

# Why observed and modelled ozone production rates and sensitivities differ, a case study at rural site in CHINA

Jun Zhou<sup>1\*#</sup>, Bin Jiang<sup>1#</sup>, Bowen Zhong<sup>1</sup>, Tao Zhang<sup>2</sup>, Duohong Chen<sup>2</sup>, Yuhong Zhai<sup>2</sup>, Li Zhong<sup>1</sup>, Zhijiong Huang<sup>1</sup>, Junqing Luo<sup>1</sup>, Minhui Deng<sup>1</sup>, Mao Xiao<sup>3,4</sup>, Jianhui Jiang<sup>5,6</sup>, Jing Li<sup>1</sup>, Min Shao<sup>1\*</sup>

<sup>1</sup>College of Environment and Climate, Institute for Environment and Climate Research, Guangdong-Hongkong-Macau Joint Laboratory of Collaborative Innovation for Environmental Quality, Jinan University, Guangzhou 511443, China

<sup>2</sup>Environmental Key Laboratory of Regional Air Quality Monitoring, Ministry of Ecology and Environment, Guangdong Ecological and Environmental Monitoring Center, Guangzhou 511443, China

<sup>3</sup>Sichuan Academy of Environmental Sciences, Chengdu 610041, China

<sup>4</sup>Biogas Institute of Ministry of Agriculture and Rural Affairs, Chengdu 610041, China

<sup>5</sup>Global Institute for Urban and Regional Sustainability, School of Ecological and Environmental Sciences, East China Normal University, Shanghai 200241, China

<sup>6</sup>Institute of Eco-Chongming, East China Normal University, Shanghai 200241, China

<sup>#</sup>These authors contribute equally to this article

\*Correspondence to: Jun Zhou (junzhou@jnu.edu.cn) & Min Shao (mshao@jnu.edu.cn)

**Abstract.** Ground-level ozone ( $O_3$ ) pollution has recently become of increasing concern in China. Studies have shown that conventional models often fail to predict accurately the net  $O_3$  production rate ( $P(O_3)_{net}$ ) due to the absence of certain mechanisms, particularly the kinetics from missing reactive volatile organic compounds (VOCs) species, and hence affects the reliability of evaluation for  $O_3$  formation sensitivity (OFS). Therefore, we conducted a field observation of  $P(O_3)_{net}$  and OFS using a  $P(O_3)_{net}$  (NPOPR) detection system based on a dual-channel reaction chamber technique at the Guangdong Atmospheric Supersite of China in Heshan, Pearl River Delta (PRD) in autumn of 2023. The in-situ monitoring data were then compared with results from a zero-dimensional model incorporating the Master Chemical Mechanism (MCM v3.3.1). We tested the model performance by incorporating parameterization for 4 processes including  $HO_2$  uptake by ambient aerosols, dry deposition,  $N_2O_5$  uptake, and  $ClNO_2$  photolysis, and found that the discrepancies between the modelled  $P(O_3)_{net}$  ( $P(O_3)_{net\_Mod}$ ) and measured data ( $P(O_3)_{net\_Mea}$ ) did not change evidently, the maximum daily  $P(O_3)_{net}$  differed by  $\sim 44.8\%$ . Meanwhile, we found that the agreement of OFS assessment results between the direct measurements and the modelling study was lower in the  $P(O_3)_{net}$  rising phase (08:00-09:00, 63.6%) than in the  $P(O_3)_{net}$  stable phase (10:00-12:00, 72.7%) and  $P(O_3)_{net}$  declining phase (13:00-17:00, 72.7%). The results in this study reflected that unmeasured oxygenated VOCs (OVOCs) were the most effective compensating factor for the discrepancies between observed and computed  $P(O_3)_{net}$  and OFS, hinting clearly at the importance of quantitative understanding the total reactivity of VOCs in  $O_3$  chemistry.

## 1 Introduction

Ground-level ozone ( $O_3$ ) pollution has garnered widespread attention due to its adverse effects on human health (Chen et al., 2023), vegetation growth (Wang et al., 2017), and climate change (Li et al., 2016). Since the implementation of the *Air Pollution Prevention and Control Action Plan* by the State Council in 2013, particulate matter pollution in China has significantly decreased. However, ground-level  $O_3$  pollution remains severe, and  $O_3$  has become the primary pollutant affecting

air quality in China (*China Environmental Status Bulletin*, 2013–2024). The variation in ground-level O<sub>3</sub> concentration is influenced by local photochemical production, surface deposition, and transport processes, which the following equation can express:

$$\frac{\partial[\text{O}_3]}{\partial t} = P(\text{O}_3)_{\text{net}} - \frac{u_d}{H}[\text{O}_3] - \nu \cdot \nabla[\text{O}_3] \quad (1)$$

In Equation (1),  $\frac{\partial[\text{O}_3]}{\partial t}$  represents the change in O<sub>3</sub> concentration,  $P(\text{O}_3)_{\text{net}}$  denotes the net O<sub>3</sub> photochemical production rate,  $u_d$  is the O<sub>3</sub> deposition rate,  $H$  stands for the mixed layer height, and  $\nu$  represents the wind speed. The in-situ photochemical production of ground-level O<sub>3</sub> primarily results from the photochemical reactions of precursors volatile organic compounds (VOCs) and nitrogen oxides (NO<sub>x</sub>: NO+NO<sub>2</sub>) under sunlight. The sensitivity of O<sub>3</sub> formation to its precursors is defined as the O<sub>3</sub> formation sensitivity (OFS), which can be classified into three regimes: NO<sub>x</sub>-limited, VOC-limited, or mixed sensitivity (Seinfeld & Pandis, 2016; Sillman, 1999). In an NO<sub>x</sub>-limited regime, the VOC/NO<sub>x</sub> ratio is high and O<sub>3</sub> production is controlled primarily by changes in NO<sub>x</sub>. In a VOC-limited regime, the VOC/NO<sub>x</sub> ratio is low, so O<sub>3</sub> decreases with additional NO<sub>x</sub> and increases with higher VOCs. In the mixed-sensitivity regime, O<sub>3</sub> rises when either NO<sub>x</sub> or VOC emissions increase (Wang et al., 2019). The  $P(\text{O}_3)_{\text{net}}$  is a critical indicator for evaluating local photochemical formation. The budget analysis of ground-level O<sub>3</sub> production ( $P(\text{O}_3)$ ) and consumption ( $D(\text{O}_3)$ ) can be calculated using the following equations:

$$P(\text{O}_3) = k_{\text{HO}_2+\text{NO}}[\text{HO}_2][\text{NO}] + \sum_i k_{\text{RO}_{2i}+\text{NO}}[\text{RO}_{2i}][\text{NO}]\varphi_i \quad (2)$$

$$D(\text{O}_3) = k_{\text{O}^1\text{D}+\text{H}_2\text{O}}[\text{O}^1\text{D}][\text{H}_2\text{O}] + k_{\text{OH}+\text{O}_3}[\text{OH}][\text{O}_3] + k_{\text{HO}_2+\text{O}_3}[\text{HO}_2][\text{O}_3] + \sum_i (k_{\text{O}_3+\text{Alkene}_i}[\text{O}_3][\text{Alkene}_i] + k_{\text{OH}+\text{NO}_2}[\text{OH}][\text{NO}_2] + k_{\text{RO}_{2i}+\text{NO}_2}[\text{RO}_{2i}][\text{NO}_2]) \quad (3)$$

$$P(\text{O}_3)_{\text{net}} = P(\text{O}_3) - D(\text{O}_3) \quad (4)$$

Equations (2)–(4) illustrate the nonlinear dependence of the  $P(\text{O}_3)_{\text{net}}$  on the oxidation of precursors generating HO<sub>x</sub> (=OH+HO<sub>2</sub>) (Tong et al., 2025). Here, the  $P(\text{O}_3)_{\text{net}}$  is the difference between  $P(\text{O}_3)$  and  $D(\text{O}_3)$ ,  $k_{M+N}$  is the reaction rate constant between two molecules,  $\varphi_i$  represents the amount of NO<sub>2</sub> generated from the reaction of RO<sub>2*i*</sub> with NO<sub>2</sub>, and  $i$  denotes different RO<sub>2</sub> species. Currently, mainstream model simulation methods for calculating the  $P(\text{O}_3)_{\text{net}}$  primarily involve indirectly solving radical concentrations. However, existing models cannot fully characterize the complex radical cycling processes in the real atmosphere (Wei et al., 2023). Specifically, the incomplete mechanisms of RO<sub>x</sub> (=OH+HO<sub>2</sub>+RO<sub>2</sub>) sources are particularly prominent, and these missing mechanisms affect the accuracy of RO<sub>2</sub> and HO<sub>2</sub> radical estimations to varying degrees. These include the neglect of contributions from carbonyl compounds, HONO, and OVOCs (Xu et al., 2022), as well as incomplete mechanisms for heterogeneous reactions on aerosol surfaces (Yang et al., 2022), dry deposition (Zhang et al., 2003), nitrosyl chloride photolysis (Whalley et al., 2021), and isomerization of isoprene peroxy radicals (Kanaya et al., 2012) remain inadequately understood. These gaps lead to systematic biases in the simulated  $P(\text{O}_3)_{\text{net}}$  (Woodward-Massey et al., 2023; Tan et al., 2017; Tan et al., 2019), thereby affecting the accurate determination of OFS.

It is noteworthy that there is a strong causal relationship between the aforementioned mechanistic biases and the misjudgment of OFS. Studies by Baier et al. (2017) and Tan et al. (2019) found that the observation-based model (OBM) significantly underestimates  $P(\text{O}_3)_{\text{net}}$  under high  $\text{NO}_x$  conditions, leading to misjudgment of OFS. They pointed out that the unresolved VOC species and unspecified chemical mechanisms in the model are the primary causes of these biases. Similarly, Whalley et al. (2021) demonstrated that the zero-dimensional (box) model exhibits deviations in simulating  $P(\text{O}_3)_{\text{net}}$  under high VOCs concentrations. Further research by Wang et al. (2024b) highlighted that the contribution of unidentified VOCs reactivity in anthropogenic emissions to  $\text{O}_3$  formation is severely underestimated, and the missing VOC species and chemical mechanisms in existing models lead to biases in the determination of OFS. Such diagnostic biases in OFS may result in misjudgment of precursor emission reduction measures, thereby affecting the effectiveness of  $\text{O}_3$  pollution control.

Direct measurement of  $P(\text{O}_3)_{\text{net}}$  based on the dual-reaction chamber technique can address the aforementioned challenges. This concept was first proposed by Jeffries (1971), who suggested determining the real value of the  $P(\text{O}_3)_{\text{net}}$  in ambient air by comparing the difference in  $\text{O}_x(=\text{O}_3+\text{NO}_2)$  between a photochemical reaction chamber and a reference chamber. To date, several  $P(\text{O}_3)_{\text{net}}$  detection systems based on the dual-reaction chamber technique have been developed, referred to as measurement of  $\text{O}_3$  production sensor (MOPS),  $\text{O}_3$  production rate measurement system (O3PR),  $\text{O}_3$  production rates instrument (OPRs), net photochemical  $\text{O}_3$  production rate detection system (NPOPR), Mea-OPR, or  $\text{O}_3$  production rate-cavity ring-down spectroscopy system (OPR-CRDS) (Baier et al., 2015; Cazorla and Brune, 2009; Cazorla et al., 2012; Sadanaga et al., 2017; Sklaveniti et al., 2018; Hao et al., 2023; Wang Y. et al., 2024; Tong et al., 2025). Through practical applications in field observations, scholars generally agree that these detection systems offer rapid stability and high precision, with measurement uncertainties ranged from 10-30 %. Comparative studies have revealed that the underestimation of the simulated  $P(\text{O}_3)_{\text{net}}$  can reach up to 50 % (Cazorla et al., 2012), highlighting the limitations of existing models in characterizing radical chemistry.

