO_x in the model resulted in overestimations of production rates of ozone by up to 98% for ozone and up to 341% for nitric acid. Our study highlights the need for further improving understanding of the sources/sinks of OH and HO_2 and representation of them in air quality models.

1. Introduction

The HO_X family, comprising hydroxyl (OH) and peroxy radicals (HO_2), plays a pivotal role in the Earth's atmosphere by driving photochemical processes that influence the air composition and chemistry. OH radicals are primarily produced by the photolysis of ozone (O_3), nitrous acid (HONO), and ozonolysis of alkenes. They initiate the oxidation of CO and most volatile organic compounds (VOCs), producing HO_2 and other peroxyl radicals (RO_2, where R represents an alkyl group). HO_2 is also generated from the photolysis of oxygenated VOCs (OVOCs) and by reactions between OVOCs and OH. In the presence of NO, RO_2 radicals are converted to HO_2 and then to OH radicals buffering OH concentrations and maintaining atmospheric oxidation capacity. (Stone et al., 2012). These interactions are crucial in the formation of photochemical smog and secondary organic aerosol (SOA), which generate NO_2, O_3 and highly oxygenated molecules. HO_X radicals are removed through reactions of OH with inorganic trace gases, self-reactions among radicals, peroxyacetyl nitrate (PAN) formation, and the heterogeneous uptake by aerosols, subsequently contributing to atmospheric acidification and aerosol formation by the production of H_2SO_4 and HNO_3. See Figure S1 and Table S1 for detailed processes and chemical reactions.

The accuracy of model-predicted OH is a crucial indicator for assessing our understanding of the atmosphere processes (Heard and Pilling, 2003). There is a longstanding debate regarding the discrepancies between simulated and observed radical concentrations under low NO_x condition which remains a significant issue (Hofzumahaus et al., 2009; Stone et al., 2012; Zou et al., 2023). Previous studies have shown that models generally predict OH levels well in polluted conditions (NO > 1 ppb), but notable overestimation were observed under low NO and aged conditions, such as coastal areas (Kanaya et al., 2007; Zou et al., 2023), marine boundary layers (Berresheim et al., 2002; Carslaw et al., 1999), and the rural area (Bottorff et al., 2023; Kanaya et al., 2012). Missing OH sinks from both measurement or chemical mechanism were proposed as the primary reason for the overestimation (Lou et al., 2010; Yang et al., 2016; Hansen et al., 2014 Thames et al., 2020). Underestimation of OH

concentrations were also observed in high biogenic VOCs (BVOCs) and low NO (<1 ppb) conditions which generally happen in the subtropical or tropical area (Hofzumahaus et al., 2009; Lelieveld et al., 2008; Tan et al., 2001; Whalley et al., 2011). After considering a new OH regeneration mechanism (Wennberg et al., 2018; Novelli et al., 2020) and a measurement interference (Feiner et al., 2016; Hens et al., 2014; Mao et al., 2012; Novelli et al., 2014; Woodward-Massey et al., 2020), daytime OH concentration could be reasonably reproduced by the model in the high BVOC conditions, with some unresolved underestimation in the evening (Jeong et al., 2022; Lew et al., 2020; Tan et al., 2019). Those results called for more measurement and modelling in the subtropical and tropical rural areas.

HO_2 concentrations were consistently underpredicted in the polluted urban sites (Ma et al., 2019; Yang et al., 2021; Ma et al., 2022) , with no clear trends in relatively clean regions. Some studies reported good agreement between measurement and model prediction (Feiner et al., 2016; Lew et al., 2020), whereas others indicated model overprediction (Bottorff et al., 2023; Griffith et al., 2013) and underprediction (Kim et al., 2013; Mallik et al., 2018 Tan et al., 2017; Whalley et al., 2010). These discrepancies may be attributed to several factors, including: measurement interference caused by RO_2 recycling in environments rich in BVOCs or aromatics (Fuchs et al., 2011), uncertainties associated with heterogeneous uptake in box models (Yang et al., 2022), and the outflow (or entrainment) of reservoir species like PAN (Griffith et al., 2013) (Whalley et al., 2010) . Despite these advances, it remains difficult to pin down the exact causes of the model-measurement discrepancies in some of the previous studies.

In the present study, we measured concentrations of OH and HO_2 using a quadrupole chemical ionization mass spectrometer (PolyU-CIMS) from November to December 2022 at a subtropical rural site of southern China. We test model's capability in reproducing the radical concentrations and elucidate factors contributing to discrepancy under varying temperature, VOCs, and NO_X conditions. The Methodology section describes the measurement site, the principle and the configuration of PolyU-CIMS, and the setup of chemical box model. The Results and Discussion section details

our findings, providing a comprehensive analysis of the radical concentrations and exploring the discrepancies between observed data and model predictions. By employing an observation-constrained box model, we analyzed the radical budgets and investigated potential causes for these discrepancies. The study concludes with a discussion of the implications of these findings.

2. Methodology

2.1 Measurement Site

The field campaign was conducted at the Conghua Liangkou Air Monitoring Station (23°44'47"N, 113°47'06"E, 200m, above sea level) from November 12 to December 19, 2022 (Figure 1). The site is located at the northern part of the Pearl River Delta (PRD), approximately 80 kilometers from the densely populated areas of the PRD and nestled within the Liuxi River National Forest Park (an evergreen broad-leaf forest). The site is situated just north of the G105 national highway and around 0.5 kilometer east from Liangkou town. Even though it is close to the road, the traffic was generally limited during the observation period due to the coronavirus disease pandemic (COVID 19). The site is subjected to the BVOCs emission, predominantly isoprene, from the surrounding forest when the daytime temperature is exceeding 20°C, and NO emissions from the nearby national highway, particularly during periods of low wind speeds. The measurements comprised trace gases including O_3, NO, NO_2, CO, HONO, VOCs, OVOCs, meteorological data such as relative humidity (RH), temperature, and photolysis frequencies of HONO, NO_2, O_3, H_2O_2, and HCHO. Details about the instruments are shown in Table S2.

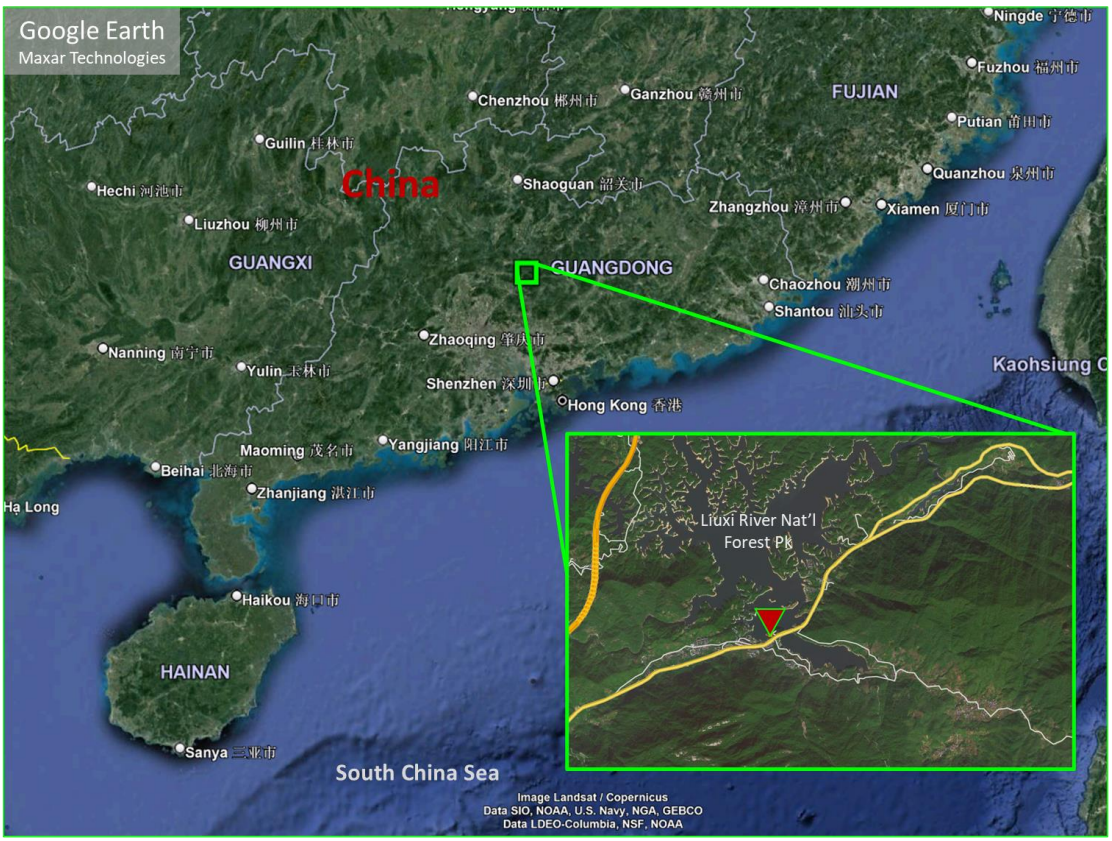

Figure 1 Geographic location of measurement site (Liangkou Air Monitoring station 23°44'47"N, 113°47'06"E, 200 m a.s.l. labelled by the red inverted triangle) in Conghua, Guangdong Province, South China. The map is sourced from © Google Earth and © Amap.

2.2 Radical measurement principle

OH and HO_2 radicals were measured using the Hong Kong Polytechnic University quadrupole Chemical Ionization Mass Spectrometer (PolyU-CIMS), which was used in a previous study for OH measurement (Zou et al., 2023). The use of CIMS for OH measurement was pioneered by Eisele and Tanner, (1991), with subsequent enhancements in measurement accuracy (Eisele and Tanner, 1993; Tanner et al., 1997; Tanner and Eisele, 1995) and adoption of inlets for simultaneous measurements of HO_2 and RO_2 (Edwards et al., 2003; Sjostedt et al., 2007), H_2SO_4 (Mauldin III et al., 2004), and OH reactivity (Muller et al., 2018).

Figure 2 illustrates the measurement principle of the PolyU-CIMS used in this campaign. Briefly, the ambient OH radicals are converted to H_2SO_4 in the sample inlet system by reacting with SO_2 (R21 in the reaction Table S1) which is then transformed to HSO_4^- ion clusters in the ionization chamber by the reactions with a reagent gas in

sheath flow (HNO_3, R24 to 27), and ultimately dissociated (R29) for detection by the mass spectrometer system at m/z 97 (S_{97SO2} in Figure 2). To mitigate interference and noise, scavenger gases (C_3F_6 in this study) were introduced to scavenge the ambient OH, creating a background signal (R23, $S_{97ScaSO2}$ in Figure 2). See details about the scavenge efficiency in Text S3 in SI. The ambient OH radicals signal (S_{OH}) is then determined by the subtracting $S_{97ScaSO2}$ from S_{97SO2}. The OH concentration is calculated using the following equation:

$$[OH] = \frac{1}{C_{OH}} \times \frac{S_{OH}}{S_{62}} \quad \text{(E1)}$$

Where C_{OH} represents the calibration factors of OH, and S_{62} is the signal corresponding to the reagent ion (NO_3^-). The detailed calibration procedure for OH is outlined in previous studies (Kürten et al., 2012; Zou et al., 2023) and also in Test S1.

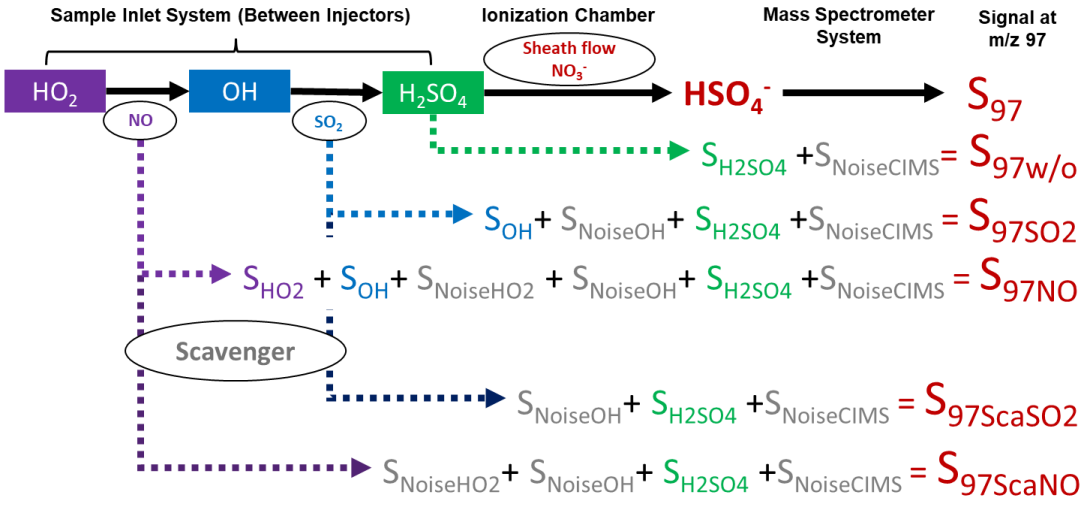

Figure 2 Flow chart depicting the relationship between measurement species and signal intensity at m/z 97 (S_{97}) with various gas injections. The color-filled grids labeled the ambient species, while oval shape labeled the species injected into the sample flow. Signal intensities with different gas additions to the sample flow are represented by $S_{97w/o}$, S_{97SO2}, S_{97NO}, $S_{97ScaSO2}$, and $S_{97ScaNO}$. The signals corresponding to ambient OH, HO_2, H_2SO_4 and noise from OH measurement, HO_2 measurement and the CIMS denoted as S_{OH}, S_{HO2}, S_{H2SO4}, $S_{NoiseOH}$, $S_{NoiseHO2}$ and $S_{NoiseCIMS}$, respectively.

