Response to Reviewer comment #1:

General comments:

The paper by Yang et al. presents results from a measurement campaign in September / October 2018 at Shenzhen in the Pearl River Delta. Unfortunately, the collected data-set is not state-of-the art and the subsequent interpretation suffers from this lack of data and thus the manuscript does not bring any useful new insight into atmospheric chemistry. The shortcomings in the data-set compared with what is current state-of-the art are:

Reply

Thanks for your helpful comments which would help us to improve the manuscript. The comments and suggestions are valuable and very helpful for us. We have taken all these suggestions into account and have made corrections in this revised manuscript. Below are our responses to the specific comments, highlighted in blue, with changes to the manuscript highlighted in green.

Specific comments:

1. OH reactivity has not been measured: the analysis of the radicals budget is based on calculated OH reactivity, which is unsatisfactorily, especially given that k_{OH} measurements are now widely available and add much confidence to the data set. Missing OH reactivity is widely observed under various conditions, and field campaigns quantifying OH and HO_2 should also measure OH reactivity to unravel possible missing OH reactivity, rather than using the calculated OH reactivity as a lower limit to evaluate the experimental OH and HO_2 data.

Reply

In this campaign, we measured k_{OH} only during 05-19 October by laser the flash photolysis-laser induced fluorescence (LP-LIF) system (Liu et al., 2019), despite the absence of k_{OH} continuous measurement during the period of radical observations (05-28 October 2018). The information on the LP-LIF system is added in Table S1 in the Supplementary Information. The timeseries of the observed and modeled k_{OH} are presented in Fig. S2, in which data gaps were caused by the maintenance of the LP-LIF system. Timeseries of the observed and modeled k_{OH} indicated that the simulations matched well with the observations within the uncertainties during 05-19 October 2018. Therefore, the model can be believed to reproduce the observed k_{OH} values within the whole campaign.

We have added Figure S2 into the Supplementary Information, and revised the description of k_{OH} in Sections 2.1, 3.3, and 4.1, and Table S1 in the Supplementary Information.

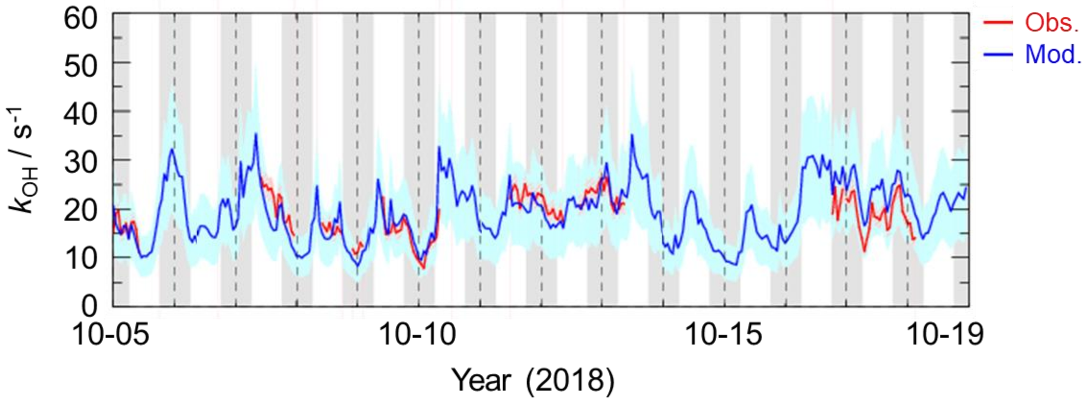

Figure S2: Timeseries of the observed and modeled k_{OH} during 05-19 October 2018. The red and blue areas denote 1-σ uncertainties of the observations and simulations by the model, respectively. The grey areas denote nighttime.

Revision

(1) Section 2.1:

k_{OH} was measured by the laser flash photolysis-laser induced fluorescence (LP-LIF) system.

(2) Section 3.3:

In this campaign, k_{OH} was measured only for several days by the LIP-LIF system, which has been reported in the previous study (Liu et al., 2019). The timeseries of the observed and modeled k_{OH} during 05-19 October 2018 are presented in Fig. S2 in the Supplementary Information. A good agreement between the observed and modeled k_{OH} within the uncertainties was achieved, and thus the model can be believed to reproduce the observed k_{OH} values within the whole campaign.

Moreover, to reflect the k_{OH} in the whole campaign, the modeled values were shown in the k_{OH} diurnal profiles (Fig. 3c) during 05-28 October 2018.

(3) Section 4.1:

As discussed in Section 3.3, it is believed that the model can reproduce the observed k_{OH}. Herein, to conduct the OH experiment budget in the whole campaign, we used the modeled k_{OH} to calculate the OH destruction rate because the k_{OH} was only measured in several days.