More importantly, the  $P(\text{O}_3)_{\text{net}}$  detection system can diagnose OFS by quantifying changes in the measured  $P(\text{O}_3)_{\text{net}}$  induced by different precursors through precursor addition experiments. Sklaveniti et al. (2018) first detected OFS in Indiana by adding NO to the sampling line of  $P(\text{O}_3)_{\text{net}}$  detection systems, demonstrating the feasibility of directly measuring OFS with this device. Morino et al. (2023) combined a smog chamber with the  $P(\text{O}_3)_{\text{net}}$  detection systems to directly measure OFS under baseline environmental conditions in Tokyo during summer. Chen et al. (2024) proposed the OPR\_Adj parameter based on the  $P(\text{O}_3)_{\text{net}}$  detection systems, which, through normalization of photolysis rates, diagnosed that  $\text{O}_3$  photochemistry in Beijing is under VOCs control. These advancements indicate that the direct measurement method of OFS based on the  $P(\text{O}_3)_{\text{net}}$  not only measures the actual OFS in ambient air but also quantifies the discrepancies between models and measurements.

In this study, we employed the developed NPOPR detection system based on the dual-reaction chamber technique to measure the  $P(\text{O}_3)_{\text{net}}$  and OFS at the Guangdong Atmospheric Supersite of China in Heshan City, Pearl River Delta (PRD), in October 2023. Based on the observational data, we used the box model equipped with the Master Chemical Mechanism (MCM v3.3.1) to simulate the radical chemistry during the observation period. We compared and investigated the differences and influencing factors between the model-simulated values (abbreviated as  $P(\text{O}_3)_{\text{net\_Mod}}$ ) and the directly measured values

(abbreviated as  $P(\text{O}_3)_{\text{net\_Mea}}$ ) in calculating the  $P(\text{O}_3)_{\text{net}}$  and assessing OFS.

## 2 Methods and materials

### 2.1 Field measurements

Field observations were continuously conducted from 4–26 October 2023 at the Guangdong Atmospheric Supersite of China in Heshan City, located in northern Jiangmen, Guangdong Province (112.93°E, 22.73°N). The supersite is situated in the downwind area of Guangzhou, Foshan, and Dongguan, a region characterized by active secondary reactions and serving as a receptor for pollution transported from the industrial and urban centers (Luo et al., 2025; Huang et al., 2020). The surrounding area is primarily composed of farmland conservation zones and forested regions, with no major industrial sources. The supersite sits on a small mountain ~ 3 km from the nearest area heavy traffic corridor; at the observed mean wind speed of 2.8 m s<sup>-1</sup>, the air mass from the corridor takes ~ 17 min to arrive. This separation limits spatial heterogeneity in both emissions and chemical composition, making the site well-suited for comprehensive monitoring and research on complex regional air pollution in the PRD (Mazaheri et al., 2019). The geographical location is shown in Fig. S1.

The  $P(\text{O}_3)_{\text{net}}$  detection system (NPOPR), based on the dual-reaction chamber technique, was used to monitor the  $P(\text{O}_3)_{\text{net}}$  and OFS. This system has been successfully applied in multiple field observation campaigns (Hao et al., 2023; Zhou et al., 2024a; 2024b). The detection system consists of a sampling unit, a monitoring unit, and a data acquisition unit. Ambient air passes through a Teflon particulate filter (7592-104, Whatman, UK) to remove particles larger than 2 μm before entering the dual chambers. The reaction chamber and the reference chamber are made of two identical quartz tubes (inner diameter: 190.5 mm, length: 700 mm, wall thickness: 5 mm). Unlike the reaction chamber, which allows ultraviolet light to penetrate and initiate photochemical reactions, the reference chamber is covered with an ultraviolet protective film (SH2CLAR, 3M, Japan) to block light with wavelengths below 390 nm, thereby preventing O<sub>3</sub> formation in the reference chamber. A custom circuit control system alternates the gas flow between the reaction chamber and the reference chamber into the NO reaction tube every 2 minutes, where the O<sub>3</sub> is converted to NO<sub>2</sub>, which is then introduced into a Cavity Attenuated Phase Shift (CAPS)-NO<sub>2</sub> analyzer (Aerodyne Research, Inc., Billerica MA, USA). The gas not introduced into the NO reaction tube is expelled through an auxiliary pump. The data acquisition system detects NO<sub>2</sub>, including both ambient NO<sub>2</sub> and NO<sub>2</sub> converted from O<sub>3</sub>. By combining the average residence time ( $\tau$ ) of the gas in the chambers and the difference in O<sub>x</sub> ( $\Delta\text{O}_x = \Delta(\text{O}_3 + \text{NO}_2)$ ) between the two chambers, the  $P(\text{O}_3)_{\text{net\_Mea}}$  can be calculated as Eq. (5):

$$P(\text{O}_3)_{\text{net\_Mea}} = P(\text{O}_x) = \frac{\Delta\text{O}_x}{\tau} = \frac{[\text{O}_x]_{\text{reaction}} - [\text{O}_x]_{\text{reference}}}{\tau} \quad (5)$$

The mean residence time in the reaction chamber is 0.15 h at the air flow rate of 2.1 L min<sup>-1</sup>, and the limit of detection (LOD) of the NPOPR detection system is 0.86 ppbv h<sup>-1</sup> at the sampling air flow rate of 2.1 L min<sup>-1</sup>, which is obtained as three times the measurement error of  $P(\text{O}_3)_{\text{net}}$  (Hao et al., 2023). The time resolution of the  $P(\text{O}_3)_{\text{net}}$  measurement is 4 min. Our previous study demonstrated that  $P(\text{O}_3)_{\text{net}}$  more directly reflects the photochemical O<sub>3</sub> formation potential from local precursors

and is less affected by transport processes compared to O<sub>3</sub> concentrations (Zhou et al., 2024b). The measurement error of  $P(O_3)_{net}$  is determined by the uncertainty in the Ox mixing ratio estimated for both the reaction and reference chambers. This uncertainty combines (i) the measurement uncertainty of the CAPS-NO<sub>2</sub> monitor used to derive Ox and (ii) the error induced by light-enhanced O<sub>3</sub> loss inside the chambers. Taken together, these contributions define the measurement precision of the NPOPR detection system. In addition, the measurement accuracy of the NPOPR detection system is 13.9 %, corresponding to the maximum systematic error arising from photochemical O<sub>3</sub> production in the reference chamber (Hao et al., 2023; Zhou et al., 2024b); details are given in Sect. S1 in the supplementary materials.

An additional system for the addition of NO or VOCs was added to the NPOPR sampling unit to assess OFS. The OFS was assessed by measuring the changes in  $P(O_3)_{net}$  induced by the addition of NO or VOCs, enabling the direct measurement of OFS. A schematic diagram of the detection system is shown in Fig. S2. In the experiments for determining OFS through direct measurements (conducted daily from 8:00-18:00), each cycle lasted 1 hour. The first 20 minutes involved the addition of NO (denoted as  $P(O_3)_{net\_Mea}^{+NO}$ ), the next 20 minutes measured the ambient baseline ( $P(O_3)_{net\_Mea}$ ), and the final 20 minutes involved the addition of VOCs (denoted as  $P(O_3)_{net\_Mea}^{+VOCs}$ ). Following Carter et al. (1995) and Wu et al. (2022), we select VOCs surrogates for the OFS measurement on the basis of ambient measurements previous to the measurements. From 4–11 October, the tracer mixture was formulated from the average daytime total VOC reactivity measured during 20 September–3 October 2023, and isopentane served as the alkane surrogate, ethylene and isoprene as the alkene surrogates, and toluene as the aromatic surrogate. For 13–26 October 2023, we used the average daytime total VOC reactivity obtained during 4–11 October 2023; ethylene represented non-methane hydrocarbons (NMHCs) and formaldehyde represented oxygenated VOCs (OVOCs). Each surrogate was mixed in proportion to its category's share of the ambient reactivity, and the effective precursor strength (NO or VOCs) should increase by 20 % relative to the original ambient level. For data treatment, we first interpolated  $P(O_3)_{net\_Mea}^{+NO}$ ,  $P(O_3)_{net\_Mea}$ , and  $P(O_3)_{net\_Mea}^{+VOCs}$  to 4-min resolution and then averaged them over 1 h to suppress data fluctuations. We caution that this 1-hour averaging may smooth out transient responses in the measured  $P(O_3)_{net}$ . The sensitivity of O<sub>3</sub> production to precursor changes was quantified using the measured OFS, derived from the incremental reactivity (IR) index. IR is defined as the change in  $P(O_3)_{net}$  per unit change in precursor concentration ( $\Delta S(X)$ ): a negative IR value indicates that reducing the precursor concentration increases O<sub>3</sub> production (e.g., decrease NO<sub>x</sub> would increase O<sub>3</sub> through OH mediate effect), while a larger absolute IR value suggests higher sensitivity of O<sub>3</sub> production to changes in the precursor. The IR was calculated as:

$$IR = \frac{P(O_3)_{net\_Mea}^{+X} - P(O_3)_{net\_Mea}}{\Delta S(X)} = \frac{\Delta P(O_3)_{net\_Mea}^{+X}}{\Delta S(X)} \quad (6)$$

where X represents VOCs or NO,  $\Delta P(O_3)_{net}^{+X}$  represents the  $P(O_3)_{net}$  values measured during the NO or VOCs addition period minus the  $P(O_3)_{net}$  values measured when only injecting ambient air.  $\Delta S(X)$  represents the concentration of the NO or VOCs precursor changed during the corresponding measurement period. We define the transition regime as the region over which the IR shows a simultaneous increase or decrease upon addition of both VOCs and NO.

In addition to  $P(\text{O}_3)_{\text{net}}$  and OFS, hourly data such as  $\text{PM}_{2.5}$ ,  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ , carbon monoxide ( $\text{CO}$ ), photolysis rates ( $j_{\text{O}^1\text{D}}$ ,  $j_{\text{NO}_2}$ ,  $j_{\text{H}_2\text{O}_2}$ ,  $j_{\text{NO}_3\text{-M}}$ ,  $j_{\text{NO}_3\text{-R}}$ ,  $j_{\text{HONO}}$ ,  $j_{\text{HCHO-M}}$ ,  $j_{\text{HCHO-R}}$ ),  $\text{HONO}$ , and VOCs concentrations were monitored (more details about the measurements are shown in Table S1). Hourly observations of conventional meteorological parameters, such as temperature, pressure, relative humidity, wind direction, and wind speed, were sourced from the European Centre for Medium-Range Weather Forecasts (ECMWF). The planetary boundary layer height (PBLH) data used in the model here was obtained from the web portal of the Real-time Environmental Applications and Display sYstem (READY) of the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<https://ready.arl.noaa.gov/READYamet.php>).

## 2.2 Box model simulation

This study employed an observation-constrained zero-dimensional photochemical reaction model (Observed 0-D box model) to simulate atmospheric photochemical processes. The chemical mechanism module is the core of the box model, and most mainstream studies use the Master Chemical Mechanism (MCM) nested within the model, incorporating processes such as solar radiation, boundary layer height, atmospheric photochemistry, and dry deposition (Zhang et al., 2022). The OBM model used in this study is AtChem2 (<https://atchem.leeds.ac.uk/webapp/>), which is equipped with the Master Chemical Mechanism (MCM v3.3.1: <https://mcm.york.ac.uk/MCM>) to simulate  $\text{O}_3$  and radical chemistry and analyze their budgets (Wang et al., 2022a; Sommariva et al., 2020). The model includes approximately 143 VOCs, 6,700 chemical species, and over 17,000 reactions. Hourly resolution observational data of  $\text{O}_3$ ,  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{CO}$ ,  $\text{SO}_2$ ,  $\text{HONO}$ , VOCs (in total 82 species), meteorological parameters (e.g., temperature, relative humidity, pressure, and boundary layer height), and photolysis rates were used as model constraints. The constraints are applied to the model every 1 h, with no free concentration evolution in between. Photolysis rates for unmeasured species were calculated using the Tropospheric Ultraviolet and Visible Radiation Model (TUV v5.3) (Table S2). Additionally, to avoid unreasonable increases in the concentrations of constrained species, a dilution rate of  $1/86400 \text{ s}^{-1}$  was applied. Before the simulation, the model underwent a 48-hour pre-run to stabilize unmeasured species (e.g., radicals).