To measure ambient HO_2, NO is injected into the sample flow, converting HO_2 to OH (R11). This converted OH then follows the same reaction pathway (R21, R24 to R27, and R29) and is measured at m/z 97 (S_{97NO} in Figure 2). Similar to the OH measurement, the background signal for HO_2 ($S_{97ScaNO}$ in Figure 2) is determined by

introducing the scavenger gas. The corresponding signal for ambient HO_2 (S_{HO2} in Figure 2) is determined by subtracting $S_{97ScaNO}$ and S_{OH} from S_{97NO}. The HO_2 concentration is calculated using a similar equation to E1, by replacing S_{OH}, and C_{OH} to S_{HO2} and C_{HO2}, respectively (E2).

$$[HO_2] = \frac{1}{C_{HO2}} \times \frac{S_{HO2}}{S_{62}} \quad \text{(E2)}$$

The procedure for determination of HO_2 calibration factor, C_{HO2}, is akin to that for C_{OH} (Text S1). The calibration tube generates equal amounts of radicals (R30 in SI, $[OH]/[HO_2] = 1$), allowing for simultaneous calibration of HO_2 and OH with and without NO addition to the sample flow.

Interference from RO_2 can affect HO_2 measurements, potentially resulting in an overestimation of ambient HO_2 levels (Edwards et al., 2003; Fuchs et al., 2014; Hanke et al., 2002). In our study, both the experimental and modelling results did not show significant interference under our environmental conditions (Text S4.3).

Compared to its configuration in the previous campaign (Zou et al., 2023), the PolyU-CIMS has been upgraded for simultaneous HO_2 measurements. See Figure S2, Text S2 on modification for HO_2 measurement; and Text S5 for measurement duty cycle. Apart from the modifications, the PolyU-CIMS's setting, and configurations remained the same as those in the previous campaign (Table S3). With the updated configuration, the PolyU-CIMS achieved the simultaneous measurement for the three gases.

The calibration factor, detection limit and accuracy were 1.09×10^{-8} cm^{-3}, 3×10^5 cm^{-3}, and 44% for OH; 6.01×10^{-9} cm^{-3}, 2×10^6 cm^{-3}, and 46% for HO_2; and 1.09×10^{-8} cm^{-3}, 1×10^5 cm^{-3}, and 40% for H_2SO_4, respectively (Table S3).

2.3 Box Model

HO_X concentrations in this study were simulated using the Framework for 0-D Atmospheric Modelling (F0AM, Wolfe et al., 2016) with the Master Chemical Mechanism (MCM) v3.3.1 (http://mcm.leeds.ac.uk/MCM), which encompasses over 6700 species and 17000 reactions. MCM v3.3.1 features a near-explicit chemical mechanism, including isoprene degradation and OH regeneration mechanisms. This

mechanism has been previously employed for investigating HO_X chemistry and conducting budget analyses (Slater et al., 2020; Tan et al., 2018; Zou et al., 2023). The gas-phase chlorine chemistry described by Xu et al., (2015) and Wang et al. (2019) were included in the model (Chen et al., 2022).

In the baseline scenario, the observation data were aggregated into one-hour intervals to provide input for the model, initially constraining it without incorporating observed OH and HO_2 data. For the assessment of ozone formation rates, the model was adjusted to include constraints based on the actual measured concentrations of OH and HO_2. Observed VOCs were categorized into anthropogenic origin (AVOCs), including species from petroleum gas and industrial solvent evaporation (alkenes, alkenes, benzene, and TEXs - toluene, ethylbenzene, and xylenes), and OVOCs comprising aldehydes, ketones, and acids. The sole BVOCs measured in this study was isoprene. Methacrolein (MACR), a derivative of isoprene, is distinctively classified among the biogenically sourced OVOCs for further discussion. Physical processes like deposition and entrainment in the model were represented by a first-order physical loss with a 24-hour lifetime for all species (Chen et al., 2022; Wolfe et al., 2016; Zou et al., 2023). The model also included the heterogeneous uptake of HO_2 by aerosols, represented as a pseudo-first order loss (Jacob, 2000):

$$\frac{d[HO_2]}{dt} = -k_{HO_2}[HO_2] \quad \text{(E3)}$$

$$k_{HO_2} = \frac{V_{HO_2} \times S_a \times \gamma_{HO_2}}{4} \quad \text{(E4)}$$

$$v_{HO_2} = \sqrt{\frac{8RT}{\pi \times M_{HO_2}}} \quad \text{(E5)}$$

Here, k_{HO_2} represents the first-order loss rate coefficient of HO_2 by aerosol uptake, determined by the effective HO_2 uptake coefficient γ_{HO2} (0.1, Guo et al., 2019), the mean molecular velocity of HO_2 (v_{HO_2}), the aerosol surface area concentration (S_a) measured by the Scanning Mobility Particle Sizing (SMPS); and the molecular mass of HO_2 (M_{HO_2}= 17 g/mol). As aerosol and aqueous phase chemistry were not included in the model, it was assumed that the heterogeneous HO_2 loss would not lead to further reactions (Guo et al., 2019). For each day, a three-day spin-up was performed with

constant inputs to establish stable model chemistry and reduce the uncertainty of unconstrained species. See Text S6 for model set up for interferences assessment.

3. Results and Discussion

3.1 Results from Observations

3.1.1 Overview

Figure 3 illustrates a time series showing observed concentrations of radical and trace gases, along with meteorological parameters, from 12 November to 19 December 2022. In November, the conditions were characterised by warm temperatures ranging from 29°C to 19°C and high relative humidity averaging 86%. In contrast, December witnessed a significant decrease in temperature (ranging from 20°C to 9°C) and a reduction in relative humidity (averaging 72%). Wind speeds during the campaign were generally low, averaging 0.9 ± 0.6 m/s and typically remaining below 3.0 m/s, with higher speeds occurring towards the end of December. In November, daytime winds predominantly blew from the south, while nighttime winds came from the north. In December, northerly winds predominated both day and night. Detailed hourly wind speed and direction data are illustrated in Figure 3, and wind roses are shown in Figure S3. On days with low wind speeds (< 0.5 m/s), NO_X emissions from the G105 national highway significantly influenced chemical measurements at the monitoring site, causing morning NO levels to peak at several parts per billion (ppb). Isoprene concentrations peaked in the afternoons, ranging from 0.2 to 1.7 ppb in November and dropping to < 0.1 ppb in December. Other trace gases and particulate matter levels were higher in November than in December.

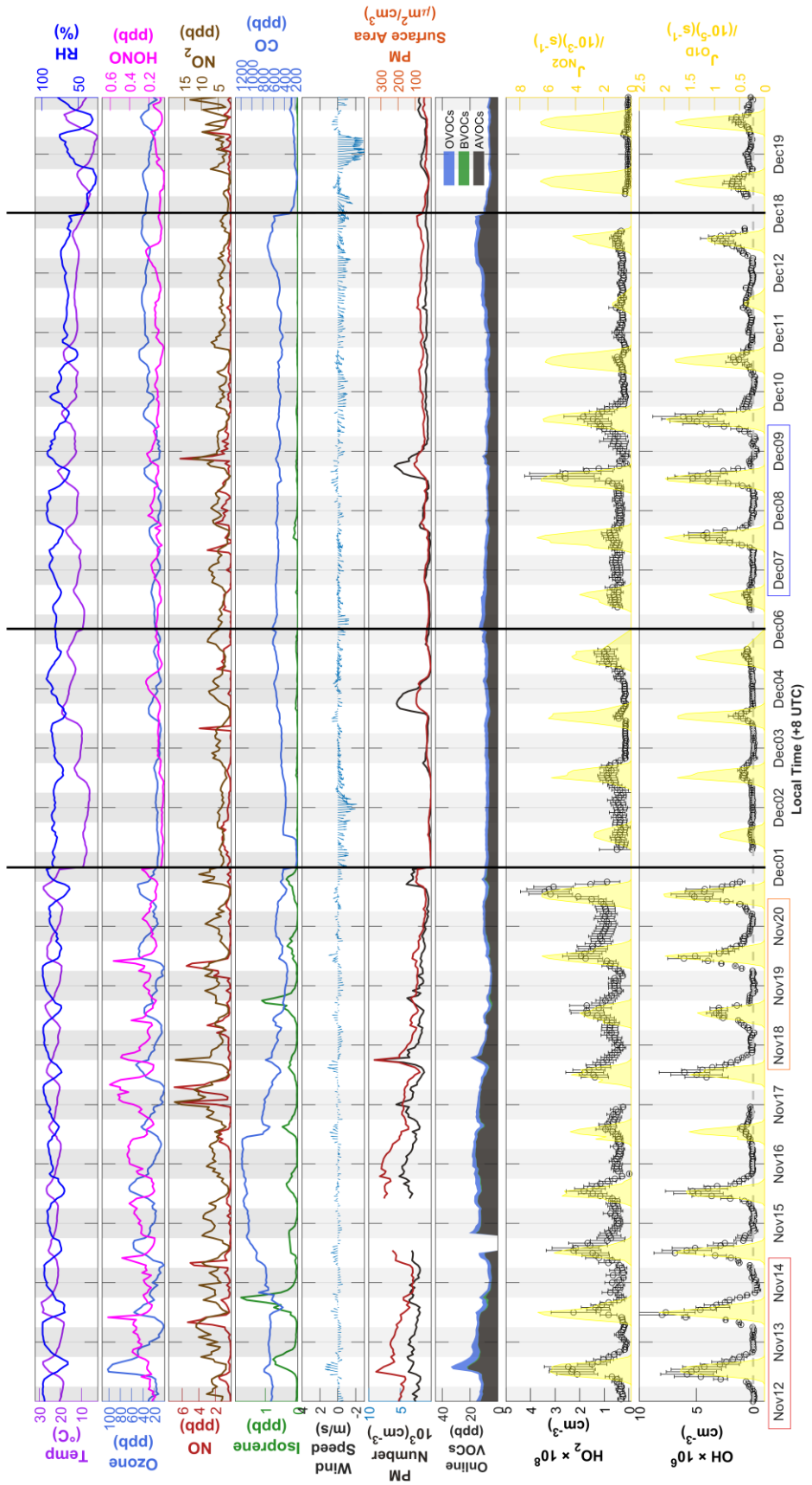
OH × 10^6 (cm^-3)
HO2 × 10^8 (cm^-3)
Online VOCs (ppb)
PM Number 10^3(cm^-3)
Wind Speed (m/s)
Isoprene (ppb)
NO (ppb)
Ozone (ppb)
Temp (°C)
J_O1D /(10^-5)(s^-1)
J_NO2 /(10^-3)(s^-1)
PM Surface Area (μm^2/cm^3)
CO (ppb)
NO2 (ppb)
HONO (ppb)
RH (%)
OVOCs
BVOCs
AVOCs
Nov12 Nov13 Nov14 Nov15 Nov16 Nov17 Nov18 Nov19 Nov20 Dec01 Dec02 Dec03 Dec04 Dec06 Dec07 Dec08 Dec09 Dec10 Dec11 Dec12 Dec18 Dec19
Local Time (+8 UTC)

Figure 3 Time series of HO_2 and OH radicals between 12 November and 19 December, including measured weather conditions (temperature, RH, wind speed, and wind direction), primary sources of HO_X radicals (ozone, HONO), important sinks of the radicals (CO, isoprene, and VOCs), and photolysis frequencies of NO_2 (J_{NO2}) and ozone (J_{O1D}). Non-continuous days during the campaign are delineated by a black line. The PRD, CEC, and CNC periods for further analysis were labelled in red, orange, and blue. The x-axis is in local time (+8 UTC).

Throughout the campaign, the daytime concentrations of OH and HO_2 consistently exceeded detection limits and showed distinct diurnal patterns. The OH concentrations typically peaked around midday, while the HO_2 levels reached their maximum approximately one to two hours later (Figure S4). The daily maximum concentration of OH varied significantly, ranging from 8.00×10^6 cm^{-3} to nearly the detection limit of 2.54×10^5 cm^{-3}, with an average of $3.50 \pm 2.47 \times 10^6$ cm^{-3} (Table 1). Similarly, the daily maximum concentration of HO_2 varied from 3.42×10^8 cm^{-3} to 2.17×10^7 cm^{-3}, averaging $1.34 \pm 0.93 \times 10^8$ cm^{-3} (Table 1). At nighttime, while the HO_2 levels generally remained above the detection threshold, the OH concentrations frequently approached the threshold. The average nighttime concentrations were 3.92×10^7 cm^{-3} for HO_2 and 1.64×10^5 cm^{-3} for OH. We compared the observed OH and HO_2 concentrations with those reported in previous studies conducted in urban, suburban, rural forest, and coastal sites. As illustrated in Figure S5, the OH concentrations were generally lower than those found in urban settings but similar to levels observed in suburban, rural, and forest environments. This suggests a moderate level of anthropogenic activity typical of mixed rural settings. In contrast, the HO_2 concentrations during these periods were significantly lower than earlier observations in rural and forest environments, likely owing to reduced photochemical activity during our measurement period.

Table 1 Average concentrations and standard deviation of measured species throughout the entire campaign (Total) and the selected 3 days cases from each cluster (PRD, CEC and CNC).