2. The reference cell for stabilizing the laser wavelength did not work during the campaign: rather high NO concentrations have therefore been used in the FAGE for HO_2 conversion, and it can be doubted that no interference from RO_2 measurements occurred under these conditions. This is even more strange, as the authors indicate line 99, that there is no obvious difference in HO_2 signal, when changing from 10 to 20 ppm. Does this mean the instrument works already under 100% HO_2 conversion? Then, an RO_2 interference seems very likely. However, 100% conversion efficiency is unlikely, as in a recent paper of the same group, describing a campaign carried out just a few months before in May / June 2018 (Ma et al., OH and HO_2 radicals chemistry at a suburban site during the EXPLORE-YRD

campaign in 2018, ACPD, doi.org/10.5194/acp-2021-1021), a conversion efficiency of 20% was obtained using 5 ppm. Or maybe the authors wanted to say that no obvious difference in HO_2 concentration was observed. Then, the HO_2 conversion rates under different NO concentrations need to be specified.

Reply

Thanks for your helpful suggestions. We have rechecked all the data and made corrections in the revised manuscript.

Revision

(1) Section 2.2:

In this campaign, NO mixing ratios were switched between 25 ppm (low NO mode) and 50 ppm (high NO mode). We calculated the HO_2 conversion rates under the two different NO concentrations by calibrating the PKU-LIF system. HO_2 conversion rates in low NO mode ranged within 80%-95%, while those in high NO mode were over 100%, demonstrating that the HO_2 measurement was affected by RO_2 radicals. Prior studies have reported the relative detection sensitivities ($\alpha_{\mathrm{RO_2}}$) for the major RO_2 species, mainly from alkenes, isoprene and aromatics, when the HO_2 conversion rate was over 100% (Fuchs et al., 2011; Lu et al., 2012; Lu et al., 2013). Therefore, only the HO_2 observations in high NO mode were chosen and they were denoted as $[\mathrm{HO_2^*}]$, which was the sum of the true HO_2 concentration and a systematic bias from the mixture of RO_2 species *i* which were detected with different relative sensitivities $\alpha_{\mathrm{RO_2}}^{i}$, as shown in Eq. (1) (Lu et al., 2012). The true HO_2 concentration was difficult to calculated due to the RO_2 concentration measurements and their speciation were not available. Herein, we simulated the HO_2 and $\mathrm{HO_2^*}$ concentrations by the model. The interference from RO_2 was estimated to be the difference between the HO_2 and $\mathrm{HO_2^*}$ concentrations.

$$[\mathrm{HO_2^*}] = [\mathrm{HO_2}] + \sum(\alpha_{\mathrm{RO_2}}^{i} \times [\mathrm{RO_2}]_i) \qquad (1)$$

(2) The figures and descriptions of HO_2 concentration were revised in Section 3.2:

The diurnal maximum of the observed $\mathrm{HO_2^*}$, the modeled $\mathrm{HO_2^*}$ and the modeled HO_2 concentrations were 4.2×10^8 cm^{-3}, 6.1×10^8 cm^{-3}, and 4.4×10^8 cm^{-3}, respectively. The difference between the modeled $\mathrm{HO_2^*}$ and HO_2 concentrations can be considered a modeled HO_2 interference from RO_2 (Lu et al., 2012). The RO_2 interference was small in the morning, while it became larger in the afternoon. It ranged within 23%-28% during the daytime (08:00-17:00), which was comparable with those in the Backgarden and Yufa sites in China, Borneo rainforest in Malaysia (OP3 campaign, aircraft), and UK (RONOCO campaign, aircraft) (Lu et al., 2012; Lu et al., 2013; Jones et al., 2011; Stone et al., 2014). The observed $\mathrm{HO_2^*}$ was overestimated by the model, indicating the HO_2 heterogeneous uptake might have a significant impact during this campaign. The diurnal maximum of $\mathrm{HO_2^*}$ concentration observed in Shenzhen was much lower than those observed in the Yufa and Backgarden sites (Lu et al., 2012; Lu et al., 2013; Hofzumahaus et al., 2009).