The configuration of model mechanisms was informed by previous research, with a particular focus on the dry deposition processes of key species (e.g.,  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$ , PAN, and HCHO), the heterogeneous uptake reactions of  $\text{HO}_2$  and  $\text{N}_2\text{O}_5$ , and the  $\text{Cl}^\cdot$  chemistry mechanism. Dry deposition is a critical pathway for the transfer of atmospheric pollutants from the gas phase to the Earth's surface, significantly influencing the concentration distribution and removal of regional pollutants. Many models have already incorporated this atmospheric physical process (Ma et al., 2022; Chen et al., 2020a). Although the heterogeneous uptake of  $\text{HO}_2$  is not the dominant loss pathway of  $\text{HO}_2$ , it accounts for approximately 10–40 % of global  $\text{HO}_2$  loss (Li et al., 2019); as a termination reaction, its direct impact on photochemical  $\text{O}_3$  production is non-negligible. Studies have shown that including the heterogeneous uptake mechanism of  $\text{HO}_2$  in simulations reduces  $P(\text{O}_3)_{\text{net}}$  concentration and alters the sensitivity to VOCs (Zhou et al., 2021; Dyson et al., 2022). Additionally,  $\text{Cl}^\cdot$  enhances atmospheric oxidation, accelerating the  $\text{OH-HO}_2\text{-RO}_2$  reaction cycle (Ma et al., 2023). By incorporating these mechanisms, this study aims to more accurately simulate the atmospheric chemical processes and their impacts on pollutant concentrations in the PRD region (Zhou

et al., 2024a). The configurations of each scenario are as follows: Case A considers only the simplified chemical reaction mechanism from the MCM, excluding dry deposition and heterogeneous reactions; Case B incorporates the HO<sub>2</sub> uptake by ambient aerosols based on Case A; Case C further includes the dry deposition processes of key species on top of Case B; and Case D<sub>1</sub> extends Case C by adding the N<sub>2</sub>O<sub>5</sub> uptake mechanism and Cl<sup>•</sup> related photochemical reactions. Detailed simulation parameter settings can be found in our previous study (Zhou et al., 2024a) and the supplementary information (Table S3).

## 2.3 Model performance evaluation

The Index of Agreement (IOA) was used to evaluate the simulation performance (Li et al., 2021).

$$IOA = 1 - \frac{\sum_{i=1}^n (O_i - S_i)^2}{\sum_{i=1}^n (|O_i - \bar{O}| + |S_i - \bar{O}|)^2} \quad (7)$$

where  $O_i$  and  $S_i$  represent the observed and simulated values, respectively,  $\bar{O}$  denote the mean of the observed values, and  $n$  is the number of samples. The IOA ranges from 0 to 1, with higher values indicating better agreement between observed and simulated values. In addition to the IOA, the Pearson correlation coefficient (R), mean bias (MB), normalized mean bias (NMB), root mean square error (RMSE), mean fractional bias (MFB) and mean fractional error (MFE) were used to evaluate the consistency between observed and simulated values (Table S7).

## 2.4 $k_{OH}$

Total OH reactivity ( $k_{OH}$ ) is a crucial indicator of atmospheric chemical cycling and oxidative capacity (Gilman et al., 2009).  $k_{OH}$  is defined as the sum of the products of the concentrations of all reactive species  $X_i$  that can react with OH radicals and their respective reaction rate constants, calculated as follows:

$$k_{OH} = \sum_i k_{OH+X_i} \cdot [X_i] \quad (8)$$

where  $X_i$  includes CO, NO<sub>x</sub>, and VOCs, among others, and  $k_{OH+X_i}$  is the reaction rate constant (s<sup>-1</sup>) between reactive species  $X_i$  and OH radicals.

## 2.5 OFP

O<sub>3</sub> Formation Potential (OFP) is an indicator used to measure the relative contribution of different VOC species to ground-level O<sub>3</sub> formation (Wu et al., 2020). The formula for OFP is as follows:

$$OFP = [VOCs]_i \times MIR_i \quad (9)$$

where  $[VOCs]_i$  represents the concentration of a specific VOC species  $i$  (μg m<sup>-3</sup>), and MIR represents the maximum incremental reactivity of the VOC species  $i$  (g<sub>O<sub>3</sub></sub>/g<sub>VOC</sub>). MIR is used to characterize the increase in O<sub>3</sub> production per unit increase in VOCs under conditions where O<sub>3</sub> formation is most sensitive to VOCs.

## 2.6 Absolute $P(\text{O}_3)_{\text{net}}$ sensitivity

We calculated the modelled OFS using the absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity, adapted from the logarithmic derivative approach of Sakamoto et al. (2019). It is defined as the change in  $P(\text{O}_3)_{\text{net}}$  with respect to the natural logarithm of  $\text{O}_3$  precursor concentrations. This method facilitates the quantitative assessment of how reductions in  $\text{O}_3$  precursors contribute to the overall reduction of  $P(\text{O}_3)_{\text{net}}$  over a period or within a region. The formula is as follows:

$$\text{Absolute } P(\text{O}_3)_{\text{net}} = \frac{dP(\text{O}_3)_{\text{net}}}{d \ln[X]} \quad (10)$$

In the equation,  $[X]$  represents  $\text{NO}_x$  or VOCs. A positive absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity indicates that reducing the precursor will lead to a decrease in the  $P(\text{O}_3)_{\text{net}}$ . In contrast, a negative value indicates that reducing the precursor will lead to an increase in the  $P(\text{O}_3)_{\text{net}}$  (Dyson et al., 2022). In this study, the analysis of absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity was conducted using the box model through an analytical calculation approach that does not involve artificial perturbation of precursor concentrations.

## 3 Results and discussion

### 3.1 Overview of observation campaign

The Supplementary Materials (SM, Fig. S3, S4, and Table S4, S5) provide the time series plots, diurnal variation, and daytime averages (daytime: 6:00–18:00) of meteorological parameters, conventional pollutants, photolysis rate constants,  $\text{NO}$ ,  $P(\text{O}_3)_{\text{net}}$  and hourly VOCs concentrations from 4–26 October 2023, at the Guangdong Atmospheric Supersite of China. The site was located downwind of the Guangzhou-Foshan area, with atmospheric pollutants primarily originating from the northeast. To access daily  $\text{O}_3$  pollution levels, the maximum daily 8-hour average  $\text{O}_3$  concentration (MDA8) was employed, in accordance with the Technical Specification for Ambient Air Quality Evaluation (Trial) (HJ 663-2013). In this study, days with MDA8- $\text{O}_3$  concentration exceeding the Class II limit stipulated by the Ambient Air Quality Standards (GB3095-2012) were defined as  $\text{O}_3$  pollution days (with MDA8- $\text{O}_3$  concentration limit of  $160 \mu\text{g m}^{-3}$  (equivalent to approximately 81.6 ppbv at  $25^\circ\text{C}$ ), while others were defined as normal days.

During the whole observation period, there were 6  $\text{O}_3$  pollution days (15–17 and 24–26 October 2023). The maximum  $\text{O}_3$  mixing ratio (136.5 ppbv) occurred at 15:00 on 25 October 2023, while the maximum  $P(\text{O}_3)_{\text{net}}$  ( $53.7 \text{ ppbv h}^{-1}$ ) occurred at 10:00 on 24 October 2023. Diurnal variation plots show that  $\text{O}_3$  and  $P(\text{O}_3)_{\text{net}}$  exhibited single-peak patterns, with  $\text{O}_3$  peaking at 15:00 and  $P(\text{O}_3)_{\text{net}}$  peaking between 9:00–10:00. On  $\text{O}_3$  pollution days, the daytime average mixing ratios concentrations of  $\text{O}_3$  and  $P(\text{O}_3)_{\text{net}}$  during the observation period were  $63.2 \pm 37.6 \text{ ppbv}$  and  $14.4 \pm 13.8 \text{ ppbv h}^{-1}$ , respectively, both approximately twice as high as on normal days (daytime average  $\text{O}_3$ :  $30.9 \pm 22.9 \text{ ppbv}$ ; daytime average  $P(\text{O}_3)_{\text{net}}$ :  $7.2 \pm 9.4 \text{ ppbv h}^{-1}$ ). The maximum values of directly measured  $P(\text{O}_3)_{\text{net}}$  in different ambient environments in previous studies are listed in Table S6, ranging from 10.5 to 100 ppbv  $\text{h}^{-1}$ , and the measured  $P(\text{O}_3)_{\text{net}}$  values in this study fall within this range, demonstrating the reasonableness of the values measured in this study.

As shown in Fig. S4, the diurnal variation of parameters on  $\text{O}_3$  pollution days and normal days indicates that the nighttime



background concentrations/mixing ratios of O<sub>3</sub> precursors (TVOC and NO<sub>x</sub>) are higher on O<sub>3</sub> pollution days. However, during the period of strongest sunlight (11:00-14:00), the concentrations/mixing ratios of TVOC and NO<sub>x</sub> on O<sub>3</sub> pollution days are lower than those on normal days. Specifically, on O<sub>3</sub> pollution days, the TVOC concentration is 11.4 µg m<sup>-3</sup>, and the NO<sub>x</sub> concentration is 13.5 ppbv, while on normal days, the TVOC concentration is 13.7 µg m<sup>-3</sup>, and the NO<sub>x</sub> concentration is 14.8 ppbv. As the PBLH on O<sub>3</sub> pollution days and normal days does not differ statistically during the period of strongest solar radiation (11:00-14:00, *t-test*, *p*=0.45, see Fig. S4k), the lower daytime concentrations/mixing ratios of O<sub>3</sub> precursors on O<sub>3</sub> pollution days than on normal days may be due to higher photolysis rates on O<sub>3</sub> pollution days (see Fig. S4a). The diurnal variation of NO concentration on O<sub>3</sub> pollution days showed an early morning peak at 8:00, rising to 12.2 ppbv and then decreasing to 1.6 ppbv. By comparing the diurnal variation data between O<sub>3</sub> pollution days and normal days, we found that both O<sub>3</sub> mixing ratios and *P*(O<sub>3</sub>)<sub>net</sub> values were significantly higher on O<sub>3</sub> pollution days, particularly during the daytime (6:00-18:00). This phenomenon aligns with the conclusion that high temperatures, low humidity, strong radiation, and stable weather conditions favor O<sub>3</sub> pollution formation.

