Response to Referee #1's comments

General Comments:

Interesting work with clear and significant conclusions, but requires more detail and explanation in some areas. For example, more context and clarity are required in the introduction and methods sections. and further experimental details to aid reproducibility. Some edits required to make the language used more fluent and precise.

Specific Comments:

Introduction:

Line 45 – "No one instrument can capture all VOCs out there and even when they can be measured there is information missing on identification and properties (Yuan et al., 2017; Wang et al., 2014)". This sentence needs expanding into a paragraph explaining what these species, instruments, and measurement methods are. Which VOC species can't currently be measured/haven't been measured and using which techniques?

Reply: Thanks for your suggestion. We have included this discussion accordingly.

Lines 46-61: Gas chromatograph–mass spectrometer/flame ionization detector (GC–MS/FID) can measure C2-C12 non-methane hydrocarbons (NMHCs) and C2-C6 oxygenated VOCs (OVOCs) while cannot measure NMHCs and OVOCs with larger carbon number (Wang et al., 2014). Proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS) is able to measure a huge number of OVOCs and aromatics and several alkanes, but cannot measure most alkanes and alkenes, and cannot distinguish isomers (Yuan et al., 2017). The 2,4-dinitrophenylhydrazine (DNPH)/high performance liquid chromatography (HPLC) method can measure several carbonyls but cannot measure non-polar organic species (Wang et al., 2009). The two-dimensional GC is able to measure some intermediate-volatile and semi-volatile non-polar organics (Song et al., 2022). A lack of standard gases prevents these technologies from accurate quantification even if these technologies can identify more

VOC species. In general, many branched alkenes, OVOCs with complex functional groups, intermediate-volatile and semi-volatile organics and complex biogenic VOCs cannot currently be well quantified even if they can be identified by instruments.

Line 47 – "By now, emission inventories of VOCs used in air quality models only include the VOC species that can be measured". This sentence needs some clarity. Would suggest changing `by now` to `currently` and giving examples of which emissions inventories and VOC species are being discussed.

Reply: Thanks for your suggestion. We have modified it in the manuscript accordingly.

Lines 62-66: Currently, emission inventories used in air quality models such as the Community Emissions Data System (CEDS) emission inventory and the multi-resolution Emission Inventory for China (MEIC) only include the VOC species that can be measured such as some C1-C9 hydrocarbons and simple-structure OVOCs with small carbon number (<C6).

Line 70 – "The inclusion of the missing VOCR can help to improve the model performance in simulating photochemistry processes". Clarify which model.

Reply: Thanks for your suggestion. We have modified it in the manuscript accordingly. The model refers to box model and air quality models.

Lines 87-89: The inclusion of the missing VOC_R can help to improve the performance of box model and air quality models in simulating photochemistry processes.

Line 90 – "Given that the missing VOCR accounts for a large part of total VOCR". This should probably read `could potentially account for`, or something similar, as this has not been determined yet.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 109-113: Given that the missing VOC_R could potentially account for a large part of total VOC_R, clearly clarifying the role of missing VOC_R in determining ozone

precursor sensitivity is an urgent need for the diagnosis of ozone sensitivity regimes and formulation of an effective emission reduction roadmap.

Method:

More details required on the experimental procedure. For example, how and where the instruments were deployed. Were continuous measurements taken from 26th Sept to 30th Oct? Were the GC, PTR, and custom-built instrument run simultaneously?

Reply: Thanks for your suggestion. We have included this discussion accordingly.

Lines 121-128:

2.1 Overview of the measurement

The field campaign was conducted from 25 September to 30 October 2018 continuously at an urban site in downtown Guangzhou (113.2ºE, 23ºN). The sampling site was located on the ninth floor of a building on the campus of Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 25 m above the ground level. This site is primarily influenced by industrial and vehicular emissions. R_{OH}, VOCs, NO_X, O_3, HONO, SO_2, CO, photolysis frequencies, and meteorological factors were simultaneously measured during the measurement period.