Species (Unit)	Total	PRD	CEC	CNC
AveMax OH_{Obs} 10^6 (cm^{-3})	3.5±2.5	6.9±1.1	4.9±1.5	5.3±0.9
OH_{Obs} 10^6 (cm^{-3})	0.9±1.5	1.6±2.2	1.4±1.6	1.2±1.8
OH_{DL} 10^6 (cm^{-3})	0.5±0.3	0.4±0.3	0.4±0.2	0.9±0.6
AveMax $HO_{2\,Obs}$ 10^8 (cm^{-3})	1.34±0.93	2.32±1.25	2.36±0.92	1.82±1.02
$HO_{2\,Obs}$ 10^8 (cm^{-3})	0.59±0.51	0.76±0.63	1.10±0.68	0.67±0.55
$HO_{2\,DL}$ 10^8 (cm^{-3})	0.19±0.11	0.17±0.10	0.25±0.08	0.26±0.15
Pressure (hpa)	995±4	992±1	992±1	995±2
Temp (°C)	16±6.1	23±3.0	23±2.6	14±2.8
RH (%)	78±15	87±11	86±10	81±9.4
Wind Speed (m/s)	0.91±0.65	0.53±0.32	0.57±0.34	0.87±0.5
j_{O1D} 10^{-6}(s^{-1})	3.2±5.4	3.5±6	3.6±5.9	4.0±6.6
j_{NO2} 10^{-3} (s^{-1})	1.3±1.9	1.3±2.1	1.4±2	1.6±2.3
HONO	0.169±0.104	0.249±0.084	0.201±0.070	0.133±0.033
SO_2	0.5±0.8	0.5±0.6	0.4±0.5	0.4±0.5
NO_2	4.89±2.37	6.25±2.47	4.84±2.23	4.52±1.97
NO	0.57±0.86	0.73±1.09	0.69±1.00	0.73±0.85
CO	557.36±225.92	739.41±153.84	464.73±74.34	513.36±22.02
Ozone	25±14	32±23	24±13	19±9.4
Particle Surface Area (um^2/cm^3)	86±72	186±51	84±28	48±19
Isoprene	0.082±0.174	0.257±0.337	0.155±0.200	0.029±0.030
*OVOCs	2.218±1.056	3.163±2.324	1.755±0.379	1.730±0.330
*AVOCs	8.346±3.223	9.662±5.031	6.886±1.755	6.801±0.864
*TEXs	0.356±0.316	0.801±0.616	0.266±0.090	0.237±0.085

Notes: Concentrations are expressed in parts per billion (ppb) unless otherwise specified. Total VOCs concentrations are categorized by origin (AVOCs, BVOCs, and OVOCs). For the average concentration of each measured VOCs, refer to Table S5.

Figure 4 illustrates the results of the 24-hour backward trajectory analysis, revealing three distinct but sequentially occurring phases. In the initial phase (Figure 4a), air masses originated from the urban and industrial zones of the Pearl River Delta (PRD). This phase was characterised by intense photochemical activity, with ambient temperatures exceeding 20°C and relative humidity levels surpassing 70%. During this period, notably high concentrations of VOCs, ozone, and radicals were observed, with the average daily maximum concentrations of OH and HO_2 radicals reaching 6.50 ± 1.19 × 10^6 cm^{-3} and 2.20 ± 0.27 × 10^8 cm^{-3}, respectively. The subsequent phase was characterised by air masses originating from Central East China (CEC, Figure 4b). This phase showed reduced photochemical reactivity and lower concentrations of the measured trace gases. The average daily maximum concentrations of OH and HO_2 during this phase were 4.35 ± 2.19 × 10^6 cm^{-3} and 1.96 ± 0.90 × 10^8 cm^{-3}, respectively. The final phase was influenced by air masses from Central North China (CNC, Figure

4c), which exhibited the lowest concentrations of trace gases and the least pronounced average daily maximum concentrations in OH and HO_2 concentrations, measured at $2.23 \pm 1.95 \times 10^6$ cm^{-3} and $7.63 \pm 7.66 \times 10^7$ cm^{-3}, respectively. This phase coincided with an increase in cloudy days and a decrease in temperatures, indicating reduced photochemical conditions.

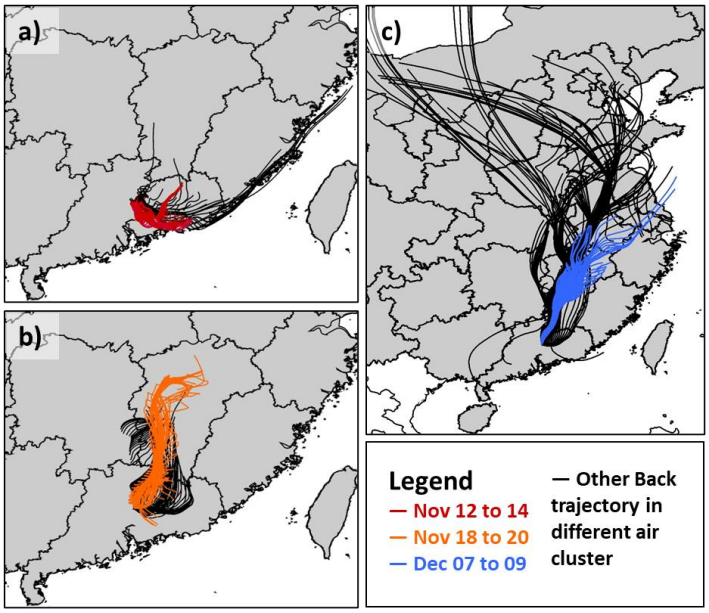

Figure 4 24-hour back trajectories for (a) Pearl River Delta (5 days), (b) Central East China (4 days), and (c) Central North China (14 days) cases. Three days selected from each cluster for model simulation are distinguished by different colours.

3.1.2 Selection of Cases

For each phase, a representative three-day period was selected for detailed analysis based on the availability of comprehensive data and sunny conditions (colored trajectories in Figure 4). In the subsequent analysis, 'PRD,' 'CEC,' and 'CNC' refer to the selected periods corresponding to the air masses originating from these regions. The average daily maximum concentrations of OH and HO_2 radicals for these periods are presented in Table 1. The average daily max OH concentrations were $6.89 \pm 1.10 \times 10^6$ cm^{-3} in PRD, $4.90 \pm 1.47 \times 10^6$ cm^{-3} in CEC, and $5.27 \pm 0.89 \times 10^6$ cm^{-3} in CNC, with a pronounce decrease from PRD to CEC (of 1.99×10^6 cm^{-3}). The average daily max HO_2 concentrations were $2.32 \pm 1.25 \times 10^8$ cm^{-3} in PRD, $2.36 \pm 0.92 \times 10^8$ cm^{-3} in CEC, and $1.82 \pm 1.02 \times 10^8$ cm^{-3} in CNC, with a slight increase of 0.04×10^8 cm^{-3} from PRD

to CEC and a more substantial drop of 0.54 × 10^8 cm^{-3} from CEC to CNC. These trends suggest a declining atmospheric oxidation capacity from PRD to CNC.

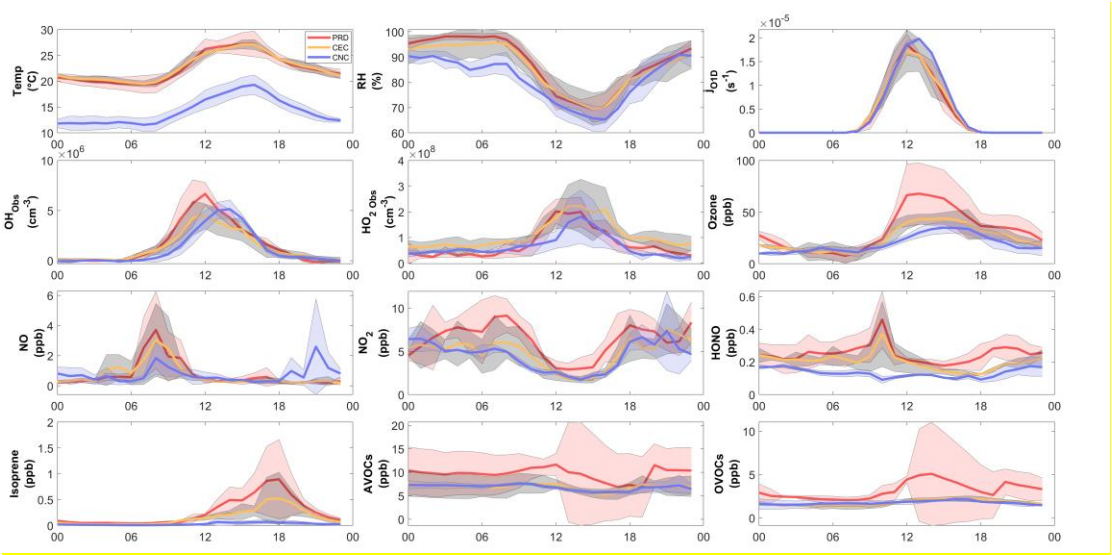

Figure 5 Average diurnal variations of (a) Temperature (b) Relative Humidity (c) J_{O1D} (d) OH (e)HO_2 (f) Ozone (g) NO (h) NO_2 (i)HONO (j)Isoprene (k) AVOCs (l) OVOCs. The solid-colored lines represent selected cases: orange for PRD, green for CEC, and blue for CNC. The light band represents the standard deviations of the mean. The increase in the standard deviations of VOCs and OVOCs during the PRD case is a result of absence of data on the afternoon of November 14th and large variations in on November 12th and 13th.

The precursor concentrations and meteorological parameters also varied across cases in terms of statistics (Tables 1 and S4) and diurnal variations (Figure 5). In the PRD case, the average concentrations are characteristic of a rural environment, with AVOCs at 9.70±5.00 ppb, OVOCs at 3.20±2.30 ppb, isoprene at 0.26±0.34 ppb, NO_2 at 6.3±2.5 ppb, and NO at 0.73±1.09 ppb. The NO concentration was affected by traffic sources as no other fresh emission source nearby and the NO diurnal variation show a morning peak in all three cases (Figure 5). In the CEC case, a general reduction in anthropogenic influence is evident. AVOCs, OVOCs isoprene and NO_2 drop significantly to 6.90±1.80 ppb, 1.70±0.38 ppb, 0.16±0.20 and 4.84±2.23 ppb respectively. Meanwhile, and NO remain close to PRD levels at 0.69±1.00 ppb. In the CNC case, the air mass is more aged with reduced biogenic emissions, reflected in further decreases in isoprene and NO_2 to 0.03±0.04 ppb and 4.52±1.97 ppb, respectively, due to colder weather conditions. The temperature decreased significantly from PRD

to CNC, whereas the average peak photolysis frequency was comparable between PRD and CNC, as shown in Table 1.

3.2 Chemical budgets of OH and HO_2

To investigate the OH and HO_2 chemical budgets during the three distinct periods, we employed a box model constrained by observed concentrations of NO_X, VOCs, and relevant meteorological parameters in the selected cases (base scenario which OH and HO_2 concentrations were not constrained by observation here). The resulting OH and HO_2 budgets, displaying typical bell-shaped patterns, are illustrated in Figure 6. During midday (10:00–15:00), the main source of HO_2 was the recycling of RO species, with rates of 3.22 ppb h^{-1} for PRD, 2.09 ppb h^{-1} for CEC, and 1.08 ppb h^{-1} for CNC. Additionally, HCHO photolysis contributed 0.75 ppb h^{-1}, 0.46 ppb h^{-1}, and 0.26 ppb h^{-1} for PRD, CEC, and CNC, respectively. The sinks of HO_2 varied among the cases with minor contribution from the uptake process, driven by radical termination mechanisms. The rate of radical self-reactions decreased from PRD to CNC. In contrast, NO_X-radical reactions between CEC and CNC were comparable, with respective rates of 0.39 ppb h^{-1}, and 0.33 ppb h^{-1}, indicating a shift in radical termination mechanisms.

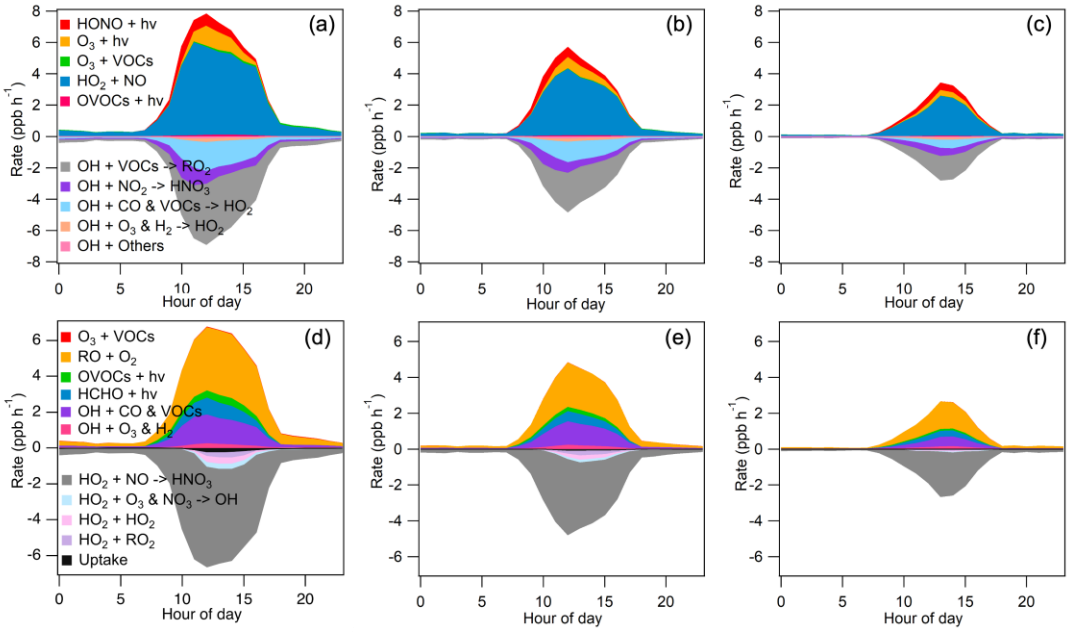

Figure 6 Chemical budgets of OH and HO_2 for PRD (a, d), CEC (b, e), and CNC (c, f) simulated using a chemical box model.