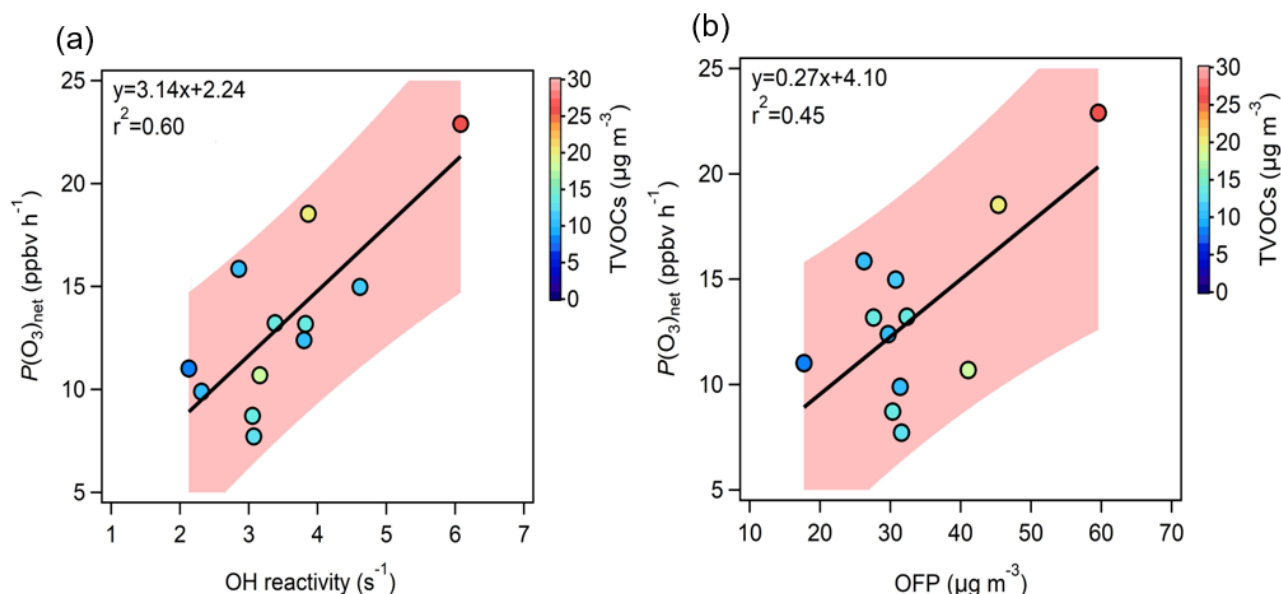
### 3.2 Characteristics of VOC concentrations and composition

This study analyzed 110 VOC species, examining the contributions of different categories to TVOC concentrations, *k*<sub>OH</sub>, and daily OFP. We also identified the top 10 VOC species contributing to these three indicators (Fig. S5), aiming to explore the atmospheric presence, chemical reactivity, and environmental impact of VOCs. Additionally, this study used two classification methods to group VOC species. Method 1 divided VOCs into alkynes (1 species), alkanes (27 species), alkenes (11 species), aromatic hydrocarbons (17 species), OVOCs (20 species), halogenated hydrocarbons (33 species), and sulfur-containing VOCs (1 species). Method 2 categorized VOCs into BVOC (Biogenic Volatile Organic Compounds), OVOCs (Oxygenated Volatile Organic Compounds), and AVOCs/NMHC (Anthropogenic Volatile Organic Compounds), with specific classifications shown in Table S4.

During the observation period, the daily average TVOC concentration ranged from 7.2 to 28.9 µg m<sup>-3</sup>. OVOCs contributed the most (40.8 %), followed by halogenated hydrocarbons (20.8 %), aromatic hydrocarbons (18.3 %), alkanes (17.9 %), alkenes (1.7 %), and alkynes (0.5 %). The *k*<sub>OH</sub> average value was 12.1±3.9 s<sup>-1</sup>, primarily contributed by OVOCs (62.9 %), followed by halogenated hydrocarbons (10.8 %), alkenes (10.4 %), aromatic hydrocarbons (9.8 %), alkanes (6.0 %), and alkynes (0.1 %). Among the alkenes in the known MCM mechanism, ethylene, as an indicator of VOCs, had the highest proportion, accounting for 10.7 % of alkenes *k*<sub>OH</sub> and 2.8 % of NMHC *k*<sub>OH</sub>. Formaldehyde, another VOCs indicator, was the most dominant species in OVOCs *k*<sub>OH</sub>, contributing about 13.3 %. Among VOC species, OVOCs contributed the most to OFP (51.6 %), followed by aromatic hydrocarbons (32.9 %), alkenes (8.0 %), alkanes (6.9 %), halogenated hydrocarbons (0.5 %), and alkynes (0.2 %). The analysis results show that although halogenated hydrocarbons dominate VOCs concentration emissions, their contribution to O<sub>3</sub> pollution is low. In contrast, alkenes, despite their lower contribution to VOCs concentration emissions, are important precursors for O<sub>3</sub> formation. Based on the comprehensive analysis of VOCs concentration, *k*<sub>OH</sub>, and OFP, OVOCs and aromatic hydrocarbons significantly contribute to O<sub>3</sub> formation and should be prioritized as key VOC species

for O<sub>3</sub> pollution control in the PRD region. This result aligns with other related studies in the PRD, such as those in Shenzhen (Yu et al., 2020; Guanghe et al., 2022), Guangzhou (Pei et al., 2022), and Jiangmen (Jing et al., 2024), which indicate that OVOCs and aromatic hydrocarbons are key VOC species for O<sub>3</sub> formation. As OVOCs arise from both direct (anthropogenic and natural) emissions and secondary atmospheric formation (Lyu et al., 2024; Yuan et al., 2012), precluding a direct quantification of their respective contributions to O<sub>3</sub> formation. Nevertheless, our previous work showed that anthropogenic primary VOCs correlate most closely with instantaneous  $P(\text{O}_3)_{\text{net}}$  on O<sub>3</sub> pollution days, and urban anthropogenic OVOC emissions markedly enhance both oxidative capacity and O<sub>3</sub> production (Qian et al., 2025; Wang et al., 2024b).

Overall, toluene, m/p-xylene, formaldehyde, 2-hexanone, ethyl acetate, and tetrahydrofuran consistently ranked in the top 10 VOC species in terms of concentration,  $k_{\text{OH}}$  and OFP contribution. These VOC species mainly originate from human activities, such as industrial production, solvent use, traffic emissions, and fuel combustion, highlighting the significant impact of anthropogenic sources on O<sub>3</sub> pollution (Cai et al., 2010; Yang et al., 2023; Zheng et al., 2019).



**Figure 1: Correlation between measured  $P(\text{O}_3)_{\text{net}}$  ( $P(\text{O}_3)_{\text{net\_Mea}}$ ) and (a) total OH reactivity ( $k_{\text{OH}}$ ) and (b) O<sub>3</sub> Formation Potential (OFP). The shaded area in the figure represents the confidence interval (90 %) of the fitting line between  $P(\text{O}_3)_{\text{net}}$  and  $k_{\text{OH}}$ , and between  $P(\text{O}_3)_{\text{net}}$  and OFP.**

Figure 1 shows the correlation between  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $k_{\text{OH}}$  and OFP (calculated using the daytime average data during the observation period). Data outside the confidence interval may be due to the fact that the calculation of  $k_{\text{OH}}$  and OFP did not fully consider the environmental conditions and atmospheric chemistry complexity at the observation site (Zhang et al., 2024; Yadav et al., 2024). The color of the scatter points represents the TVOC concentration. The  $r^2$  values between  $P(\text{O}_3)_{\text{net}}$  measurements and  $k_{\text{OH}}$  and OFP are 0.6 and 0.5, respectively, indicating that VOCs with higher  $k_{\text{OH}}$  and OFP significantly enhance the  $P(\text{O}_3)_{\text{net}}$ .

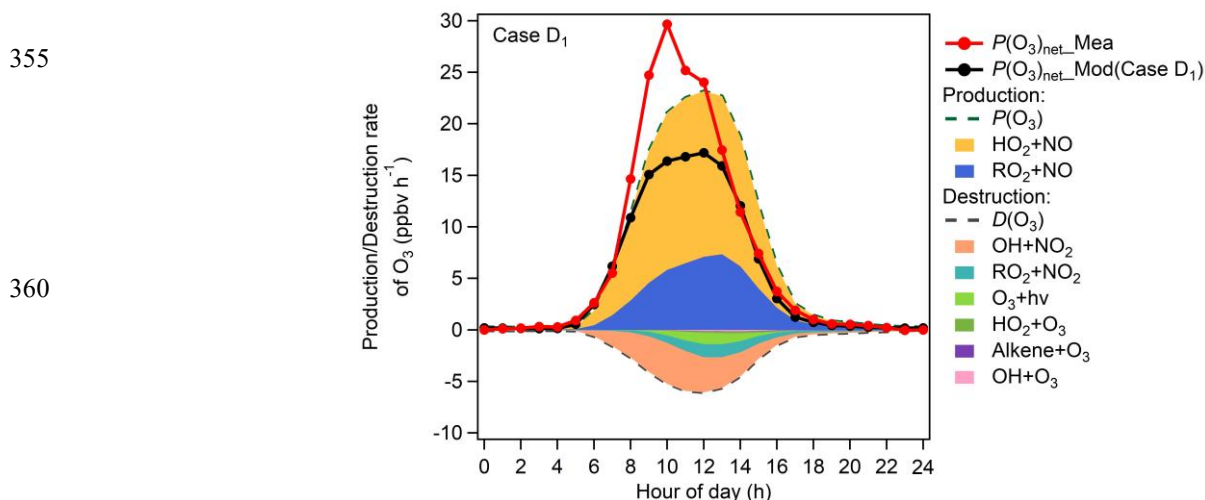
### 3.3 Comparison and optimization of simulated and measured $P(\text{O}_3)_{\text{net}}$ values

Based on our previous research (Zhou et al., 2024a), we named the scenario considering only the current chemical reaction mechanism from the MCM v3.3.1 in the box model as Case A. Subsequently, we gradually incorporated the  $\text{HO}_2$  uptake by ambient aerosols, dry deposition,  $\text{N}_2\text{O}_5$  uptake, and  $\text{ClNO}_2$  photolysis mechanisms into the MCM mechanism in the box model, implemented as modelling scenarios labeled Case B, Case C, and Case D<sub>1</sub>. The specific parameter settings for each scenario are shown in Table S3. The time series and diurnal variations of the  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  for Cases A–D<sub>1</sub> are shown in Fig. S7. To evaluate the model's performance,  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  data were used to calculate IOA, R, MB, NMB, RMSE, MFB and MFE values under different scenarios (Table S7). The IOA values between  $P(\text{O}_3)_{\text{net\_Mod}}$  and  $P(\text{O}_3)_{\text{net\_Mea}}$  was  $> 0.86$  for all cases, and R ranged from 0.84 to 0.98, indicating that the model can reasonably reproduce the variations in  $P(\text{O}_3)_{\text{net}}$ . However, MB and NMB were  $-3.0$  to  $-2.4$  ppbv  $\text{h}^{-1}$  and  $-30.5$  % to  $-24.9$  %, respectively, revealing a systematic underestimation of  $P(\text{O}_3)_{\text{net}}$ . RMSE ranged from 7.0 to 7.2 ppbv  $\text{h}^{-1}$ , while MFB and MFE ranged from  $-3.1$  % to  $-1.7$  % and 53.8 % to 55.5 %, respectively. These results suggest that, although the model captures the overall trends well, there is room to reduce simulation biases.