PTR - Was this run in selected ion monitoring mode? If so, which reagent and product ions were selected? (Would suggest including a table of these in the SI.) Other missing details include drift tube pressure, temperature, and voltage, etc.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 173-181: During the campaign, the PTR-ToF-MS automatically switched between H_3O^+ and NO^+ chemistry every 10–20 min. The H_3O^+ mode was used to measure OVOCs and aromatics while the NO^+ model was used to measure alkanes with more carbons (C8-C20). When running in the H_3O^+ ionization mode, the drift tube was at a temperature of 50 °C, a pressure of 3.8 mbar, and a voltage of 920 V, leading to an

operating E/N (E is the electric field, and N is the number density of the gas in the drift tube) ratio of 120 Td. When running in the NO^+ ionization mode, the drift tube was at a temperature of 50 ℃, a pressure of 3.8 mbar, and a voltage of 470 V, leading to an operating E/N ratio of 60 Td.

Include details of GC–MS/FID parameters.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 161-170: After removal of water vapor, VOCs were trapped at -155 ℃ in a deactivated quartz capillary column (15 cm×0.53 mm ID) and a Porous Layer Open Tubular (PLOT) capillary column (15 cm×0.53 mm ID) for the MS channel and the FID channel, respectively. The system was calibrated weekly by TO-15 (Air Environmental Inc., USA) and PAMS gas standards (Spectra Gases Inc., USA). Detection limits for various compounds were in the range of 0.002–0.070 ppbv. A total of 56 NMHCs species were measured (**Table S1**). The time resolution of the measurement was 1 h. The uncertainties of VOC measurements by GC–MS/FID are in the range of 15 %–20 %. More details of this method can be found in previous studies (Wang et al., 2014;Yuan et al., 2012).

Line 119 – Can the correction curve be supplied in the SI?

Reply: Thanks for your suggestion. We have supplied the correction curve in the SI.

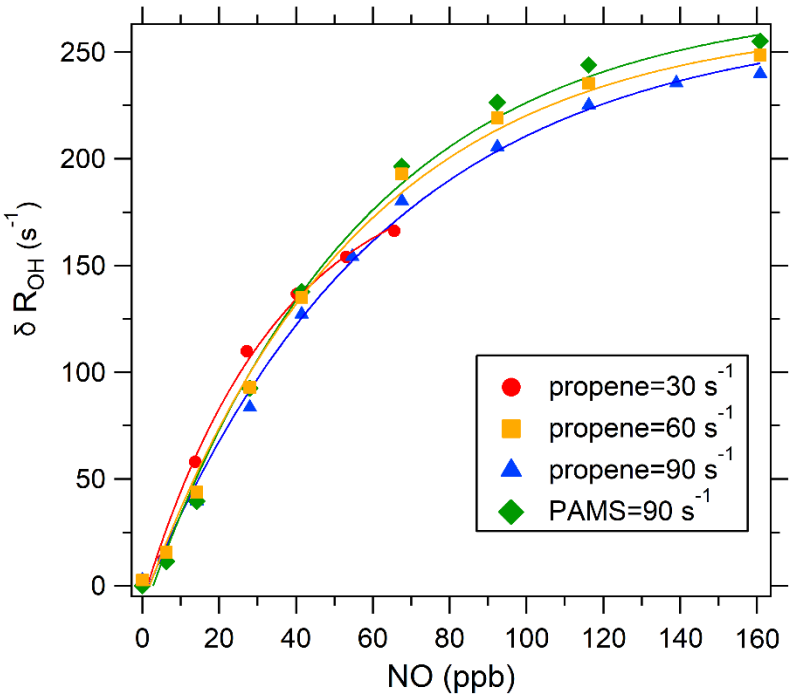

Figure S1. NO-correction experiments and fitting curves in Guangzhou in 2018 at different R_{OH} of propene standard gas and mixture standard gas. The mixture standard gas used is the mixture PAMS (photochemical assessment monitoring stations) of 56 non-methane hydrocarbons (NMHCs; SpecialGas Ltd, USA).

Line 134 - `A total of 56 NMHCs species were measured`, provide information in SI.

Reply: Thanks for your suggestion. We have provided the information in SI.