OH formation was predominantly driven by the HO_2 + NO reaction, contributing 5.18 ppb h^{-1}, 3.51 ppb h^{-1}, and 1.81 ppb h^{-1} (average for 10:00 – 15:00, hereafter in this section) for PRD, CEC, and CNC, respectively. Additionally, contributions from ozone photolysis and HONO increased from PRD to CEC and then to CNC, with rates of 21.4%, 22.7%, and 24.6%, respectively. The primary sinks for OH included reactions with VOCs to produce RO_2, with rates of 3.31 ppb h^{-1}, 2.02 ppb h^{-1}, and 1.13 ppb h^{-1}, and reactions with CO and other VOCs to generate HO_2, contributing 1.55 ppb h^{-1}, 1.06 ppb h^{-1}, and 0.38 ppb h^{-1} for PRD, CEC, and CNC, respectively. These findings highlight the critical role of OH + VOC reactions in the chemical budget of OH.

3.3 Comparison of model with observation results

The modeled and observed concentrations of OH and HO_2 radicals were compared to evaluate the performance of the model. In the PRD case (Figure 7), which is the most polluted and warmest among the three cases, the OH concentration was only slightly overestimated, whereas the HO_2 concentration was substantially overpredicted by the model during the daytime. Similar result has been observed at another rural site (Kanaya et al., 2012). For the CEC case (Figure 8), the model moderately overestimated both radicals during the daytime but underestimated the nighttime HO_2 concentration, which is similar to the findings at a rural forest site (Bottorff et al., 2023). In the CNC case (Figure 9), the model results were generally within the measurement uncertainty, with some daytime overestimation of HO_x on December 7 (similar to the PRD case) and nighttime underestimation of HO_2 (similar to the CEC case). In the following section, we conduct sensitivity tests to explore the possible reasons for the model observation discrepancy in the PRD and CEC cases.

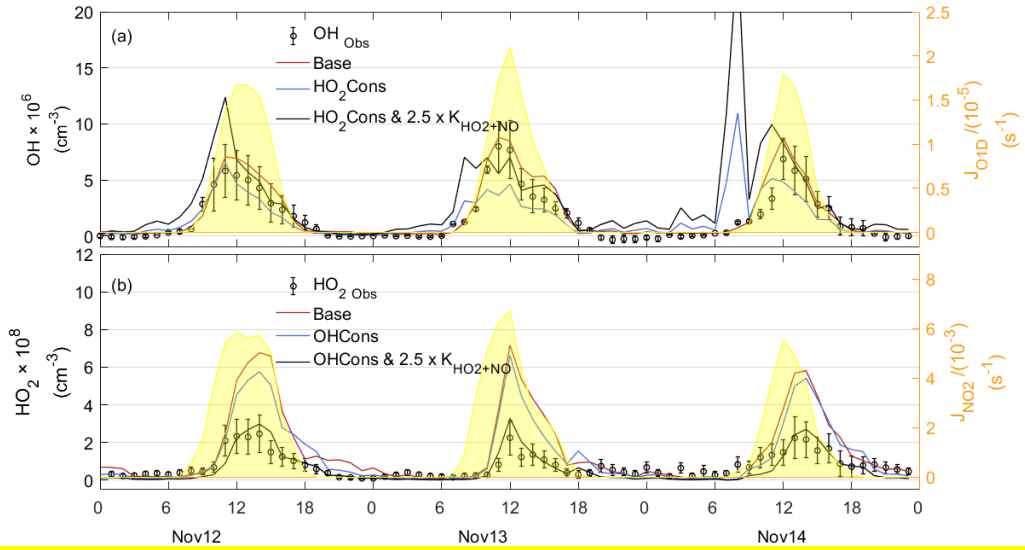

Figure 7 observed and simulated time series of OH and HO_2 for the PRD case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described in Box Model section. "Cons" denotes the results with additional constrained species compared to Base. "2.5 × K_{HO2+NO}" denotes the results with increasing the reaction rate coefficient of R11 by a factor of 2.5.

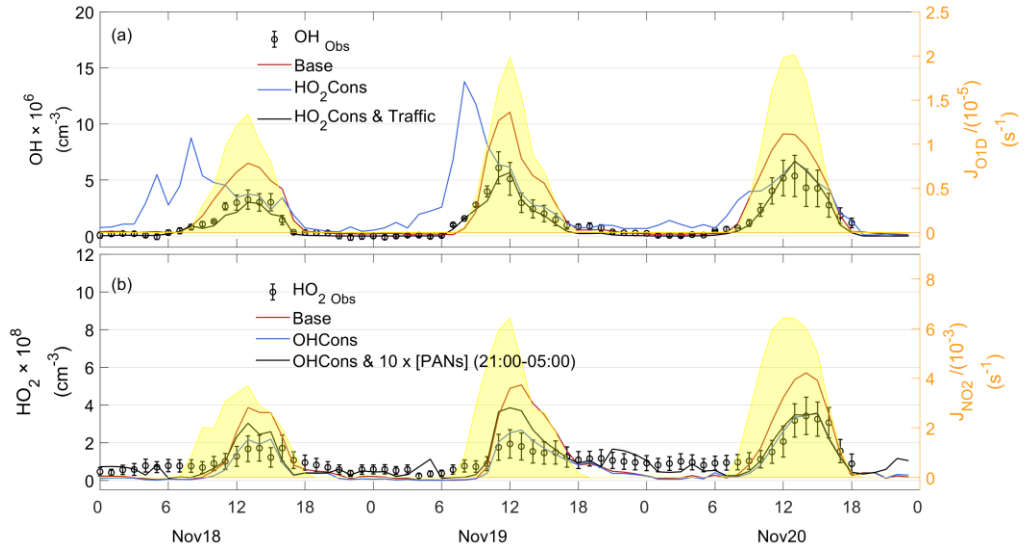

Figure 8 observed and simulated time series of OH and HO_2 for the CEC case. The "Obs" subscript denotes the observation data. "Base" denotes the result of Baseline scenario as described in Box Model section. "Cons" denotes the results with additional constrained species compared to Base. "Traffic" denotes the sensitivity test results with consideration of vehicular emission (see Test S7 in SI). "10 × [PANs] (21:00-05:00)" denotes the results with increasing nighttime secondary concentration of PAN by a factor of 10.

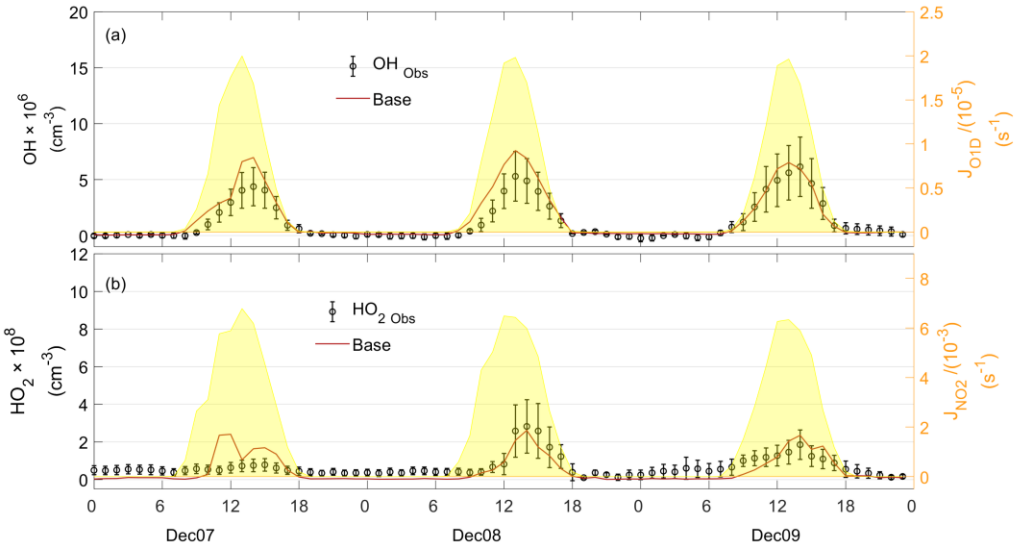

Figure 9 observed and simulated time series of OH and HO_2 for the CNC case. "Base" denotes the result of Baseline scenario as described in Box Model section.

3.3.1 Substantial overestimation of HO_2 in PRD case

To explain the HO_2 over-simulation by the base model, we constrain OH or HO_2 and compared to the base case (without constraining OH and HO_2). Result shows that constraining HO_2 causes the model to underestimate OH (blue line in Figure 7a), while constraining OH leads the model to still substantially overestimate HO_2 (blue line in Figure 7b). This result suggests that aligning the modeled OH and HO_2 with observations may require introducing a strong, unknown process for HO_2 that efficiently recycles OH with a high yield (Kanaya et al., 2012). A sensitivity analysis shows that increasing the reaction rate coefficient of $HO_2 + NO \rightarrow OH + NO_2$ (R11) by a factor of 2.5 would largely reduce both the HO_2 overestimation and the OH underestimation as shown by the black line in Figure 7. However, it is not clear what such OH cycling reaction is. Thus, the exact cause of the overestimation of HO_2 in the PRD case remain unresolved.

3.3.2 Moderate overestimation of both OH and HO_2 radicals in CEC case

Unlike the PRD case, constraining either OH or HO_2 in the CEC case generally reduces the daytime overestimation of both HO_2 and OH. These results indicate an additional sink for both OH and HO_2, as suggested by Bottorff et al. (2023). However, the OH concentration shows an overestimation in the morning when HO_2 was constrained, which may suggest missing OH reactivity in the morning. To further

investigate the underlying causes, we examined the correlations between various pollutants. The significant negative correlation between CO and NO (R^2=0.49, p=0.01, Figure S6b) suggests that CEC in the morning may have been influenced by emission from fresh complete combustion during the CEC case, whereas such correlations for PRD and CNC are not significant (Figure S6a and c). This indicates that the missing OH reactivity of CEC in the morning is possibly related to fresh vehicle emissions.

Diesel vehicle exhausts are rich in OVOCs relative to total VOCs (Yang et al., 2023). In our study, OVOCs were measured, except formaldehyde and acetaldehyde. We conducted a sensitivity analysis by adding these two OVOCs in the model (see Text S7 for details). After accounting for their influence, the overestimation of OH in the morning with constraining HO_2 could be significantly reduced (Figure 8a black line).

3.3.3 Nighttime underestimation of HO_2 in CEC case

Ozone and NO_3 reactions with alkenes can produce HO_2 at night (Walker et al., 2015). In our study, alkenes are unlikely to be the main cause for the underestimation because the major alkenes were measured, and the alkenes concentrations in the CEC case were much lower compared to the PRD case in which no underestimation of nighttime HO_2 was found. A previous study (Whalley et al., 2010) showed that nighttime HO_2 underestimation at a clean tropical Atlantic site was significantly reduced by constraining the model with higher PAN. In our study, PAN was not measured. The model simulated nighttime PAN mixing ratios (0.1-0.7 ppb) were lower than previous observed nighttime results in the coastal (up to 1 ppb) (Xu et al., 2015) and mountain site (up to 2 ppb) (Wang et al., 2023) in southern China. To assess the impact of PAN concentration on nighttime HO_2 levels, a sensitivity analysis was conducted in which the PAN concentration was increased. The results show that only when the PAN concentrations were increased by tenfold, the model simulated nighttime PAN level could match the observations (Figure 8b, black line). This suggests that underestimated PAN might have contributed to the model's nighttime HO_2 underestimation, but other processes must have a larger contribution.

4. Implication for model overestimation of HO_X

OH and HO_2 are key species that determine the atmosphere's oxidative processes. Inaccurate modelling of their sinks can lead to significant overestimation of oxidation capacity, resulting in skewed assessments of the impact of HO_X on air pollution and climate change. This problem is particularly pronounced in the case of ozone, a widespread photochemical pollutant. To demonstrate this issue, we compared simulation results from two modelling scenarios: the first scenario was constrained by observational parameters except OH and HO_2 (as described in section 3.2), while the second scenario included constraints from all observational parameters, including OH and HO_2 measurements.

As illustrated in Figure 10, not constraining free-radical measurement data in the chemical model (the red line) led to overestimates of ozone's photochemical production rates. In the PRD case, simulated midday O_X (O_3 + NO_2) formation rates were overestimated by 59 % on average and 57% at peak values. In the CEC case, the overestimation was 98% on average and 91% at peak O_X rates, while the CNC case exhibited the smallest overestimation, 52% on average and 25% at peak values.

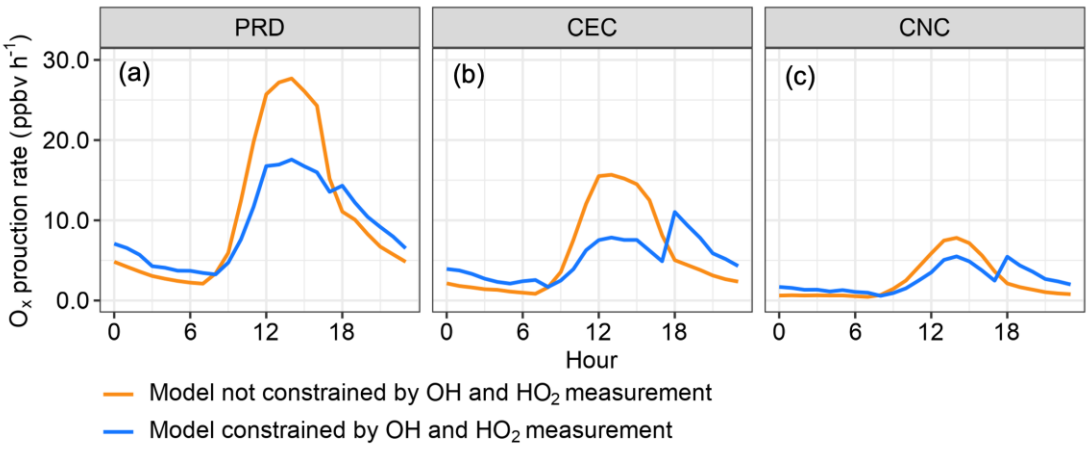

Figure 10 O_X (O_3+NO_2) photochemical production rates in three comparative cases: (a) PRD, (b) CEC, and (c) CNC. The red lines represent rates modelled with constraints on all observed data except OH and HO_2, while the green lines include constraints on all data, including OH and HO_2.