In all modelling scenarios from Case A–Case D<sub>1</sub>,  $P(\text{O}_3)_{\text{net\_Mod}}$  values were generally lower than  $P(\text{O}_3)_{\text{net\_Mea}}$  (see Fig. 3). Although the correlation between  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  was good (Fig. S9,  $r^2=0.73$ ), even after incorporating mechanisms that may affect  $\text{O}_3$  production simulation biases into the box model (labeled as Case D<sub>1</sub>), the simulated daytime average  $P(\text{O}_3)_{\text{net\_Mod}}$  was still 3.4 ppbv  $\text{h}^{-1}$  lower than  $P(\text{O}_3)_{\text{net\_Mea}}$  (26.3 % bias), with a peak deviation of up to 13.3 ppbv  $\text{h}^{-1}$  (44.8 %), as shown in Fig. 2. We defined the difference between  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  as  $P(\text{O}_3)_{\text{net\_Missing}}$ , and its distribution of each day is shown in Fig. S10. Due to the measurement error of HONO by MARGA in this study, the modelled  $P(\text{O}_3)_{\text{net}}$  tends to be underestimated (as shown in SM: S2); thus, we define the  $P(\text{O}_3)_{\text{net\_Missing}}$  obtained from all simulation cases as the upper-limit values. During the observation period, 7–10 October and 18–22 October were rainy days, with a median  $P(\text{O}_3)_{\text{net\_Missing}} < 1.1$  ppbv  $\text{h}^{-1}$ ; therefore, these days were excluded when calculating the diurnal variations of different  $\text{O}_3$  production and consumption pathways. On non-rainy days, the averaged daytime  $P(\text{O}_3)_{\text{net\_Missing}}$  reached  $4.5 \pm 7.6$  ppbv  $\text{h}^{-1}$ , accounting for 31% of the total measured  $P(\text{O}_3)_{\text{net}}$ . Furthermore, the enlarged days in Fig. 2 reveal day-to-day variations in  $P(\text{O}_3)_{\text{net\_Mod}}$  across the different cases, underscoring that the overall diurnal pattern described above does not resolve this variability. The averaged daytime  $P(\text{O}_3)_{\text{net\_Missing}}$  values on  $\text{O}_3$  pollution days were statistically higher than those on normal days ( $t$ -test,  $p < 0.05$ ), suggesting that while the supplementary mechanisms explored in the model may contribute to some extent, they are unlikely to be the dominant cause of the  $P(\text{O}_3)_{\text{net\_Missing}}$ .

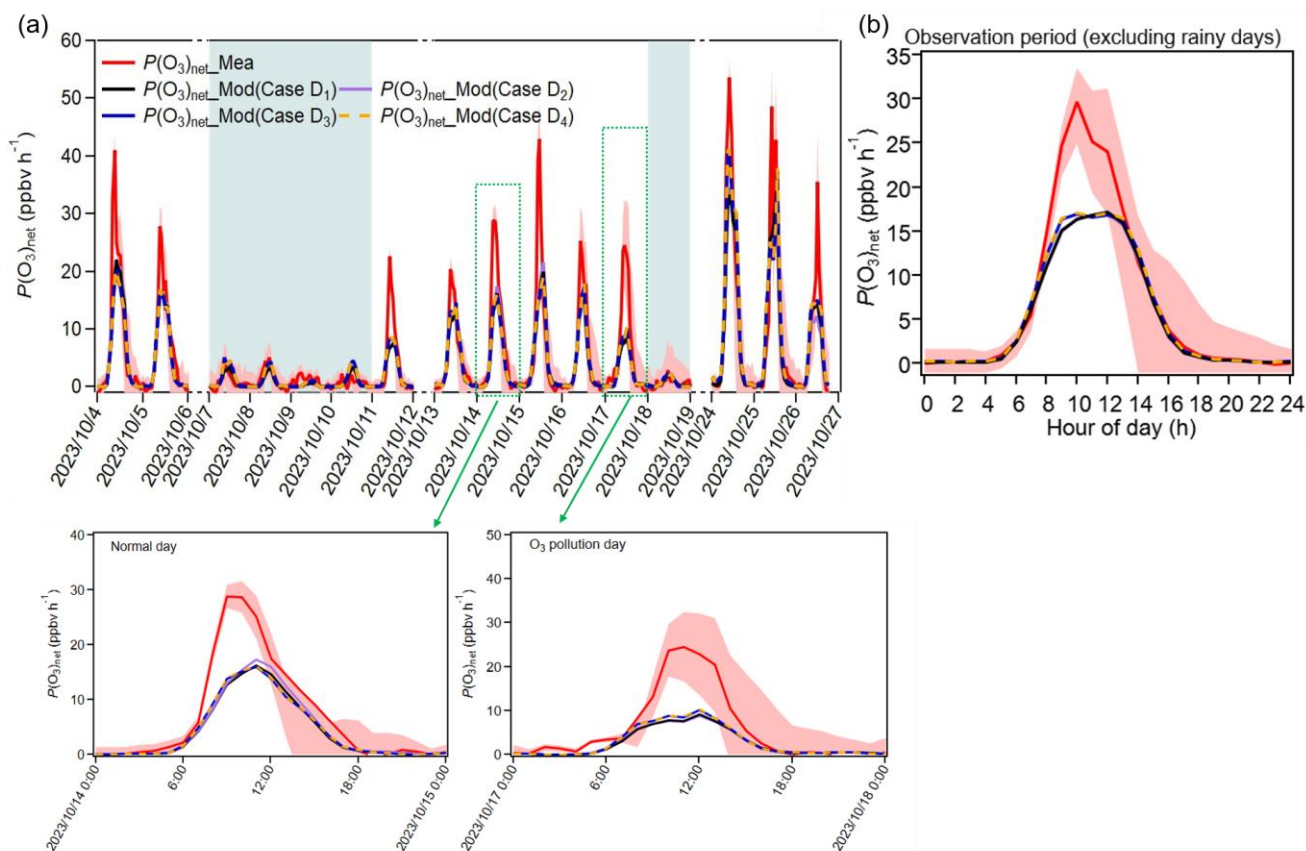
We further explore the possible reasons for the discrepancies between  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  using the modelling results of Case D<sub>1</sub>. The ratio of cumulative  $P(\text{O}_3)_{\text{net\_Mea}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  derived from Case D<sub>1</sub> was 1.4, calculated by summing the daytime data with 1 h resolution during the observation period. This result is consistent with previous findings: Cazorla and Brune (2009) reported a ratio of 1.3, and Ren et al. (2013) and Hao et al. (2023) both reported 1.4. As shown in Fig. 2, the  $\text{HO}_2 + \text{NO}$  reaction dominates  $\text{O}_3$  production, accounting for 71.4 % of total  $\text{O}_3$  production pathways. In contrast, the

main  $O_3$  loss pathways were  $OH+NO_2$  and  $RO_2+NO_2$ , accounting for 67.9 % and 16.5 % of total  $O_3$  consumption pathways, respectively. The importance of the  $HO_2/RO_2$  reaction pathways indicates that simulation biases in  $HO_2$  or  $RO_2$  will propagate into  $P(O_3)_{net\_Mod}$ .



**Figure 2: Diurnal variations (excludes rainy days) of  $O_3$  production and destruction rates modelled in Case D<sub>1</sub>, and measured ( $P(O_3)_{net\_Mea}$ ) and modelled ( $P(O_3)_{net\_Mod}$ )  $P(O_3)_{net}$ .**

To explore the possible drivers of  $P(O_3)_{net\_Missing}$ , we correlated it with TVOC,  $NO_x$ ,  $J_{O1D}$ ,  $T$ , and  $O_x$  separately for  $O_3$  pollution days and normal days (Fig. S11). On  $O_3$  pollution days,  $P(O_3)_{net\_Missing}$  exhibited a moderate positive correlation with VOCs ( $r^2=0.4$ ,  $R=0.2$ ,  $t=2.9$ ) and  $NO_x$  ( $r^2=0.5$ ,  $R=0.2$ ,  $t=3.8$ ), confirming that the  $P(O_3)_{net\_Missing}$  is larger at higher precursor concentrations/mixing ratios (both  $t > \text{critical } 2.0$ ,  $p < 0.05$ ), consistent with earlier box-model studies (Whalley et al., 2021; Ren et al., 2013; Zhou et al., 2024a). A moderate positive correlation is also found with  $J_{O1D}$  on both  $O_3$  pollution days and normal days, with  $r^2$  values of 0.5 and 0.4, respectively. On normal days all correlations collapse ( $r^2 < 0.2$ ,  $p > 0.1$ ), implying that the model deficit is not tied to the measured precursors under low- $NO_x$  conditions and may instead related to the missing mechanisms for unmeasured photolabile VOCs. Wang et al. (2022b) indicates that constraining OVOCs in the model is crucial for the accuracy of  $P(O_3)_{net\_Mod}$ , and photochemical models without OVOCs constraints significantly underestimate  $P(O_3)_{net}$ . In our previous study on the industrial city of Dongguan (Zhou et al., 2024a), we used parameter equations developed by Wang et al. (2024a; 2024b) to quantify the impact of missing  $k_{OH}$  on  $P(O_3)_{net\_Missing}$  and qualitatively tested the potential compensating effects of unmeasured OVOCs on  $P(O_3)_{net\_Missing}$ . This study measured more VOC species compared to the Dongguan campaign (Table S4). Therefore, we further compensate for the Case D<sub>1</sub> scenario by constraining more measured VOC species compared to the study in Dongguan (e.g., OVOCs, halogenated hydrocarbons) to explore their impact on  $P(O_3)_{net\_Mod}$ . The specific simulation scenario settings are described in Table S3.



**Figure 3: The time series and diurnal variations of  $P(O_3)_{net\_Mea}$  and  $P(O_3)_{net\_Mod}$  (Case D<sub>1</sub>–D<sub>4</sub>) during the observation period, with an enlarged view for an O<sub>3</sub> pollution day (October 26, 2023) and a normal (O<sub>3</sub> non-pollution) day (October 14, 2023); The shaded areas in (a) represent rainy days.**

Figure 3 shows the time series and diurnal variations of  $P(O_3)_{net\_Mea}$  and  $P(O_3)_{net\_Mod}$  (under Case D<sub>1</sub>–D<sub>4</sub>) during the observation period. Specifically, we added constraints for measured acetaldehyde, acrolein, acetone, and butanone (OVOCs, which were considered as potential contributors for  $P(O_3)_{net\_Missing}$  in Dongguan) to the model based on Case D<sub>1</sub>, which is labeled as Case D<sub>2</sub>. However, the daytime mean  $P(O_3)_{net\_Mod}$  in Case D<sub>2</sub> decreased by 0.5 % compared with Case D<sub>1</sub>, indicating that the dominant OVOC species responsible for  $P(O_3)_{net\_Missing}$  may differ between Heshan and Dongguan. We further constrained all measured OVOC species in Heshan (which included additional OVOCs species compared to that added to Case D<sub>2</sub>, such as propionaldehyde, butyraldehyde, and valeraldehyde) that could be input into the box model in the Case D<sub>3</sub> simulation scenario (more details can be found in Table S8). The results showed that the averaged daytime  $P(O_3)_{net\_Mod}$  from Case D<sub>3</sub> increased by 4.4 % compared to that in Case D<sub>2</sub>. Notably, in Case D<sub>3</sub>, constraining all OVOC species significantly improved  $P(O_3)_{net\_Mod}$  during the morning period (8:00–9:00), with an increasing rate of approximately 10.2 % (~1.3 ppbv h<sup>-1</sup>).

<sup>1</sup>). Additionally, Case D<sub>4</sub> scenario added constraints for chlorine-containing VOCs (i.e., all measured VOC species listed in Table S8 that could be input into the OBM model were constrained). The daytime average  $P(\text{O}_3)_{\text{net\_Mod}}$  values from Case D<sub>4</sub> changed by only 1.1 % compared to those derived from Case D<sub>3</sub>, indicating that the potential contribution of OVOCs to compensating  $P(\text{O}_3)_{\text{net\_Missing}}$  is greater than that of chlorine-containing VOCs. The negligible (or even negative) change in  $P(\text{O}_3)_{\text{net\_Mod}}$  when OVOCs are constrained in Cases D1-D4 may arise because the OVOC constraint masks deficiencies in the model's chemical mechanism and artificially suppresses diagnostic signals of missing secondary formation pathways. Until the underlying chemical mechanisms are improved, observational nudging of OVOCs offers a practical compromise—it helps maintain concentration accuracy while limiting unrealistic chemical feedbacks (more details can be found in Supplementary Materials S5). However, in modelling scenario Case D<sub>4</sub>, the daytime average  $P(\text{O}_3)_{\text{net\_Mod}}$  still showed a 22.2 % underestimation compared to the measured values. Accurate quantification of  $P(\text{O}_3)_{\text{net}}$  missing is possible here because the diurnal patterns of measurement uncertainty and the modelling bias responsible for the  $P(\text{O}_3)_{\text{net}}$  missing do not co-vary; consequently, measurement uncertainty is much smaller than modelling bias for most of the daytime, especially around noon.