Table S1. VOC species measured in this study

Classes	VOC species
Alkane	ethane, propane, isobutane, n-butane, cyclopentane, isopentane, n-pentane, 2,2-dimethylbutane, 2,3-dimethylbutane, 2-methylpentane, 3-methylpentane, n-hexane, 2,4-dimethylpentane, methylcyclopentane, 2-methylhexane, cyclohexane, 2,3-

	dimethylpentane, 3-Methylhexane, 2,2,4-trimethylpentane, n-heptane, methylcyclohexane, 2,3,4-trimethylpentane, 2-methylheptane, 3-methyl Heptane, octane, n-nonane, n-decane, n-undecane, n-dodecane
Alkene	ethylene, propylene, trans-2-butene, 1-butene, cis-2-butene, 1,3-butadiene, 1-pentene, trans-2-pentene, isoprene, cis- 2-pentene, 1-hexene
Aromatic	benzene, ethylbenzene, m/p-xylene, o-xylene, styrene, n-propylbenzene, 3-ethyltoluene, 4-ethyltoluene, 1,3,5-trimethyl Benzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, 1,2,3-trimethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene, toluene

Line 142 - `A total of 31 VOCs were calibrated using either gas or liquid standards`, provide information in SI.

Reply: Thanks for your suggestion. We have supplied this information in the SI.

Table S2. The 31 VOCs which were calibrated using either gas or liquid standards. The ion formula of these VOCs detected by PTR-ToF-MS and corresponding sensitivity are provided.

VOC species	Ion formula	Sensitivity, cps/ppb
Formaldehyde	CH_2OH^+	1042
Methanol	CH_4OH^+	629.3
Acetonitrile	$C_2H_3NH^+$	3374
Acetaldehyde	$C_2H_4OH^+$	2767

Ethanol	$C_2H_6OH^+$	99.23
Acrolein	$C_3H_4OH^+$	4107
Acetone	$C_3H_6OH^+$	4299
Furan	$C_4H_4OH^+$	2544
Isoprene	$C_5H_8H^+$	1888
MVK+MACR	$C_4H_6OH^+$	3868
MEK	$C_4H_8OH^+$	4467
Benzene	$C_6H_6H^+$	3151
2-Pentanone	$C_5H_{10}OH^+$	4510
Toluene	$C_7H_8H^+$	3978
Phenol	$C_6H_6OH^+$	4076
Furfural	$C_5H_4O_2H^+$	7460
Methyl Isobutyl Ketone	$C_6H_{12}OH^+$	3988
Styrene	$C_8H_8H^+$	4289
xylene	$C_8H_{10}H^+$	4241
Cresol	$C_7H_8OH^+$	4299
Trimethylbenzene	$C_9H_{12}H^+$	4413
Naphthalene	$C_{10}H_8H^+$	5117
a-Pinene	$C_{10}H_{16}H^+$	2332
Formic acid	$CH_2O_2H^+$	856.6
Acetic acid	$C_2H_4O_2H^+$	1711
Propionic acid	$C_3H_6O_2H^+$	2072
Butyric acid	$C_4H_8O_2H^+$	2358
Pyrrole	$C_4H_5NH^+$	2842
Formamide	CH_3NOH^+	2871
Acetamide	$C_2H_5NOH^+$	3992

Line 143 - `For other measured VOCs`, provide details in SI.

Reply: Thanks for your suggestion. The other measured VOCs include 128 VOC species. The detailed information can be seen in Wu et al. (2020) and all VOC species measured by PTR-ToF-MS were provided in table S4 of that article.

Lines 190-193: By this method, PTR-ToF-MS can additionally measure 128 VOCs which were included in the analysis of this study. The detailed information for this method can be found in Wu et al. (2020) and all VOC species measured by PTR-ToF-MS were provided in table S4 of that article.

Results and Discussion:

Line 206 - How many extra species were measured by PTR?

Reply: Thanks for your suggestion. By using PTR-ToF-MS, we measured 159 VOCs and 128 of them were difficult to be measured before. We have provided this information accordingly.

Lines 265-271: By using GC-MS/FID, we measured 56 NMHCs. By using PTR-ToF-MS, we measured 159 VOCs and 128 of them were difficult to be measured before. Besides the alkanes with carbons less than 12, PTR-ToF-MS can also measure alkanes with more carbons (C12–C20). With regard to OVOCs, not only common OVOC species including formaldehyde and C2-C4 carbonyls but also carbonyls with more carbons (C5-C10) and some N-containing OVOC species such as nitrophenol and methyl nitrophenol were measured by PTR-ToF-MS.

Technical Corrections:

Line 53 – "The measurement of total OH reactivity (ROH) provides an effective approach to quantify the total amount of reactive gases in terms of reacting with OH radicals." I think this sentence could be reworded to be clearer and more concise.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 70-71: The total OH reactivity (R_{OH}), which can be directly measured, is an index for evaluating the amounts of reductive pollutants in terms of ambient OH loss.