The overestimation of HO_X also significantly affected the simulated concentration of nitric acid (HNO_3), which is crucial for new particle formation and growth (Wang et al., 2020). Figure 11 illustrates that the chemical model drastically overestimated nitric acid production rates without constraints of free-radical measurements (the orange line).

The midday production rates of nitric acid were overestimated by factors of 3.16, 2.02, and 3.41 in the PRD, CEC, and CNC cases, respectively. Such overestimations can considerably impact assessments of new particle formation and growth processes and their impact on air pollution and climate change.

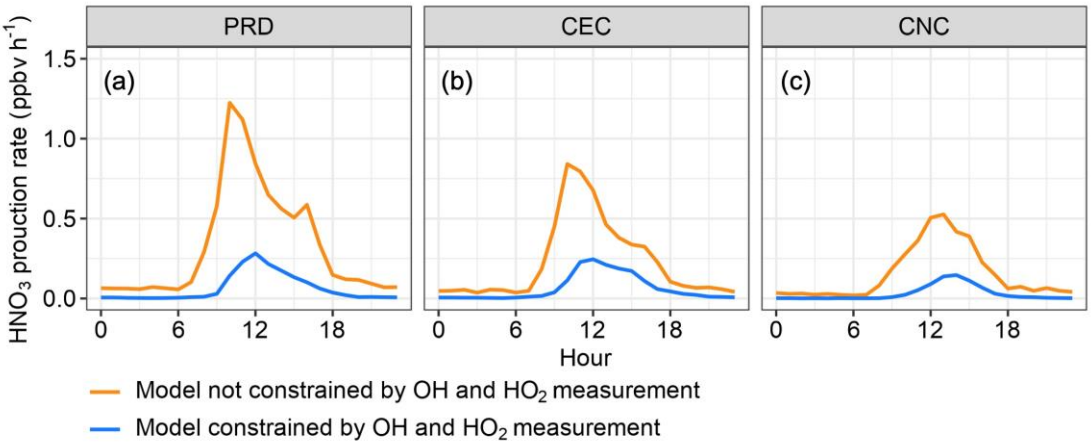

Figure 11 Modelled HNO_3 production rates in three comparative cases: (a) PRD, (b) CEC, and (c) CNC. The red lines represent rates modelled with constraints on all observed data except OH and HO_2, while the green lines include constraints on all data, including OH and HO_2.

5. Conclusion

HO_2 and OH concentrations were measured using a chemical ionization mass spectrometer at a subtropical rural site in southern China from 12 November to 19 December 2022. The measurements indicated generally lower concentrations of OH and HO_2 than those observed in previous studies at various sites. Backward trajectory analysis revealed three distinct phases characterised by sequentially decreasing pollution levels and temperatures. During the cold, clean period, model simulations closely matched the observed OH and HO_2 concentrations. However, during the warm, polluted period, the models overestimated HO_2 or both radicals. Model sensitivity analysis indicates that adding an OH cycling reaction from HO_2 or additional sinks of OH and HO_2 would largely reduce the model-observation discrepancy in different cases of this study. However, the exact chemical reactions remain to be identified. Our results are in line with previous studies indicating substantial gaps in our understanding of the sources and sinks of OH and HO_2 in certain environments. Our study provides additional evidence for current incomplete understanding of the HO_X sources or sinks

and calls for more research to resolve the model–observation mismatch found in this work and previous studies.

The over-prediction of HO_X resulted in significant over simulation of the production rates of other secondary pollutants such as ozone and nitric acid at the site. It is critical to evaluate the capability of OH and HO_2 simulations in major chemical transport models and earth system models as inaccurate simulations of OH and HO_2 may misguide the development of air pollution and global warming control strategies.

Data availability. All of the data used to produce this paper can be obtained by contacting Tao Wang (tao.wang@polyu.edu.hk).

Supplement. The online supplement for this article is available at:

Author contributions. TW conceived the HO_x research. TW, XW and YZ planned and organized the overall field campaign at Conghua. ZZ conducted the OH measurements using CIMS, with contributions from TW and WS, QC, and SH. XF, ZR, XL, AG, QW, CP, and XT performed the JNO_2 VOCs and OVOCs measurements. ZZ performed the chemical box modelling with contributions from TC and QC. TC, ZZ, and TW analysed the data and interpreted the result (ZZ analysed the time series and diurnal variations of observation data; TC interpreted the results of box model, investigated the missing sources; TW supervised and guided these processes). TC, ZZ, and TW wrote the paper. All of the authors reviewed and commented on the paper.

Competing interests. One author (Tao Wang) is a member of the editorial board of Atmospheric Chemistry and Physics. The authors have no other competing interests to declare.

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Supporting Information for

Observation and modelling of OH and HO_2 radicals at a subtropical rural site and implications for secondary pollutants

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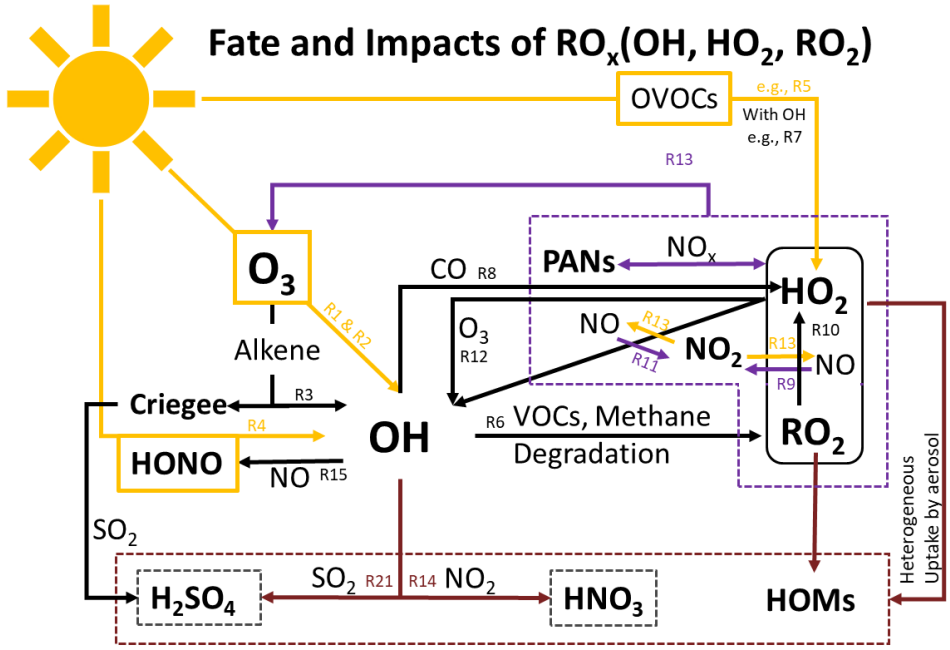

Figure S1 Schematic of the RO_x family's photochemical pathway. Photolysis reactions are highlighted in yellow, reactions contributing to secondary aerosol production are marked in brown, and reactions associated with photochemical pollution are indicated in purple. The chemical reactions (R1 to R21) referred to Table S1.

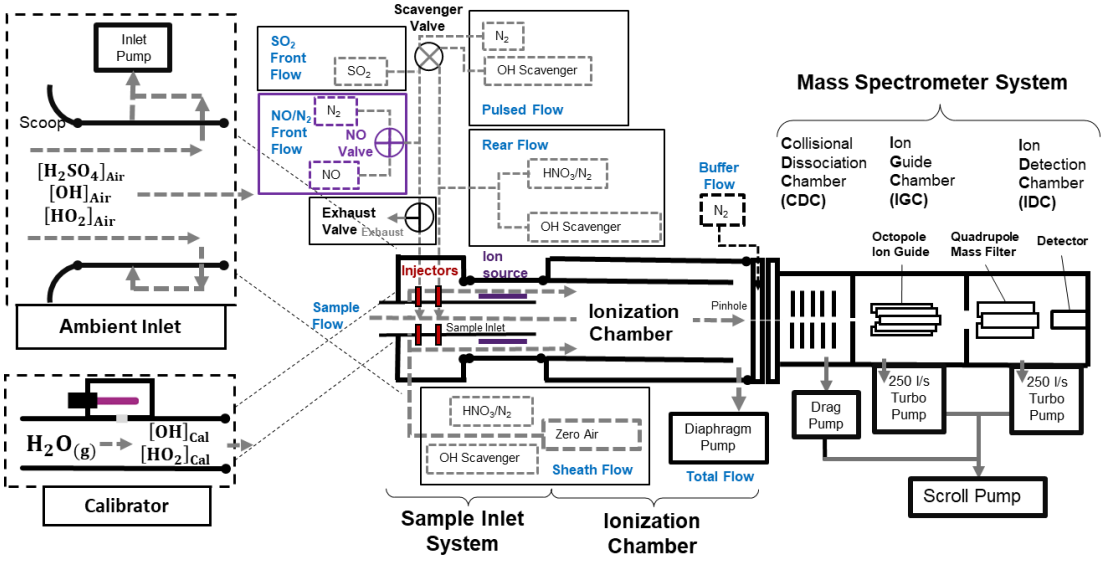

Figure S2 Schematic diagram of the PolyU-CIMS system. The CIMS composed of two detachable components: the ambient inlet and the calibrator; and the main body, which includes the sample inlet system, ionization chamber, and the mass spectrometer system. The frames labeled in purple highlight the additional valve

incorporated for HO_2 measurement. Further details on setup, measurement principles of the CIMS are available in a previous study in a previous study (Zou et al., 2023) and Test S1.

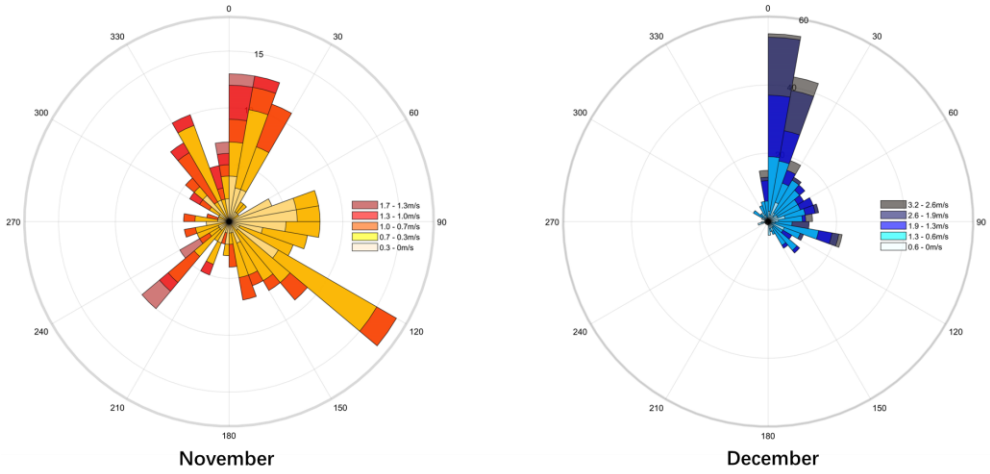

Figure S3 The wind rose for November and December.

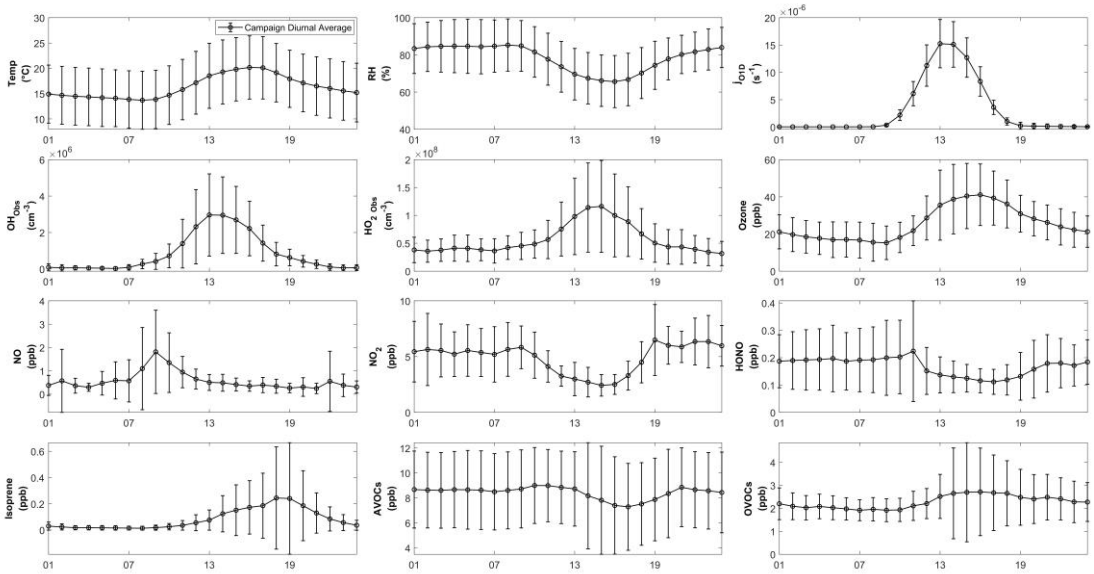

Figure S4 Diurnal profiles of average concentration of HO_2, OH, meteorology data and trace gases of the whole campaign. The shade error bars represent standard deviations of the averaged data.