The diurnal variations of  $\text{O}_3$  production pathways in Case D<sub>4</sub> are shown in Fig. S12. Compared to Case D<sub>1</sub>, the  $\text{RO}_2+\text{NO}$  reaction rate in Case D<sub>4</sub> was higher by 0–2.1 ppbv h<sup>-1</sup> in the diurnal variations during the whole measurement period (excluded the rainy days). The  $\text{RO}_2$  species with higher contributions to this pathway included  $\text{CH}_3\text{O}_2$ ,  $\text{HO}_2\text{C}_4\text{O}_2$ ,  $\text{HO}_{13}\text{C}_4\text{O}_2$ ,  $\text{HOCH}_2\text{CH}_2\text{O}_2$ ,  $\text{HO}_3\text{C}_4\text{O}_2$ ,  $\text{CH}_3\text{COCH}_2\text{O}_2$ , and  $\text{COCCOCH}_2\text{CO}_2$ . This indicates that the constraints on additional OVOCs in Case D<sub>4</sub> (such as aldehyde and ketone compounds with specific functional groups, e.g., carbonyl and hydroxyl) increased the intermediate  $\text{RO}_2$  products, leading to a significant enhancement in the  $\text{RO}_2+\text{NO}$  reaction rate. This suggests their large potential to contribute to  $P(\text{O}_3)_{\text{net\_Missing}}$ .

The modelling results of scenarios Case D<sub>1</sub>–D<sub>4</sub> show that although constraining the measured VOC species in the box model mechanism can reduce  $P(\text{O}_3)_{\text{net\_Missing}}$  to some extent, there is still a significant gap between the simulated and measured  $P(\text{O}_3)_{\text{net}}$  values. Previous studies have shown that the  $\text{RO}_2$  isomerization (Crounse et al., 2012), autoxidation (Wang et al., 2017), and the accretion reactions (Berndt et al., 2018) can also effect modelled  $P(\text{O}_3)_{\text{net}}$ , but these processes have not been investigated here. Also, the potential contribution of unmeasured VOC species to compensating  $P(\text{O}_3)_{\text{net\_Missing}}$  in the box model mechanism cannot be ignored. Yang et al. (2017) and Tan et al. (2019) conducted radical measurements at the Guangdong Atmospheric Supersite of China in autumn of 2014, revealing missing  $k_{\text{OH}}$  contributions of approximately 32 % and 50 %, respectively. Yang et al. (2017) pointed out that the missing  $k_{\text{OH}}$  contributions in the Heshan region may originate from OVOCs such as aldehydes, acids, and dicarbonyls. Tan et al. (2019) indicated that about 60 % of the  $\text{O}_3$  produced in the Heshan region was contributed by unmeasured VOCs. We hypothesize that the remaining  $P(\text{O}_3)_{\text{net\_Missing}}$  is caused by unknown VOCs that are not constrained in the box model.

The method of estimating missing VOC concentrations through the empirical linear relationship between OH reactivity ( $k_{\text{OH}}$ ) and  $P(\text{O}_3)_{\text{net}}$  is used in this study, the scientific basis lies in the fact that  $P(\text{O}_3)_{\text{net}}$  is closely related to the production rate of  $\text{RO}_X$  radicals ( $P(\text{RO}_X)$ ), which are primarily formed through the reaction of OH with VOCs. Since  $P(\text{RO}_X)$  is directly influenced by the OH reactivity ( $k_{\text{OH}}$ ),  $P(\text{O}_3)_{\text{net}}$  is consequently correlated with  $k_{\text{OH}}$ . Previous study has shown that  $P(\text{O}_3)_{\text{net}}$

exhibits a linear relationship with both  $P(\text{HOx})$  and  $k_{\text{OH}}$  when  $\text{O}_3$  formation is located in VOCs-limited regime (Baier et al., 2017), and this approach reflects nearly actual atmospheric chemistry if  $P(\text{O}_3)_{\text{net}}$  missing is driven by VOCs reactivity missing (Wang et al., 2024b). Furthermore, we examined whether unconstrained secondary products affect  $P(\text{O}_3)_{\text{net}}$  missing—and thus the linear relationship between  $P(\text{O}_3)_{\text{net}}$  missing and  $k_{\text{OH}}$ —by analysing its dependence on the ethylbenzene/m,p-xylene ratio. Because this ratio increases with the degree of air-mass aging (de Gouw et al., 2005; Yuan et al., 2013), the observed decrease in the  $P(\text{O}_3)_{\text{net}}$  missing with increasing ratio (Fig. S11f) indicates that the  $P(\text{O}_3)_{\text{net}}$  missing is not likely caused by unaccounted secondary production. By quantifying the relationship between  $k_{\text{OH}}$  and  $P(\text{O}_3)_{\text{net}}$ , the contribution of missing  $k_{\text{OH}}$  ( $k_{\text{OH\_Missing}}$ ) to  $P(\text{O}_3)_{\text{net\_Missing}}$  can be assessed, and compensating for  $k_{\text{OH\_Missing}}$  in the box model can help reduce  $P(\text{O}_3)_{\text{net\_Missing}}$ . Figure 4 shows the relationship between  $k_{\text{OH}}$  and  $P(\text{O}_3)_{\text{net\_Mod}}$  calculated under the Case D<sub>1</sub> scenario, which can be expressed as:

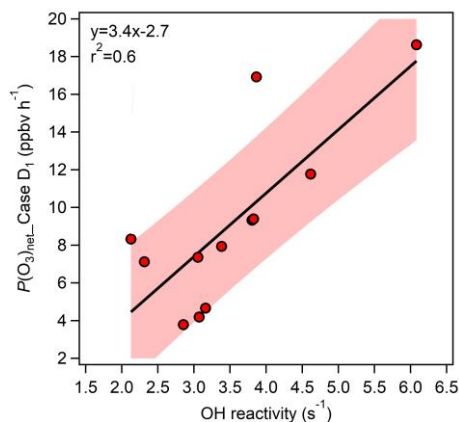
$$P(\text{O}_3)_{\text{net\_Missing}} = 3.4 \times k_{\text{OH\_Missing}} - 2.7 \quad (11)$$

where  $P(\text{O}_3)_{\text{net\_Missing}}$  and  $k_{\text{OH\_Missing}}$  in the equation represent the daytime averaged values for each day. Based on this relationship, we calculated  $k_{\text{OH\_Missing}}$  according to calculated  $P(\text{O}_3)_{\text{net\_Missing}}$  for each day. This value was then used to compensate for the unmeasured VOCs in the model (with a daytime  $k_{\text{OH}}$  compensation range of 1.2–2.4 s<sup>-1</sup>, approximately 27.6–45.1% of missing values). Based on the significant contribution of OVOCs to  $P(\text{O}_3)_{\text{net\_Missing}}$  mentioned earlier, we designed three modelling scenarios to compensate for  $k_{\text{OH\_Missing}}$ , with the specific multiples varying each day. We note that these scenarios are idealized sensitivity tests to explore potential bounds of OVOCs' contribution to  $P(\text{O}_3)_{\text{net\_Missing}}$  compensation, rather than realistic emission assumptions. Specifically, we tested how much the  $P(\text{O}_3)_{\text{net\_Missing}}$  could be accounted for if the  $k_{\text{OH}}$  were attributed to different VOCs categories. The specific scenarios include: (1) Case E<sub>1</sub>: by expanding the constrained overall VOCs concentrations in Case D<sub>1</sub> (daily mean compensation range for TVOCs: 0.5–2.8 µg m<sup>-3</sup>) the daily TVOC concentration was increased by 1.1 to 1.7 times; (2) Case E<sub>2</sub>: according to  $k_{\text{OH}}$  ratio of NMHC to OVOCs in the constrained VOCs of Case D<sub>1</sub>, the concentrations of ethylene (a representative NMHC species) and formaldehyde (OVOCs indicator) were expanded separately. The ethylene concentration (daily mean compensation range for TVOCs: 0.5–2.8 µg m<sup>-3</sup>) was increased by 5.9 to 85.6 times, and the formaldehyde concentration (daily mean compensation range for TVOCs: 0.0–0.5 µg m<sup>-3</sup>) was increased by 1.4 to 2.0 times; (3) Case E<sub>3</sub>: by expanding only the formaldehyde concentration to compensate for  $k_{\text{OH\_Missing}}$ , in this case, the daily formaldehyde concentration (daily mean compensation range for TVOCs: 0.6–1.4 µg m<sup>-3</sup>) was increased by 1.8 to 9.2 times, to verify the role of OVOCs in compensating for  $P(\text{O}_3)_{\text{net\_Missing}}$ . The time series and overall diurnal variations of modelled Cases E1-E3 are presented alongside Case D1 in Fig. 5.

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**Figure 4: The relationship between  $k_{OH}$  and  $P(O_3)_{net\_Mod}$  calculated under the Case D1 scenario (using the daily daytime average values during the observation period).**