Line 166 – "The multiple linear regression (MLR) have been successfully applied to quantify the sources of air pollutants (Li et al., 2019; Yang et al., 2016a)." Grammar – `have` should be `has`.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 211-212: The Multiple Linear Regression (MLR) has been successfully applied to quantify the sources of air pollutants (Li et al., 2019; Yang et al., 2016a).

Line 176 – "Calculated from observed isoprene and its photochemical products MVK and MACR". Define acronyms.

Reply: Thanks for your suggestion. We have modified it accordingly.

Lines 222-223: calculated from observed isoprene and its photochemical products methyl vinyl ketone (MVK) and methacrolein (MACR).

Line 261 - ` Given the larger missing VOCR level during the high missing- VOCR days, we focus on the high missing- VOCR days in the following analysis.` This line seems unnecessary and repetitive.

Reply: Thanks for your suggestion. We have removed this sentence.

Line 290 – Compensate rather than compensates.

Reply: Thanks for your suggestion. We have modified it.

Define units for all equations and variables where appropriate throughout.

Reply: Thanks for your suggestion. We have defined units for all equations and variables in the SI.

Lines 128-129: The units of all parameters used in this study is shown in table S3.

Table S3. The units of variables used in this study.

Variables	Units
R_{OH}	s^{-1}
k_{OH+Xi}	$ppb^{-1}\ s^{-1}$
$[X_i]$	ppb
VOC_R	s^{-1}
$Missing\ VOC_R$	s^{-1}
$C_{backgound}$	s^{-1}
$P(O_3)$	$ppb\ h^{-1}$
$L(O_3)$	$ppb\ h^{-1}$
$j(O^1D)$	s^{-1}
L_N/Q	unitless

Some of the details of how the box model was run from section 3.3 might be more appropriate in the methods section than in the results.

Reply: Thanks for your suggestion. We have moved the details of how the box model was run to the methods section 2.6.

Lines 249-260:

The box model was used to evaluate the impact of missing VOC_R on the O_3 production rate. In the base scenario, the box model was constrained by all measured inorganic and organic gases but the missing VOC_R was not considered. To consider the missing VOC_R in the box model, we additionally increased the concentration of NMHCs to exactly compensate for the missing VOC_R by multiplying a factor, on the basis of measured NMHC concentrations. We simulated four scenarios by increasing the concentration of: (1) n-pentane, (2) ethylene, (3) toluene, (4) all measured 56 NMHCs. For the scenario of increasing all 56 NMHCs, concentrations of 56 NMHC

species were increased by multiplying the same factor. Given that the VOC_R of unconstrained secondary products increases with the increase in the concentration of NMHCs, several attempts of different values are needed to determine the increasing factor.

References:

Song, K., Gong, Y., Guo, S., Lv, D., Wang, H., Wan, Z., Yu, Y., Tang, R., Li, T., Tan, R., Zhu, W., Shen, R., and Lu, S.: Investigation of partition coefficients and fingerprints of atmospheric gas- and particle-phase intermediate volatility and semi-volatile organic compounds using pixel-based approaches, Journal of Chromatography A, 1665, 462808, https://doi.org/10.1016/j.chroma.2022.462808, 2022.

Wang, H., Zhang, X., and Chen, Z.: Development of DNPH/HPLC method for the measurement of carbonyl compounds in the aqueous phase: applications to laboratory simulation and field measurement, Environmental Chemistry, 6, 389-397, https://doi.org/10.1071/EN09057, 2009.

Wang, M., Zeng, L., Lu, S., Shao, M., Liu, X., Yu, X., Chen, W., Yuan, B., Zhang, Q., and Hu, M.: Development and validation of a cryogen-free automatic gas chromatograph system (GC-MS/FID) for online measurements of volatile organic compounds, Anal. Methods, 6, 9424-9434, 2014.

Wu, C., Wang, C., Wang, S., Wang, W., Yuan, B., Qi, J., Wang, B., Wang, H., Wang, C., and Song, W.: Measurement report: Important contributions of oxygenated compounds to emissions and chemistry of volatile organic compounds in urban air, Atmos. Chem. Phys., 20, 14769-14785, 2020.

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