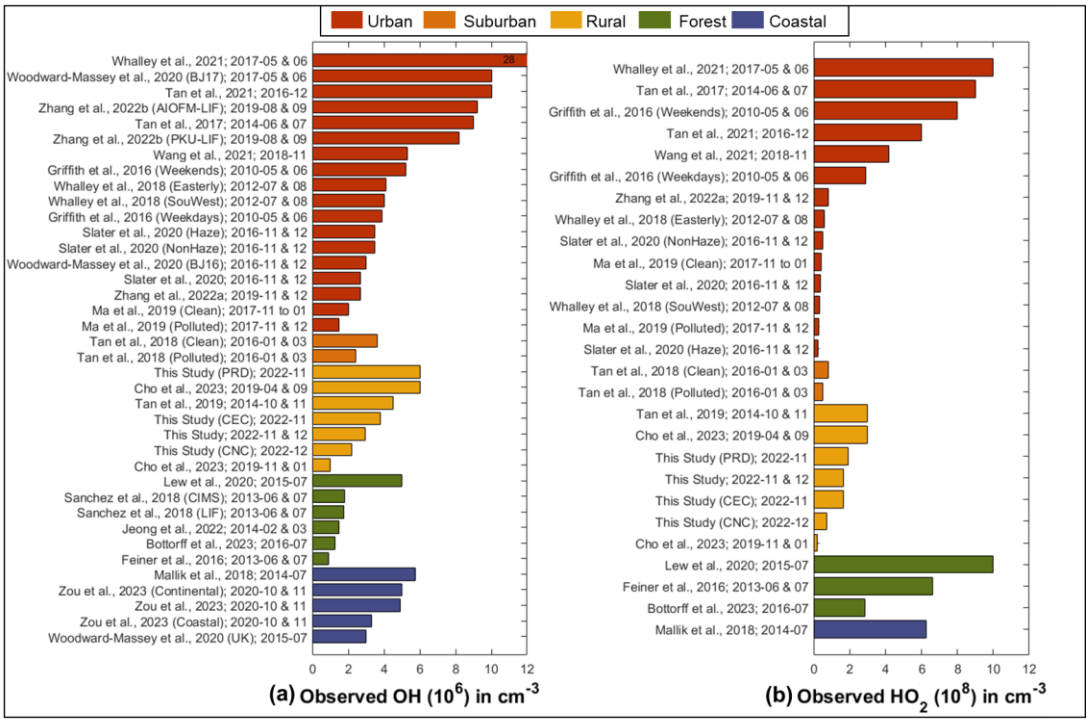

Figure S5 Typical daily averaged maximum concentration of (a) OH and (b) HO_2 observed in various geophysical regions including coastal (blue), forest (green), rural (yellow) and urban (red).

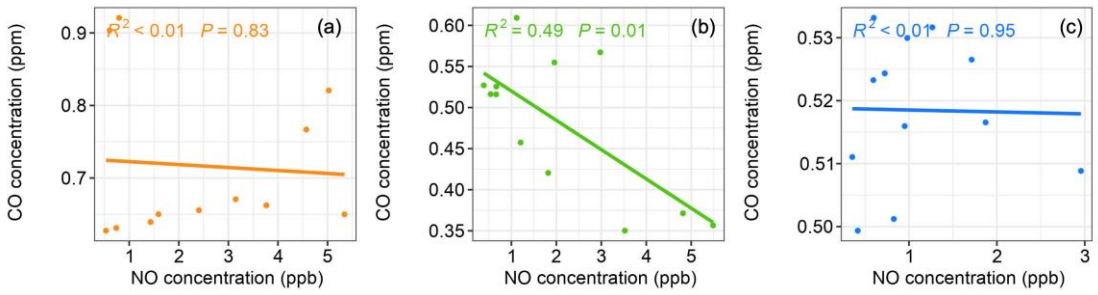

Figure S6 Relationship between NO and CO concentrations in (a) PRD, (b) CEC and (c) CNC from 7:00 to 10:00. The solid lines depict the linear regression fit, with the corresponding equations R^2 and P values annotated on the plot.

Table S1 The HO_X related reactions in the model.

Ambient: HO_x Productions	
(R1)	$O_3 + h\nu(<340\ nm) \rightarrow O(^1D) + O_2$
(R2)	$O(^1D) + H_2O \rightarrow OH + OH$
(R3)	Alkenes + $O_3 \rightarrow RO_X$ + Products
(R4)	$HONO + h\nu(<400\ nm) \rightarrow OH + NO$
(R5)	$HCHO + h\nu\ (<335\ nm) + 2O_2 \rightarrow 2HO_2 + CO$
Ambient: HO_x Interconvertions	
(R6)	$OH + RH + O_2 \rightarrow RO_2 + H_2O$
(R7)	$HCHO + OH + O_2 \rightarrow CO + H_2O + HO_2$
(R8)	$CO + OH + O_2 \rightarrow CO_2 + HO_2$
(R9)	$RO_2 + NO \rightarrow RO + NO_2$
(R10)	$RO + O_2 \rightarrow R'CHO + HO_2$
(R11)	$HO_2 + NO \rightarrow OH + NO_2$
(R12)	$HO_2 + O_3 \rightarrow OH + 2O_2$
(R13)	$NO_2 + h\nu(<420\ nm) + O_2 \rightarrow NO + O_3$
Ambient: HO_x Loss	
(R14)	$OH + NO_2 \rightarrow HNO_3$
(R15)	$OH + NO \rightarrow HONO$
(R16)	$RO_2 + NO \rightarrow RONO_2$
(R17)	$RO_2 + RO_2 \rightarrow$ products
(R18)	$RO_2 + HO_2 \rightarrow ROOH + O_2$
(R19)	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$
(R20)	$HO_2 + HO_2 + H_2O \rightarrow H_2O_2 + H_2O + O_2$
(R21)	$OH + SO_2 + O_2 + H_2O + M \rightarrow H_2SO_4 + HO_2 + M$
CIMS: Reactions in Sample Inlet System	
(R21)	$OH + SO_2 + O_2 + H_2O + M \rightarrow H_2SO_4 + HO_2 + M$
(R11)	$HO_2 + NO \rightarrow OH + NO_2$
(R22)	$RO_2 + NO + O_2 \rightarrow R'CHO + HO_2 + NO_2$
(R23)	Scavenger gas + $OH \rightarrow$ Products
CIMS: Reactions in Ionization Chamber	
(R24)	$HNO_3 + e^- \rightarrow NO_2^- + OH$
(R25)	$HNO_3 + NO_2^- \rightarrow NO_3^- + HONO$
(R26)	$NO_3^- + (HNO_3)_m + (H_2O)_n + M \rightarrow NO_3^-\cdot(HNO_3)_m\cdot(H_2O)_n + M$
(R27)	$H_2SO_4 + NO_3^-\cdot(HNO_3)_m\cdot(H_2O)_n \rightarrow HSO_4^-\cdot(HNO_3)_m(H_2O)_n + HNO_3$
CIMS: Reactions in Collisional Dissociation Chamber	
(R28)	$NO_3^-\cdot(HNO_3)_m\cdot(H_2O)_n + M \rightarrow NO_3^- + (HNO_3)_m + (H_2O)_n + M$
(R29)	$HSO_4^-\cdot(HNO_3)_m\cdot(H_2O)_n + M \rightarrow HSO_4^- + (HNO_3)_m + (H_2O)_n + M$
CIMS: Calibration	
(R30)	$H_2O + h\nu(184.9nm) + O_2 \rightarrow HO_2 + OH$

Table S2 Summary of instruments used, and species measured during the field campaign.

Instruments	Species	Resolution	Detection Limits	Accuracy
Q-CIMS (NO_3^-)	OH	1 hours	3×10^5 cm^{-3}	± 46%
	HO_2	1 hours	20×10^5 cm^{-3}	± 44%
Thermo 42i-TL	NO	1 min	60 ppt	± 5.2%
Thermo 49i	O_3	1 min	0.5 ppb	± 6.0%
NO_2-11r-EP	NO_2	1 min	60 ppt	± 6.0%
Online GC-MS	VOCs	1 hour	10 ppt	± 20%
Thermo 43i	SO_2	1 min	1 ppb	± 6.1%
Thermo 48i	CO	1 min	40 ppb	± 7.4%
Thermo 17i	NH_3	2 mins	1 ppb	± 8%
LOPAP-03	HONO	5 mins	1 ppt	± 10%
SMPS	Aerosol Particles	5 mins	1 particle cm^{-3}	± 10%

Tabel S3 Configurations of the PolyU CIMS in Hok Tsui 2020 and Conghua 2022 campaigns. The changes from the last configuration were labelled by red color.

a) Hok Tsui 2020

Efficiency Related	Parameters	Gas	Values	Units	Specification for Measurement	Values	Units
E_{Conv}	**Front Injection**	SO_2 (0.9%)	5	sccm	Sample Flow [SO_2]	12	ppm
	Pulse Valve	N_2	2	sccm	Cycle Duration (OH)	6	mins
		C_3F_6 (99.9%)	2	sccm	B/S Ratio for OH measurement	8%	
	Rear Injection	C_3F_6 (99.9%)	2	sccm	Sample Flow [C_3F_6]	1072	ppm
		HNO_3	10	sccm	Reaction Time	47	ms
	Sample Flow		3.7	slpm	Sample Flow Speed	55	cm/s
E_{Ion}	**Sheath Flow**	Zero Air	12.6	slpm	Reynolds Number in Ionization Chamber	>4000 Turbulent flows	
		HNO_3	10	sccm			
		C_3F_6 (99.9%)	2	sccm	Sheath Flow [C_3F_6]	159	ppm
	Total Flow		16.8	slpm	Sheath Flow Speed	25	cm/s
	Sheath Voltages		-80	V	Voltages Difference for ionization	48	V
	Sample Voltages		-32	V			
E_{Trans}	**Buffer Gas**	N_2	440	sccm	Voltages Difference for transmission	80	V
	Buffer Voltages		-70	V			
	Pinhole Voltages		-40	V			
Cal	**Calibration Flow**		10	slpm	Calibration Factor C_{OH} (Reagent ion: $N^{18}O_3^-$)	$1.21*10^{-8}$	cm^3
	Flow Speed		65	cm/s			
	Product It Value		$8.8*10^{10}$ photon/cm^2				
Uncertainties	**Sigma**		2		**Detection Limit ($\times10^5$ cm^{-3}) (3σ)**	In lab	1.7
	Calibration		38%			Day	12
	Overall		44%			Night	8.5

b) CongHua 2022

Efficiency Related	Parameters	Gas	Values	Units	Specification for Measurement	Values	Units
E_{conv}	**Front Injection**	SO_2 (0.9%)	5	sccm	Sample Flow [SO_2]	12	ppm
		NO (0.9%)	0.5		Sample Flow [NO]	1.2	ppm
	Pulse Valve	N_2	2	sccm	Cycle Duration (OH)	6	mins
					Cycle Duration (HO_2)	60	mins
		C_3F_6 (99.9%)	2	sccm	B/S Ratio (OH)		10%
					B/S Ratio (HO_2)		20%
	Rear Injection	C_3F_6 (99.9%)	2	sccm	Sample Flow [C_3F_6]	1072	ppm
		HNO_3	10	sccm	Reaction Time	47	ms
	Sample Flow		3.7	slpm	Sample Flow Speed	55	cm/s
E_{Ion}	**Sheath Flow**	Zero Air	12.6	slpm	Reynolds Number in Ionization Chamber	>4000 Turbulent flows	
		HNO_3	10	sccm			
		C_3F_6 (99.9%)	2	sccm	Sheath Flow [C_3F_6]	159	ppm
	Total Flow		16.8	slpm	Sheath Flow Speed	25	cm/s
	Sheath Voltages		-80	V	Voltages Difference for ionization	48	V
	Sample Voltages		-32	V			
E_{Trans}	**Buffer Gas**	N_2	440	sccm	Voltages Difference for transmission	80	V
	Buffer Voltages		-70	V			
	Pinhole Voltages		-40	V			
Cal	**Calibration Flow**		10	slpm	Calibration C_{OH}	$1.09*10^{-8}$	
	Flow Speed		65	cm/s	Factors C_{HO2}	$1.07*10^{-8}$	cm^3
	Product It Value		$8.8*10^{10}$ photon/cm^2		($N^{18}O_3^-$) C_{H2SO4}	$6.01*10^{-9}$	
Overall Uncertainties (2σ)		OH	44%		**Detection Limit in Field Study ($\times10^5$ cm^{-3}) (3σ)**	OH	3
		H_2SO_4	40%			H_2SO_4	1
		HO_2	46%			HO_2	20

Notes: B/S Ratio - background to signal ratio

Table S4 Average mixing ratios (ppbv) and standard deviations of measured VOCs that are constrained in the box model in the entire campaign and in different cases.