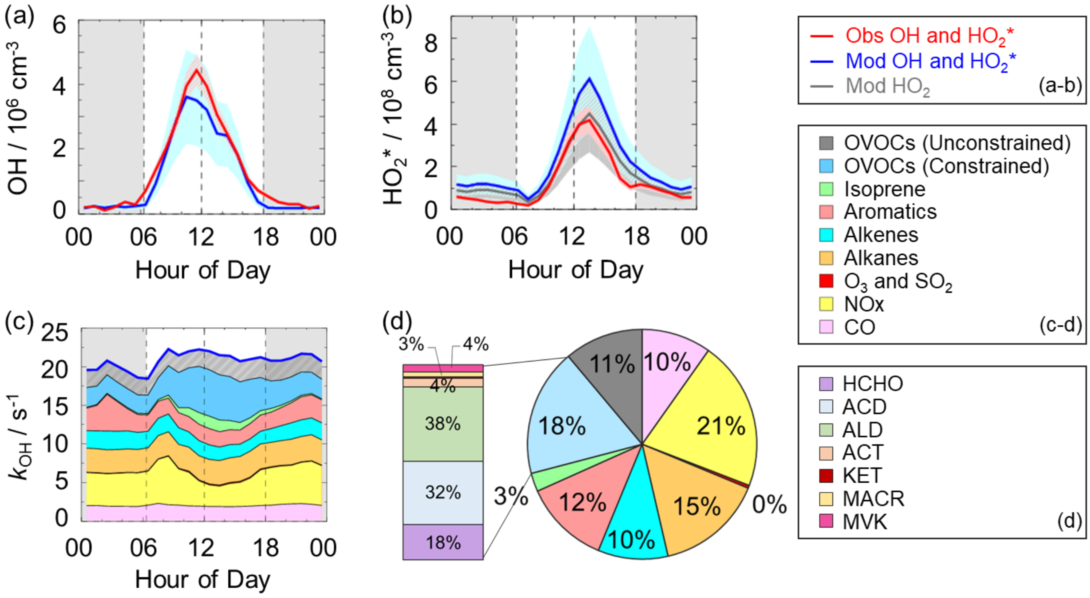

Figure 3: (a-b) The diurnal profiles of the observed and modeled OH, HO_2^* and HO_2 concentrations. (c) The diurnal profiles of the modeled k_{OH}. (d) The composition of the modeled k_{OH}. The red areas in (a-b) denote 1-σ uncertainties of the observed OH and HO_2^* concentrations. The blue areas in (a-b) denote 1-σ uncertainties of the modeled OH and HO_2^* concentrations, and the grey area in (b) denotes 1-σ uncertainties of the modeled HO_2 concentrations. The grey areas in (a-c) denote nighttime. ACD denotes acetaldehydes. ALD denotes the C3 and higher aldehydes. ACT and KET denote acetone and ketones. MACR and MVK denote methacrolein and methyl vinyl ketone.

(3) The timeseries of HO_2 concentrations were revised in Figure S1:

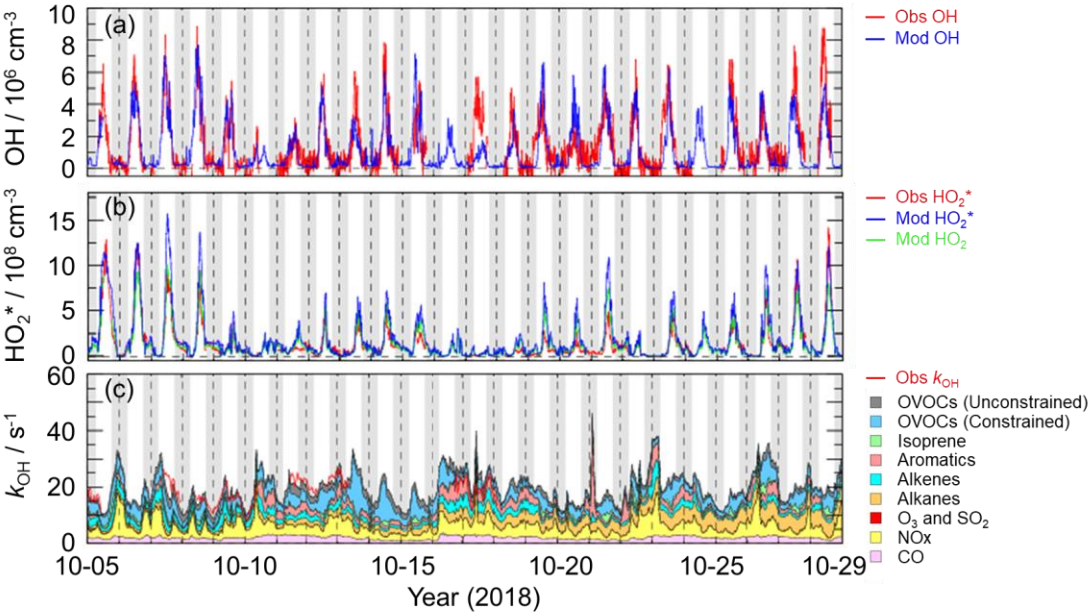

Figure S1: Timeseries of the OH, HO_2^*, HO_2 concentrations and k_{OH} in this study. The grey areas denote nighttime.