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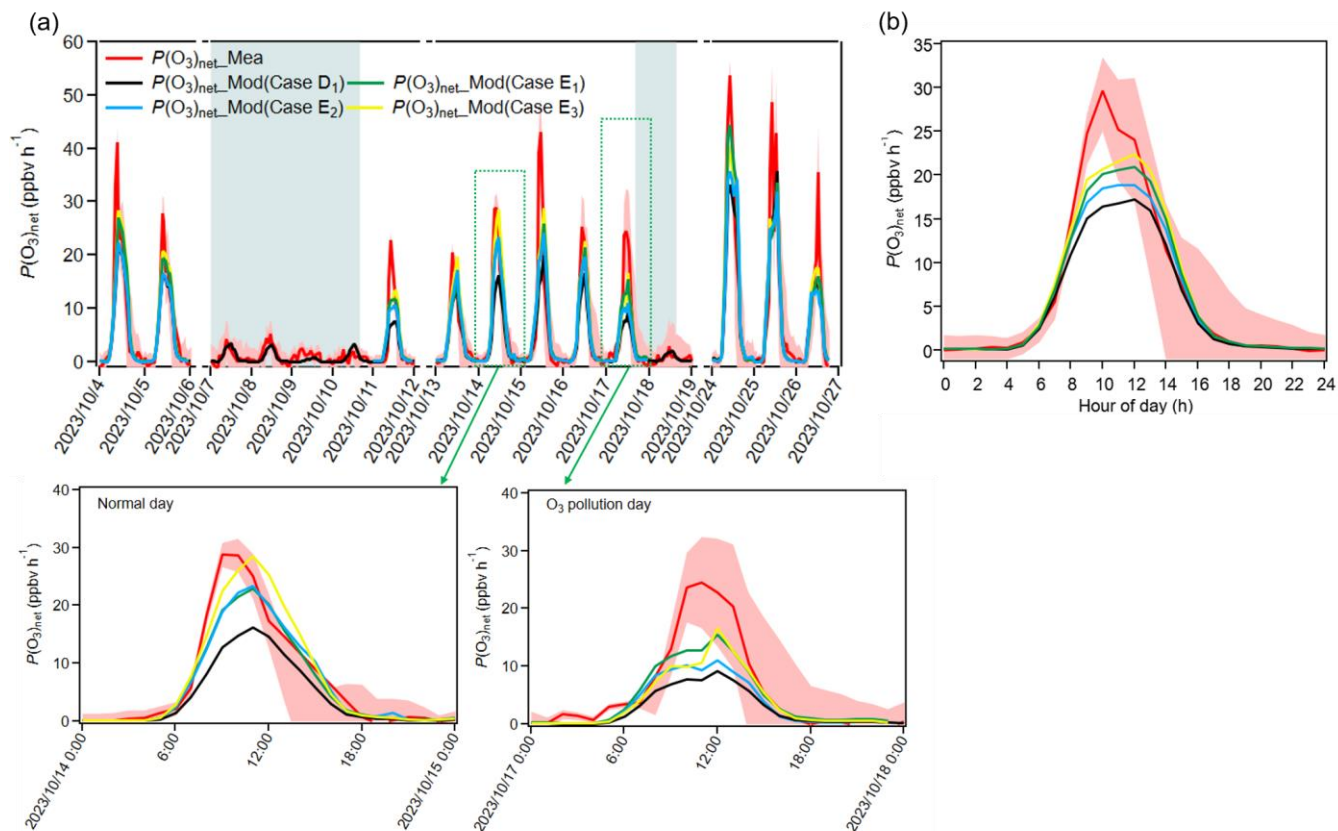
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In Case E<sub>1</sub>, where the overall TVOC concentration was increased to compensate for  $k_{OH\_Missing}$  without distinguishing VOCs categories, the compensation effect was limited due to the dilution effect of low-reactivity VOCs, resulting in a reduction of the daytime average  $P(O_3)_{net\_Missing}$  proportion from 26.3 % (calculated as  $P(O_3)_{net\_Missing}/P(O_3)_{net\_Mea}$ ) to 10.3 %. In Case E<sub>2</sub>, where the concentrations of ethylene and formaldehyde were expanded to compensate for  $k_{OH\_Missing}$ , the daytime average  $P(O_3)_{net\_Missing}$  proportion reduced from 26.3 % to 17.2 %. This proportion is higher than that obtained from Case E<sub>1</sub>, which may be due to the relatively low reactivity of ethylene limited the overall compensation effect. In contrast, Case E<sub>3</sub> compensated for  $k_{OH\_Missing}$  solely by expanding the formaldehyde concentration. More details concerning the cases settings are shown in Table S3. Since formaldehyde, as a representative high-reactivity OVOC species, contributes more directly and significantly to O<sub>3</sub> generation through photochemical pathways (Mousavinezhad et al., 2021), it achieved the best compensation effect, reducing the daytime average of  $P(O_3)_{net\_Missing}$  from 26.3 % to 5.1 %. However,  $P(O_3)_{net\_Missing}$  during the peak period of diurnal variation remained at 9.0 ppbv h<sup>-1</sup>. This result confirms the critical role of high-reactivity OVOCs (especially those with the same photochemical reaction characteristics as formaldehyde) in compensating for  $P(O_3)_{net\_Missing}$ . Further, it suggests the potential presence of other unmeasured high-reactivity VOC species in the ambient atmosphere. Constraining these species could help further improve the model's simulation accuracy (Lyu et al., 2024; Wang et al., 2024b). Overall, the degree of compensation for  $P(O_3)_{net\_Missing}$  follows the order Case E<sub>3</sub>>Case E<sub>1</sub>>Case E<sub>2</sub>, which may be related to the reactivity of the selected VOCs. However, we observe a slight difference in the diurnal trends of  $P(O_3)_{net}$  across different days (enlarged view in Fig. 5); this depicts the overall pattern for the observation period described above does not capture day-to-day variability.



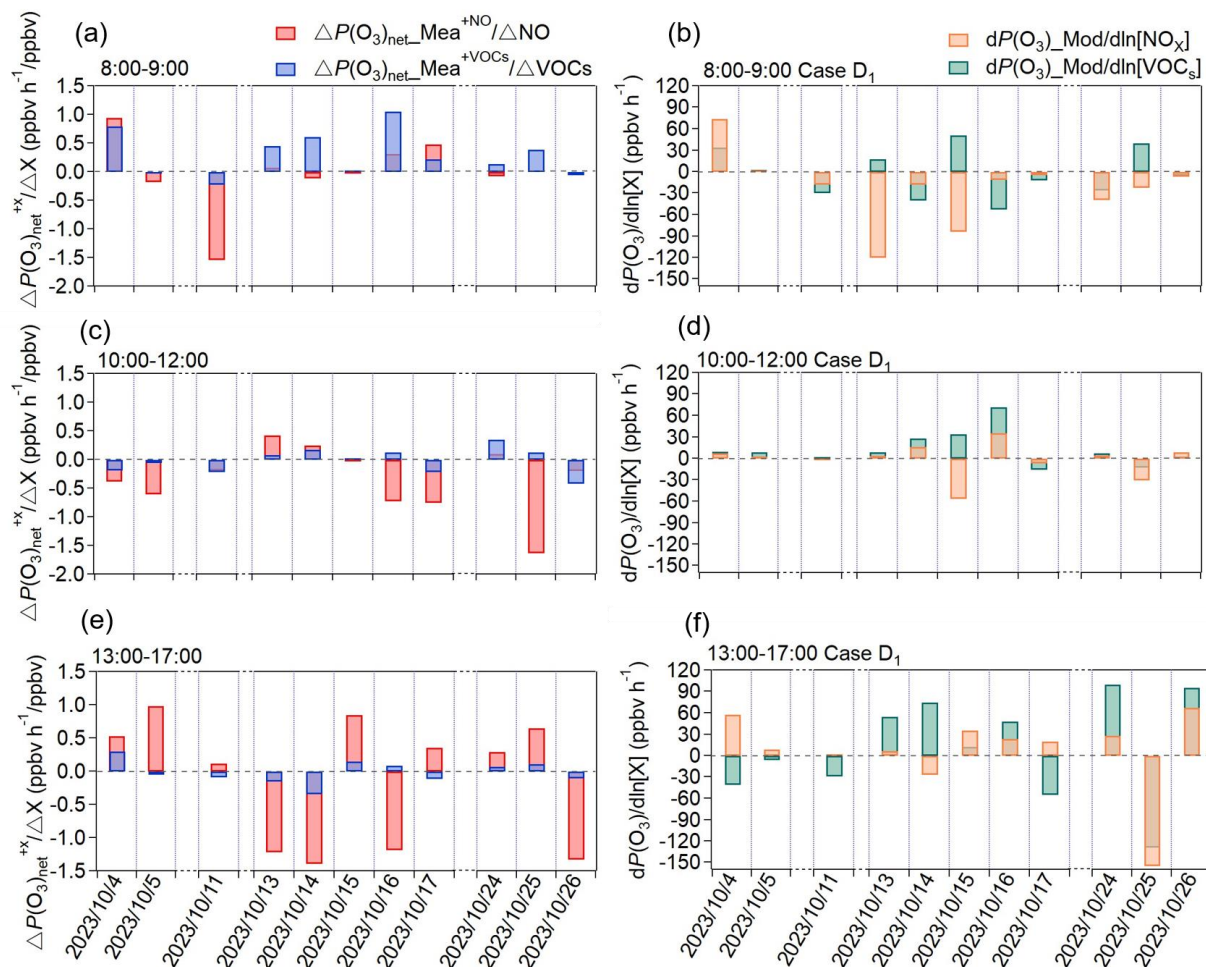


**Figure 5: (a) Time series and (b) diurnal variations of  $P(O_3)_{net\_Mea}$  and  $P(O_3)_{net\_Mod}$  (Case D<sub>1</sub>–E<sub>3</sub>) during the observation period, with an enlarged view for an O<sub>3</sub> pollution day (October 26, 2023) and a normal (O<sub>3</sub> non-pollution) day (October 14, 2023); (b) Diurnal variations excluding rainy days. The shaded areas in (a) represent rainy days.**

#### 4. OFS assessment based on measurements and simulations

This study systematically estimated OFS during the observation period (4–5, 11, 13–17, and 24–26 October 2023) using measured OFS (see Sect. 2.1) and modelled OFS (see Sect. 2.6). The time series of measured  $P(O_3)_{net\_Mea}$ ,  $P(O_3)_{net}^{+NO}$  and  $P(O_3)_{net}^{+VOCs}$  based on sensitivity experiments using the NPOPR detection system are shown in Fig. S13. We see the measurement uncertainty decreased with increasing  $P(O_3)_{net}$  values: it reaches approximately 23% when  $P(O_3)_{net}$  is around 0 ppbv h<sup>-1</sup>, but falls below 3% when  $P(O_3)_{net}$  is around 50 ppbv h<sup>-1</sup>. Fig. S14 shows the diurnal variation of the directly measured IR index compiled from all 11 days of OFS experiments, together with the absolute  $P(O_3)_{net}$  sensitivity to NO<sub>x</sub> and VOCs calculated with the box model (Case D<sub>1</sub>, Eq. (10)). It therefore depicts the overall trend across the observation period and does not reflect the day-to-day variability. We see that both measured OFS and modelled OFS captured the same diurnal OFS trend: an early morning (8:00–12:00) VOCs-limited/transition regime shifting to a NO<sub>x</sub>-limited regime around midday (13:00),

followed by a return to VOCs-limited/transition conditions in the afternoon (14:00-18:00). This midday transition to NO<sub>x</sub>-limited conditions is chemically reasonable, where intensified NO<sub>2</sub> photolysis boosts O<sub>x</sub> production while persistent photochemistry consumption without replenishment (Wang et al., 2023). The overall OFS classification (mainly VOCs-limited and transition regimes) aligns with previous studies in Guangdong in autumn (Song et al., 2022; Chen et al., 2020b; Wu et al., 2020; Jing et al., 2024). However, the OFS assessment results from measured and modelling methods showed only 60 % agreement in hourly OFS variations (see Fig. S14).



**Figure 6:** Average values of IR derived from the direct measurement data using the NPOPR detection system (e.g.,  $\Delta P(O_3)_{net}^{+NO}$  and  $\Delta P(O_3)_{net}^{+VOCs}$ ) and absolute  $P(O_3)_{net}$  sensitivity from the box model during (a)–(b)  $P(O_3)_{net}$  rising phase (8:00-9:00); (c)–(d)  $P(O_3)_{net}$  stable phase (10:00-12:00) (e)–(f)  $P(O_3)_{net}$  declining phase (13:00-17:00).

In order to gain a deeper understanding of the similarities and differences between the direct measurement and the model simulation methods in diagnosing OFS, we divided the daytime observation period into three characteristic phases: the  $P(O_3)_{net}$

525 rising phase (8:00-9:00), the  $P(\text{O}_3)_{\text{net}}$  stable phase (10:00-12:00), and the  $P(\text{O}_3)_{\text{net}}$  declining phase (13:00-17:00). Fig. 6 (a), (c), and (e) present the diurnal cumulative average results of IR derived from direct measurements of  $\Delta P(\text{O}_3)_{\text{net}}^{+\text{NO}}$  and  $\Delta P(\text{O}_3)_{\text{net}}^{+\text{VOCs}}$  using the NPOPR detection system for each phase. Fig. 6 (b), (d), and (f) show the diurnal cumulative average results of the absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity calculated from the box model (Case D<sub>1</sub>) for each phase. We found that during the  $P(\text{O}_3)_{\text{net}}$  rising phase, both the direct measurement and the model simulation methods identified the OFS as being in either the transition regime or VOCs-limited regime. However, the agreement between these two methods was only 63.6 %. During the  $P(\text{O}_3)_{\text{net}}$  stable phase, the consistency between these two methods improved significantly, reaching 72.7 %, with the OFS predominantly located in the transition regime. This higher consistency occurred during periods of higher solar radiation intensity, when photochemical reactions were more stable, leading to improved model simulation accuracy. During the  $P(\text{O}_3)_{\text{net}}$  declining phase, the two methods achieved an agreement of 72.7 % in the OFS assessment; both predominantly identified the OFS as being in either the transition regime or NO<sub>x</sub>-limited regime. This relatively high agreement may be attributed to the reduced intensity of solar radiation and the decreased complexity of photochemical reactions in the afternoon. As Chen et al. (2025) showed that lower solar radiation simplifies reaction pathways, thereby enhancing model simulation accuracy. To illustrate that the diurnal shift in OFS depicted in Fig. 6 is not random noise but reflects the general rule, we grouped the 11 days of direct measurements by their initial O<sub>3</sub>-formation regime, calculated their average diurnal variations, and thus reproduced the “morning-transition” phenomenon in Fig. S13c–d.