Species	Total	PRD	CEC	CNC	MCM Abb.
Ethane	2.3±0.83	1.6±0.88	1.9±0.53	2±0.14	C2H6
Ethylene	0.69±0.33	0.62±0.26	0.58±0.21	0.58±0.16	C2H4
Propane	1.6±0.62	2.1±0.81	1.2±0.31	1.2±0.27	C3H8
Propene	0.072±0.077	0.13±0.17	0.059±0.023	0.067±0.035	C3H6
i-Butane	0.44±0.28	0.89±0.49	0.35±0.1	0.31±0.061	IC4H10
n-Butane	0.65±0.41	1.3±0.71	0.48±0.14	0.44±0.083	NC4H10
Acetylene	0.92±0.42	0.91±0.35	0.82±0.31	0.76±0.072	C2H2
trans-2-Butene	0.015±0.0071	0.015±0.0046	0.017±0.011	0.016±0.0057	TBUT2ENE
cis-2-Butene	0.083±0.038	0.17±0.033	0.083±0.013	0.08±0.014	CBUT2ENE
Butene	0.044±0.021	0.047±0.049	0.037±0.014	0.048±0.01	BUT1ENE
Chloromethane	0.84±0.22	0.51±0.076	0.84±0.15	0.86±0.15	CH3CL
1,3-Butadiene	0.0079±0.0078	0.012±0.0087	0.0076±0.0071	0.007±0.0045	C4H6
Acetaldehyde	0.92±0.35	1.5±0.37	NaN	0.53±0.16	CH3CHO
Bromomethane	0.0093±0.0022	0.01±0.0019	0.009±0.0015	0.0088±0.00098	CH3BR
Chloroethane	0.023±0.012	0.015±0.011	0.021±0.0088	0.02±0.0039	CH3CH2CL
i-Pentane	0.34±0.17	0.61±0.22	0.31±0.059	0.24±0.042	IC5H12
1-Pentene	0.043±0.016	0.067±0.024	0.033±0.0079	0.037±0.0056	PENT1ENE
n-Pentane	0.19±0.1	0.34±0.18	0.12±0.034	0.14±0.022	NC5H12
trans-2-Pentene	0.0032±0.0045	0.011±0.0052	0.0025±0.0024	0.0012±0.0012	TPENT2ENE
Isoprene	0.082±0.17	0.26±0.34	0.16±0.2	0.029±0.03	C5H8
cis-2-Pentene	0.0017±0.0028	0.007±0.003	0.0012±0.0013	0.0039±0.0055	CPENT2ENE
Acrolein	0.06±0.031	0.092±0.043	0.053±0.019	0.043±0.015	ACR
Propanal	0.011±0.0059	0.015±0.011	0.0095±0.004	0.0091±0.0036	C2H5CHO
Vinylidene chloride	0.0036±0.0027	0.003±0.0016	0.002±0.002	0.0049±0.003	CCL2CH2
2,2-Dimethylbutane	0.017±0.015	0.046±0.025	0.012±0.0031	0.01±0.0015	M22C4
Dichloromethane	1.1±0.84	2.5±1.4	1±0.35	0.93±0.18	CH2CL2
2,3-Dimethylbutane	0.026±0.023	0.064±0.033	0.025±0.0066	0.015±0.004	M23C4
2-Methylpentane	0.071±0.045	0.24±0.053	0.06±0.016	0.056±0.012	M2PE
3-Methylpentane	0.052±0.039	0.12±0.061	0.04±0.011	0.036±0.0085	M3PE
Methyl tert-butyl ether	0.072±0.042	0.14±0.051	0.068±0.016	0.055±0.012	MTBE
1-Hexene	0.0048±0.0052	0.013±0.004	0.0036±0.004	0.002±0.0008	HEX1ENE
n-Hexane	0.066±0.043	0.13±0.063	0.049±0.016	0.042±0.012	NC6H14
Methacrolein	0.062±0.062	0.12±0.058	0.11±0.069	0.025±0.0097	MACR
1,1-Dichloroethane	0.0086±0.0046	0.0079±0.0038	0.008±0.0036	0.0069±0.0014	CHCL2CH3
Butyraldehyde	0.54±0.21	0.45±0.18	0.5±0.14	0.45±0.16	C3H7CHO
1,2-Dichloroethylene	0.049±0.076	0.14±0.17	0.032±0.014	0.026±0.014	DICLETH
2-Butanone	0.25±0.24	0.55±0.49	0.21±0.086	0.13±0.05	MEK
Ethyl acetate	0.27±0.39	0.71±0.87	0.17±0.076	0.15±0.076	ETHACET
Chloroform	0.082±0.032	0.13±0.042	0.087±0.015	0.069±0.01	CHCL3
Methylchloroform	0.0021±0.0011	0.0037±0.00044	0.001±4.4e-19	0.0018±0.00042	CH3CCL3
2-Methylhexane	0.015±0.017	0.046±0.028	0.0097±0.0038	0.0074±0.002	M2HEX
Cyclohexane	0.019±0.015	0.041±0.021	0.011±0.0052	0.011±0.0037	CHEX
Tetrachloromethane	0.073±0.0055	0.07±0.0036	0.066±0.0036	0.075±0.0031	CCL4
3-Methylhexane	0.02±0.024	0.064±0.042	0.012±0.0042	0.0095±0.0026	M3HEX
Benzene	0.35±0.14	0.29±0.11	0.32±0.1	0.31±0.029	BENZENE
Ethylene dichloride	0.36±0.17	0.26±0.11	0.34±0.18	0.41±0.097	CH2CLCH2Cl
n-Hepane	0.035±0.023	0.072±0.038	0.024±0.0053	0.022±0.0035	NC7H16
Crotonaldehyde	0.45±0.14	0.46±0.0079	0.48±0.0065	0.5±0.0081	C3MDBAL
Trichloroethene	0.021±0.023	0.061±0.037	0.018±0.013	0.013±0.0033	TRICLETH
1,2-Dichloropropane	0.085±0.038	0.12±0.03	0.096±0.016	0.071±0.011	CL12PROP
Pantanal	0.018±0.011	0.033±0.017	0.019±0.0078	0.013±0.006	C4H9CHO
1,3-Dichloro-1-propene	0.0025±0.0011	0.0029±0.00071	0.0015±0.00099	0.0024±0.00092	CLC3H4CL
4-Methyl-2-pentanone	0.0046±0.0073	0.019±0.0045	0.0011±0.00091	0.0031±0.0051	MIBK
Toluene	0.28±0.27	0.71±0.5	0.21±0.057	0.17±0.049	TOLUENE
n-Octane	0.0093±0.0071	0.022±0.0067	0.0046±0.0014	0.0051±0.0012	NC8H18
1,1,2-Trichloroethane	0.014±0.0097	0.011±0.0084	0.013±0.0093	0.015±0.0048	CH2CLCHCL2
Tetrachloroethylene	0.015±0.013	0.04±0.019	0.014±0.004	0.0085±0.0011	TCE
2-Hexanone	0.05±0.025	0.087±0.029	NaN	0.038±0.011	HEX2ONE
Hexanal	0.041±0.022	0.076±0.025	NaN	0.03±0.0091	C5H11CHO
1,2-Dibromoethane	0.002±0.0016	0.0038±0.0012	0.0013±0.0012	0.0015±0.0011	DIBRET
Ethylbenzene	0.042±0.031	0.072±0.035	0.028±0.022	0.034±0.023	EBENZ
o-Xylene	0.039±0.03	0.077±0.039	0.027±0.018	0.031±0.017	OXYL
Styrene	0.02±0.013	0.034±0.008	0.012±0.0054	0.013±0.0074	STYRENE
Isopropylbenzene	0.006±0.0058	0.016±0.0026	0.0027±0.0011	0.0029±0.00099	IPBENZ
1,1,2,2-Tetrachloroethane	0.0031±0.0019	0.0053±0.0012	0.0029±0.0017	0.0023±0.0012	CHCL2CHCL2
n-Propylbenzene	0.0048±0.0045	0.013±0.0033	0.0032±0.0013	0.0024±0.001	PBENZ
m-Ethyltoluene	0.0073±0.0067	0.019±0.0083	0.0057±0.0026	0.0041±0.0018	METHTOL
p-Ethyltoluene	0.0048±0.0047	0.013±0.0045	0.0033±0.002	0.0024±0.0015	PETHTOL
1,3,5-Trimethylbenzene	0.0051±0.0054	0.015±0.0054	0.004±0.0022	0.0021±0.0015	TM135B
n-Decane	0.0031±0.0031	0.0088±0.0028	0.0017±0.00075	0.0013±0.00062	NC10H22
Benzaldehyde	0.0047±0.0044	0.013±0.0039	0.0032±0.0013	0.0023±0.00098	BENZAL
1,2,4-Trimethylbenzene	0.0088±0.009	0.024±0.013	0.0075±0.0031	0.0044±0.0019	TM124B
1,2,3-Trimethylbenzene	0.0037±0.0035	0.01±0.0037	0.0029±0.0015	0.0018±0.001	TM123B
Undecane	0.0019±0.0024	0.0061±0.0012	0.0018±0.00091	0.0037±0.0056	NC11H24
Dodecane	0.0094±0.0035	0.015±0.0034	0.0066±0.0014	0.01±0.0017	NC12H26

Text S1 Calibration procedures

The calibration of Chemical Ionization Mass Spectrometer (CIMS) involves the generation of OH and HO_2 radicals through photolysis of water vapor by 184.9 nm light, as outlined in Reaction R30. The concentration of radicals produced during calibration is determined from the known concentration of water vapor [H_2O], which is calculated from water vapor pressure and the relative humidity and temperature. Other essential parameters include the photolysis cross-section of water vapor (σ_{H2O} = 7.14×10^{-20} cm^2; Cantrell et al., 1997), the photolysis quantum yield (Φ, assumed to be 1, Kürten et al., 2012) and the photon flux (*It* value, see details about *It* value determination on Kürten et al., 2012). The generated radical concentrations ([OH] and [HO_2]) are calculated using the following equations:

$$[OH] = [HO_2] = [H_2O] * \sigma_{H_2O} * \Phi * It$$

From these values, the calibration factors for OH and HO_2 (C_{OH} and C_{HO2}) are calculated using the signals obtained during calibration (S_{OHcal} and S_{HO2cal}), as expressed in the transformed equations E1 and E2:

$$C_{OH} = \frac{1}{[OH]_{cal}} \times \frac{S_{OHcal}}{S_{62}} \quad \text{(E1, transformed)}$$

$$C_{HO2} = \frac{1}{[HO_2]_{cal}} \times \frac{S_{HO2cal}}{S_{62}} \quad \text{(E2, transformed)}$$

The calibrator produced OH and HO_2 concentrations in the range of 3×10^7 to 1×10^9 cm^{-3} depending on RH conditions in 10 LMP synthetic air. The more detailed information on calculation procedures is given in our previous study (Zou et al., 2023).

Text S2 Modification for HO_2 measurement

To measure the HO_2, a valve is added to switch the injection gas between NO and N_2 as indicated by purple frame in Figure S2. When adding N_2, the CIMS is in OH measurement mode. When NO is added to the sample flow, the CIMS changes to HO_2 mode for total HO_x measurement.

During HO_2 measurement, ambient HO_2 converted by NO to OH. It should be noted that in HO_2 mode, the increasing NO concentration can enhance HO_2

conversion to OH (R11), but excessive NO levels trigger the HONO formation when reacts with OH (R15), competing with the OH conversion process by SO_2 (R21) and lowering the detection efficiency for OH. Consequently, the NO to SO_2 concentration ratio is crucial for HO_2 measurements. Sensitivity tests revealed an optimal [NO]/[SO_2] ratio of 0.1 for the PolyU-CIMS and 100% conversion of HO_2 in the laboratory ([H_2SO_4]/[HO_2] = 1), aligning with prior research recommendations (Edwards et al., 2003; Sjostedt et al., 2007). Because the concentrations of both SO_2 and NO injected to sample flow are maintained at levels over 100-1000 times higher than those in the ambient atmosphere and the injection flow rates are fixed, the efficiency of the HO_2 to OH conversion remains stable and is believed to be at completion.

Text S3 The Background mode and scavenge efficiency

In the background mode, scavenger gases C_3F_6 are introduced into the sample flow along with SO_2. Given that the concentration of C_3F_6 is 100 times higher than that of SO_2, the ambient OH and any ambient HO_2 converted to OH are scavenged by C_3F_6, rather than being converted to H_2SO_4.

To determine the amount of C_3F_6 that is needed to achieve complete OH scavenge, we gradually increased C_3F_6 added to high concentrations of OH and HO_2 ([HO_x] ≈ 10^9 cm^{-3}) generated from the calibrator in synthetic air until no further reduction in the measured signal, which indicates complete scavenging of OH. This point defines the background noise which is attributed to any Criegee intermediates and ambient sulfuric acid. In our setup, there is residual C_3F_6 present after CIMS switches from background to signal mode, but it does not affect the measurement results. As shown in Figure S7, after switching off C_3F_6, the measurement signals rapidly return to their initial levels within 20 seconds. Data affected by C_3F_6 residual are excluded to minimize the impact of the residual C_3F_6 on the measurements.

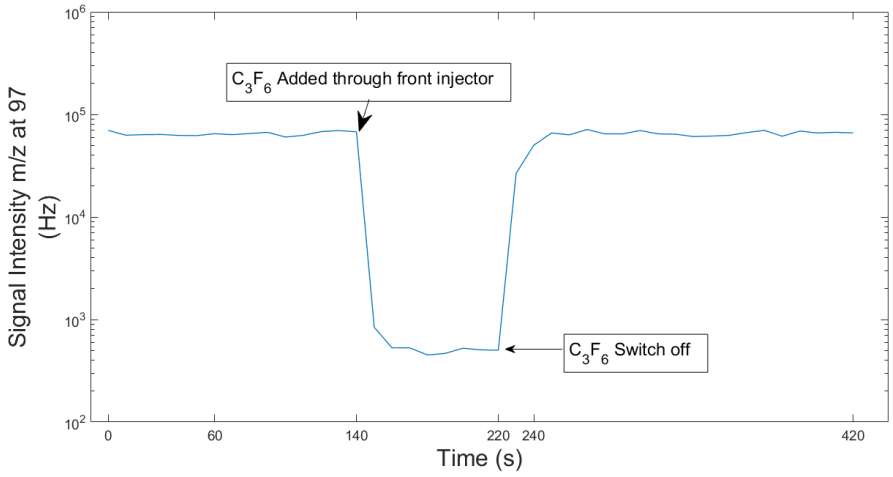

Figure S7 Variation of signal intensity m/z at 97 before C_3F_6 addition with time, after addition and switching off of C_3F_6 in synthetic air containing OH of ~5×10^8 cm^{-3}.