540 The absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity for scenarios Case E<sub>1</sub>–Case E<sub>3</sub> are shown in Fig. S15. The agreement between these scenarios and the direct measurement results changes across different periods, with consistency levels of 54.5–63.6 %, 45.5–72.7 %, and 63.6–72.7 % during  $P(\text{O}_3)_{\text{net}}$  rising phase,  $P(\text{O}_3)_{\text{net}}$  stable phase, and  $P(\text{O}_3)_{\text{net}}$  declining phase, respectively. In cases where  $P(\text{O}_3)_{\text{net}}$  Missing was reduced (Case E<sub>1</sub>–Case E<sub>3</sub>), the OFS sometimes shifted to NO<sub>x</sub>-limited conditions during certain periods, such as in Case E<sub>2</sub> during the  $P(\text{O}_3)_{\text{net}}$  rising phase and Case E<sub>3</sub> during the  $P(\text{O}_3)_{\text{net}}$  stable phase on October 4, 2023. This contradictory phenomenon may be related to the model’s incomplete representation of unknown high-reactivity VOCs chemical mechanisms (e.g., aldehyde and ketone). Additionally, previous studies have pointed out that the diagnostic method based on the box model tends to overestimate the sensitivity to VOCs in certain regions of China due to neglecting the reactivity of unidentified VOCs in anthropogenic emissions (Xu et al., 2022; Lu et al., 2010). To more accurately simulate O<sub>3</sub> formation and precursor sensitivity, Xu et al. (2022) incorporated formaldehyde as input data in the box model, and found that this improvement significantly reduced the model’s bias in diagnosing OFS, particularly in misjudging the VOCs-limited regime. These results demonstrate that the bias between measured and modeled OFS arises chiefly from missing VOCs or shortcomings in the model’s chemical mechanism.

555 It is noteworthy that there are differences in the precursor sensitivity response mechanisms between the absolute  $P(\text{O}_3)_{\text{net}}$  sensitivity assessment method based on the box model and the IR method based on the direct measurement method. For example, during the  $P(\text{O}_3)_{\text{net}}$  stable phase (10:00-12:00 period) on 4–5 October, although both methods identified the OFS as being in the transition regime, the direct measurement showed that an increase in precursor concentrations suppressed  $P(\text{O}_3)_{\text{net}}$ , while the model simulations indicated that a reduction in precursor concentrations led to a decrease in  $P(\text{O}_3)_{\text{net}}$ . However, these

findings only explain regional differences in sensitivity determinations, and the underlying reasons for the differing precursor sensitivity response mechanisms between the two methods may require further investigation.

## 5 Conclusions

Understanding ozone ( $O_3$ ) production mechanisms is critical for accurate  $O_3$  pollution assessment and control, as photochemical production directly effects  $O_3$  concentration levels. Due to the absence of certain mechanisms in conventional models, particularly the kinetics from missing reactive volatile organic compounds (VOCs) species, the reliability of net photochemical  $O_3$  production rates ( $P(O_3)_{net}$ ) and  $O_3$  formation sensitivity (OFS) evaluation is compromised. To address this issue, we employed the custom-made online  $O_3$  production rate (NPOPR) detection system based on the dual-reaction chamber technique to measure the  $P(O_3)_{ne}$  and OFS. The system was applied in field observations at the Guangdong Atmospheric Supersite of China in Heshan, Pearl River Delta during the autumn of 2023. By combining the NPOPR detection system and the box model, a systematic investigation of  $P(O_3)_{net}$  and OFS was carried out. During the observation period (4–26 October 2023), a total of 6  $O_3$  pollution days were recorded, with the maximum  $O_3$  mixing ratio reaching 136.5 ppbv. The  $P(O_3)_{net}$  levels on  $O_3$  pollution days were significantly higher than those on normal days, indicating that high temperatures, low humidity, strong solar radiation, and stagnant weather conditions favor the  $O_3$  pollution formation. The observational results show that oxygenated volatile organic compounds (OVOCs) and aromatic hydrocarbons contributing 51.6 % and 32.9 % to OFP, respectively, which are the primary contributors to  $O_3$  formation.

Systematic underestimation of modelled  $P(O_3)_{net}$  ( $P(O_3)_{net\_Mod}$ ) was found when compared to the measured  $P(O_3)_{net}$  ( $P(O_3)_{net\_Mea}$ ); this difference is defined as upper-limit  $P(O_3)_{net\_Missing}$  due to the overestimation of HONO by MARGA in this study. When gradually incorporating mechanisms such as  $HO_2$  uptake by ambient aerosols, dry deposition,  $N_2O_5$  uptake, and  $ClNO_2$  photolysis (Case D<sub>1</sub>), the daytime average  $P(O_3)_{net\_Missing}$  was 3.4 ppbv h<sup>-1</sup> (26.3 % underestimation). After adding constraints for VOC species such as acetaldehyde, acrolein, acetone, and butanone compared to Case D<sub>1</sub> (defined as Case D<sub>2</sub>), the  $P(O_3)_{net\_Mod}$  decreased by 0.5 % compared with Case D<sub>1</sub>. However, after further constraining all measurable OVOC species (Case D<sub>3</sub>),  $P(O_3)_{net\_Mod}$  values increased by 4.4 % compared with Case D<sub>2</sub>, with a notable improvement of 10.2 % (approximately 1.3 ppbv h<sup>-1</sup>) during the  $P(O_3)_{net}$  rising phase (8:00-9:00). This indicates that OVOCs play a particularly significant role in  $O_3$  formation during the morning. Additionally, after adding chlorine-containing VOCs (Case D<sub>4</sub>),  $P(O_3)_{net\_Mod}$  increased by only 1.1 % compared with Case D<sub>3</sub>, further confirming the dominant role of OVOCs in compensating for  $P(O_3)_{net\_Missing}$ . These results also demonstrate that incorporating the aforementioned missing mechanisms and measured VOC species cannot fully eliminate simulation bias. Other processes, i.e., the  $RO_2$ , autoxidation, and the accretion reactions can also affect modelled  $P(O_3)_{net}$ , but they have not been examined here. The negative correlation of  $P(O_3)_{net\_Missing}$  with the air mass aging indicates that the  $P(O_3)_{net}$  missing is not likely caused by unaccounted secondary production.

To quantify the effect of unmeasured VOCs and their related reactions, especially those involving OVOCs, we developed a compensation approach based on the observed relationship between daytime averaged  $P(O_3)_{net\_Missing}$  and  $k_{OH\_Missing}$ .

This approach hypothesizes that upscaling measured VOCs can compensate for the  $k_{OH\_Missing}$  attributed to unmeasured species, thereby reducing  $P(O_3)_{net\_Missing}$ . Building upon Case D<sub>1</sub>, we designed three modelling scenarios (Case E<sub>1</sub>: expanded TVOC; Case E<sub>2</sub>: expanded ethylene and formaldehyde; Case E<sub>3</sub>: expanded formaldehyde) to compensate for  $P(O_3)_{net\_Missing}$ . Among these modelling scenarios, the daytime averaged  $P(O_3)_{net\_Missing}$  was reduced to 10.3 %, 17.2 %, and 5.1 % for Case E<sub>1</sub>, Case E<sub>2</sub>, and Case E<sub>3</sub>, respectively. Notably, Case E<sub>3</sub> achieved the greatest reduction solely by increasing formaldehyde concentrations, validating the critical role of highly reactive OVOCs (particularly formaldehyde) in compensating for  $P(O_3)_{net\_Missing}$ . This suggests that there other unmeasured highly reactive VOC species may exist in the ambient atmosphere, and constraining them in the model could further improve the simulation accuracy.

Additionally, the sensitivity assessment results derived from the different measured and modelled OFS approaches were compared: (1) in direct measurement using the NPOPR detection system, NO or VOCs were added to quantify changes in  $P(O_3)_{net}$ , with OFS determined through the incremental reactivity (IR) index ( $IR = \Delta P(O_3)_{net}^{+x} / \Delta S(x)$ , where  $X = NO_x$  or VOCs and  $\Delta S(x)$  represents the added concentration); (2) in model simulations, where the box model calculated  $P(O_3)_{net}$  and derived absolute  $P(O_3)_{net}$  sensitivity ( $dP(O_3)_{net} / d[X]$ , where  $X = NO_x$  or VOCs). Meanwhile we found that the agreement of OFS assessment results between the direct measurements and the model results was lower in the  $P(O_3)_{net}$  rising phase (8:00-9:00, 63.6 %) than those in the  $P(O_3)_{net}$  stable phase (10:00-12:00, 72.7 %) and  $P(O_3)_{net}$  declining phase (13:00-17:00, 72.7 %). This again highlights the importance of highly reactive OVOCs in improving the accuracy of OFS assessment. These results indicate that reducing  $P(O_3)_{net\_Missing}$  can enhance the accuracy of OFS assessment to some extent, but fully eliminating the discrepancies still requires further constraints on unmeasured VOC species and further research.

In conclusion, we quantitatively assessed the  $P(O_3)_{net}$  simulation deficits and their impact on OFS diagnosis by comparing the measured and modelled  $P(O_3)_{net}$ , and found that the unmeasured VOCs —rather than the secondary atmospheric formation—are the primary causative factor of  $P(O_3)_{net\_Missing}$ . Furthermore, both direct measurements and model results reveal a diurnal OFS shift dominated by the morning regime; transition and VOC-limited conditions prevailed, so prioritizing VOCs while co-controlling  $NO_x$  is the most effective approach to  $O_3$  pollution control in PRD region. Our results also demonstrate that the persistent model biases risk under-estimating the local photochemical formation contribution to  $O_3$  pollution, thereby has weakening its perceived impact relative to physical transportation. Future studies should expanded VOCs measurements and combine direct  $P(O_3)_{net}$  observations with regional transport model to separate local production from up-wind advection.

**Date availability.** The datasets supporting this research are included in this manuscript and its supplementary information files. The data for this study are also publicly available at <https://doi.org/10.5281/zenodo.15052519>. Meteorological data were sourced from the European Centre for Medium-Range Weather Forecasts (ECMWF, <https://www.ecmwf.int/>). Box model simulations were conducted using the AtChem2 model (<https://atchem.leeds.ac.uk/webapp/>) with the Master Chemical Mechanism (MCM v3.3.1, <https://mcm.york.ac.uk/MCM>). Figures in this study were created using Igor Pro 6.7. Additional data or materials related to this study can be made available upon reasonable request to the corresponding author ([junzhou@jnu.edu.cn](mailto:junzhou@jnu.edu.cn)), subject to restrictions on data resources.

625 **Supplement.** The supplement related to this article is available online at: <https://doi.org/>

**Author contributions.** Author contributions. JZ and MS designed this study. JZ and BZ wrote the manuscript with contributions from all co-authors. JZ, BJ, BZ, TZ, DC, YZ, J. Li, MD, MX, JHJ, and J. Luo collected and analyzed the data. All authors reviewed and revised the manuscript.

**Competing interests.** The contact author has declared that none of the authors has any competing interests.

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