Text S4 Measurement interferences

4.1 Sampling Loss

Wall losses in the ambient inlet were evaluated by varying the distances of the calibration lamp from the inlet to assess potential effects on signal attenuation. The instrument was calibrated in two distinct configurations: initially, the lamp was positioned close to the CIMS sample inlet (Figure S6a, and subsequently, moved away from the CIMS sample inlet (Figure S6b. By comparing the observed signals from these two configurations, we were able to calculate the wall losses associated with the ambient inlet. The results indicated no significant difference (<1%) between the two measurements, suggesting negligible wall losses in the sampling system.

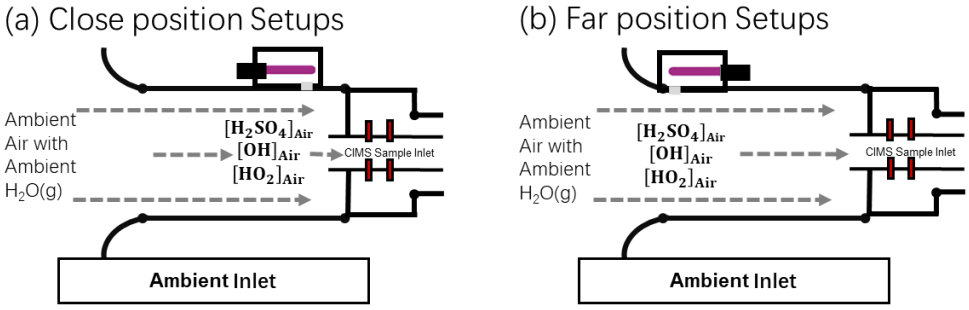

Figure S8 calibration process during ambient sampling in (a) close and (b) far positions.

Furthermore, the potential for radical-radical loss after radicals exit the calibrator and enter the sampling inlet was considered. Given the flow speed of the ambient inlet (12.2 m/s), the sample inlet (55 cm/s), and the distances involved—the calibration lamp is less than 1 cm from the sample inlet, and the sampling port to the front injectors is 1 cm—it can be calculated that the transport time for radicals to the front injectors for reactions is less than 20 ms. This brief transport time is sufficiently short to prevent significant radical-radical losses. Additionally, since the sample inlet draws the central part of the airflow within the ambient inlet, and the flow in the sample inlet is laminar, wall losses at this stage are also considered negligible.

4.2 OH interference

The OH interference in PolyU-CIMS, resulting from ambient HO_2 recycling (R11) and ionization process (R24, artificial OH), was accounted for and included in the measurement uncertainty, as outlined by Zou et al. (2023). However, in this study, PolyU-CIMS encountered additional interference from residual NO in the injectors when switching from NO (used for HO_2 measurement) to N_2 (used for OH measurement). To prevent residual NO buildup, the inlet was cleaned daily, and a one-hour calibration was performed at both the start and end of daily measurement to monitor the NO residuals. The monitoring results showed that the NO residual time for PolyU - CIMS was approximately 26 mins which is similar to the residual time reported in earlier studies (Edwards et al., 2003; Sjostedt et al., 2007). Consequently, data collected during the residual period (30 mins after switching the measurement target from HO_2 to OH) was discarded to eliminate any NO residual interference from the final results. See details about how the duty cycle setup achieved the monitoring of NO residual interference in Text S5.

4.3 HO_2 interference

The concentration of injected NO is the primary source of HO_2 measurement interference in this study. High NO concentrations convert ambient RO_2, particularly alkene and aromatic-related RO_2, into HO_2 and then OH, leading to a positive bias in HO_2 measurements (Fuchs et al., 2014). To mitigate this interference, the NO

concentration at the sample inlet was set to 1.2 ppm—lower than the levels recommended in previous studies to minimize RO_2 interference (Fuchs et al., 2014).

To assess the possible HO_2 interference from RO_2, we first simulated with a box model production of HO_2 from RO_2 in the inlet system with addition of 1.2 ppm NO to ambient air composition observed in previous field study in Hok Tsui (a coastal site in Hong Kong) by our team in 2020 (Zou et al., 2023) before this observation. The observation-constrained MCM model (described in the Text S6) was run for three days, and the RO_2 outputs were taken as used as the initial concentrations entering the inlet. Then another model run was conducted by setting j-values setting to zero and reaction time as the residence time (47 ms) to simulate the conversion of RO_2 by NO in the CIMS inlet. We compared the OH concentrations (from RO_2 conversion to HO_2 and then to OH) at the outlet with the total concentration of HO_2+OH after spinning up. The result shows a difference of less than 2% suggesting negligible conversation of RO_2 to HO_2 in the inlet at 1.2 ppm NO injection. Similar model tests with real time conditions were also done for Conghua study after field study and show less than 2% interference.

To verity the model results, experiment tests were conducted in both laboratory and field settings (Hok Tsui in Hong Kong and Conghua) by comparing the HO_2 calibration factor obtained in synthetic air (with minimal interference of RO_2 due to very low VOCs concentrations in the synthetic air) and that conducted in indoor and outdoor air (with potential interference due to presence of VOCs). The results in Table S6 show difference of 1% - 3% between the HO_2 calibration factor in the synthetic air with that in the lab indoor air and that in the ambient air at Hok Tsui (with $[O_3]$ <70 ppb $[NO_x]$ < 10 ppb) as well as Cong Hua (with $[O_3]$ <60 ppb $[NO_x]$ < 10 ppb), confirming little interference of RO_2 to HO_2 measurements (See Table S6 below). These results might be due to the low concentrations of biogenic volatile organic compounds (BVOCs) in our two study sites ($[C_5H_8]$ <0.2 ppb) as previous studies show large interference of BVOC than anthropogenic VOC to HO_2 measurements (Fuchs et al., 2014).

Table S5 Calibration factors of OH and HO_2 obtained in different conditions to estimate the RO_2 interference.

Year of experiements	Calibration Conditions	Calibration Factor (cm^3) OH	HO_2	Notes
2021	Synthetic air in lab	7.912E-10	9.156E-10	On the afternoon of Nov 20, 2021
	Indoor air in lab	8.146E-10	9.275E-10	
	Synthetic air at Hok Tsui	8.212E-10	9.181E-10	On the morning of Dec 23, 2021
	Outdoor air at Hok Tsui	8.252E-10	9.378E-10	
2022	Synthetic air in lab	1.043E-09	1.080E-09	On the morning of May 04, 2022
	Indoor air in lab	1.035E-09	1.119E-09	
	Synthetic air at Conghua	1.033E-09	1.085E-09	On the morning of Nov 17, 2022
	Outdoor air at Conghua	1.025E-09	1.092E-09	

Notes:
The difference between calibration factors obtained at 2022 and 2020 is due to the changes of CIMS's settings
Chemical Condition of outdoor air of Hok Tsui $[O_3]$ <70 ppb, $[NO_x]$ < 10 ppb, $[C_5H_8]$ < 0.2 ppb
Chemical Condition of outdoor air of Cong Hua $[O_3]$ <60 ppb, $[NO_x]$ < 10 ppb, C_5H_8] < 0.2 ppb

Text S5 The measurement duty cycle of CIMS

As detailed in Section 2.2, the PolyU-CIMS was configured to sequentially measure HO_2, H_2SO_4, and OH within each hour during the field study, corresponding to changes in injection gases. Table S3 outlines the hourly schedule and injection gases Figure S9 a 1-hour duty cycle.

Table S6 Duty cycle and injection gases for targeted chemical analysis.

Purpose	Measurement Mode	Signal 97 Label	Chemicals injected to the sample flow through different injectors: Front Injectors	Rear Injectors	Duty time (s)	Repeat times	Total Duration (mins)
HO_2	SIG	S_{97NO}	NO, $N_{2(p)}$, SO_2,	Sca, $Sca_{(p)}$	60	3	6
	BKG	$S_{97NOSca}$	NO, $Sca_{(p)}$, SO_2	Sca, $N_{2(p)}$	60		
H_2SO_4	SIG	$S_{97w/o}$	-	Sca, $Sca_{(p)}$	60	2	4
	BKG	$S_{97w/o}$	-	Sca, $N_{2(p)}$	60		
OH	SIG	S_{97SO2}	$N_{2(p)}$, SO_2,	Sca, $Sca_{(p)}$	60	25	50
	BKG	$S_{97SO2Sca}$	$Sca_{(p)}$, SO_2	Sca, $N_{2(p)}$	60		

Notes:

Front and Rear Injectors - The injector pairs as demonstrated in the Figure S2

SIG & BKG – the signal and background modes.

Sca - scavenger gas, C_3F_6 in this study.

$Sca_{(p)}$ - scavenger gas added through the pulsed flow.

$N_{2(p)}$- nitrogen gas, added through the pulsed flow.

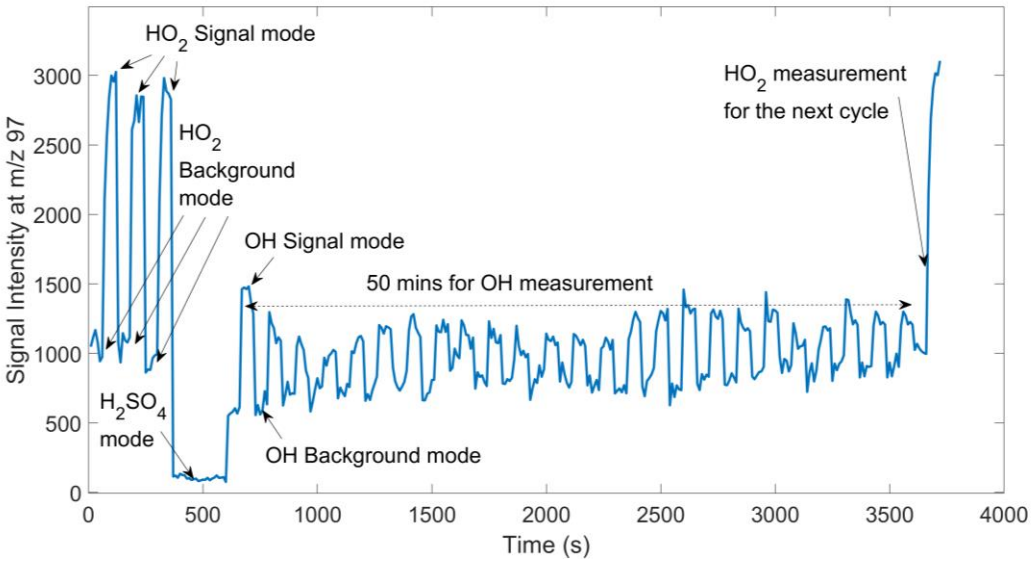

Figure S9 Variation of signal intensity at m/z 97 during a 1-hour duty cycle of CIMS measurement.

Text S6 The model efforts to correct measurement interference.

Ambient NO can cause interference to OH measurement by concerting HO_2 to OH in the inlet system. To assess and correct this effect, model simulations were conducted, which also simulated conversion of RO_2 to HO_2 by NO (i.e., interference to HO2 measurements as discussed before). We first constrained all measured species (except OH and HO_2) in the model, and a three-day spin-up was used to simulate the chemical conditions of the sampled air during measurement. Then the outputs were used as inputs for another simulation with the injection gases (SO_2 and/or NO) to simulate chemical reactions in the inlet with reaction time of 47 ms to match the reaction time in the CIMS. Photolysis frequencies were maintained at zero to reflect the dark environment of the inlet. The modeled OH concentrations without NO addition and OH concentrations with NO addition represent ambient NO interference to OH and HO_2, respectively.

The calculated interferences for OH and HO_2 measurements were in the range 1×10^4 cm^{-3} to 1×10^5 cm^{-3} (mean: 3×10^4) and 8×10^5 cm^{-3} to 2×10^6 cm^{-3} (mean: 1.2×10^6), respectively. These lead to correction of measurement data of OH and HO_2 less than 2%.

Text S7: Sensitivity Test to assess impact of the fresh vehicle exhaust in CEC

A sensitivity test was conducted for the CEC case to account for the missing OH reactivity in the morning. This missing OH reactivity was attributed to unmeasured species in the fresh diesel exhaust. To estimate this, we first calculated the total OH reactivity of the exhaust based on the reactivity of NO_x and CO, along with the diesel exhaust source profile. The contributions from NO_x and CO were then subtracted. The remaining OH reactivity was allocated to formaldehyde and acetaldehyde, with their concentrations adjusted accordingly. This allocation was justified by the significant contribution of OVOCs to the total reactivity of diesel exhaust (Yao et al., 2015; Mo et al., 2016), as formaldehyde and acetaldehyde were not measured in this study. The sensitivity test was performed following these steps:

1. First, we calculated the OH reactivity of freshly emitted NOx and CO at each time step. We assumed that the pollutant concentrations at the time of the highest NO concentration did not undergo significant photochemical loss. For each time step, we calculated the ratio of the OH concentration at the time of the highest NO concentration to the OH concentration at that time step. This ratio was then multiplied by the OH reactivity of ambient NO_x and CO at that time step to estimate the OH reactivity from the emitted NO_x and CO.

2. The observed exhaust OH reactivity was determined by dividing the OH reactivity of emitted NO_x and CO by 20%, which represents the minimum contribution of NO_x and CO to the observed OH reactivity in exhaust in China (Yang, 2023).

3. The total exhaust OH reactivity was derived by dividing the observed exhaust OH reactivity by 60%, to account for the approximately 40% of OH reactivity missing in Chinese diesel exhaust (Yang, 2023). The OH reactivity of emitted NO_x and CO was then subtracted from the total exhaust OH reactivity.

4. The remaining OH reactivity was allocated to formaldehyde and acetaldehyde in a 1:1.6 ratio, and their concentrations were adjusted accordingly. This ratio was

calculated based on the concentration ratios of formaldehyde and acetaldehyde in diesel exhaust (Yao et al., 2015) and their respective OH reactivity coefficients.

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