(4) The observed HO_2 concentrations can influence the OH experimental budget, so the description in Section 4.1 was revised:

It is noted that the OH production rate was overestimated because we used HO_2^* concentrations instead of HO_2 concentrations here. Thus, the missing OH source was the lower limit here, demonstrating more unknown OH sources need to be further explored.

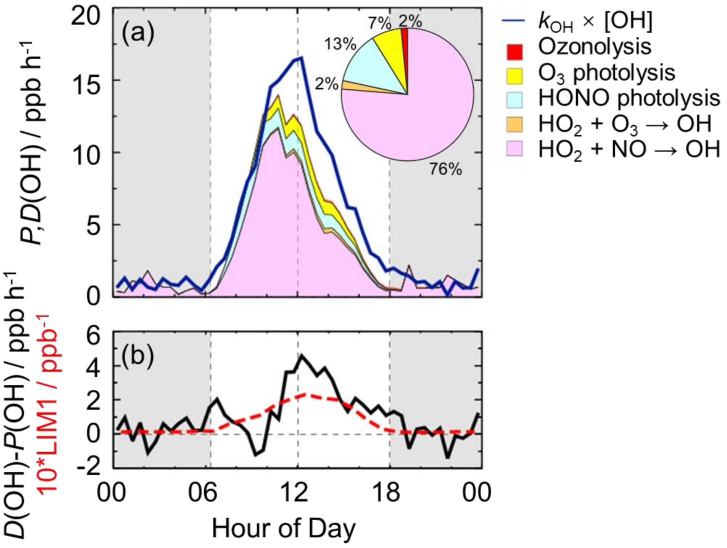

Figure 4: (a) The diurnal profiles of OH production and destruction rates and the proportions of different known sources in the calculated production rate during the daytime. The blue line denotes the OH destruction rate, and the colored areas denote the calculated OH production rates from the known sources. (b) The missing OH source which was the discrepancy between the OH destruction and production rates, and the OH production rate which was ten times the production rate derived from LIM1 mechanism. The grey areas denote nighttime.

(5) The NO dependence of HOx radicals in Fig. 5 was revised:

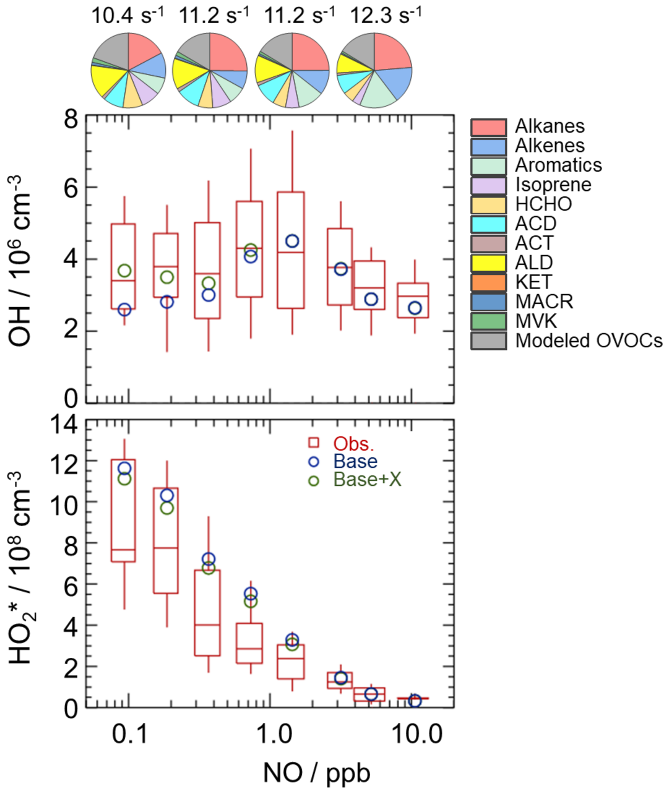

Figure 5: NO dependence of OH and HO_2^*radicals. The red box-whisker plots give the 10%, 25%, median, 75%, and 90% of the HOx observations. The blue circles show the median values of the HOx simulations by the base model, and the green circles show the HOx simulations by the model with X mechanism. Total VOCs reactivity and their organic speciation are presented by pie charts at the different NO intervals at the top. Only daytime values and NO concentration above the detection limit of the instrument were chosen. ACD and ACT denote acetaldehyde and acetone, respectively. ALD denotes the C3 and higher aldehydes. KET denotes ketones. MACR and MVK, which are both the isoprene oxidation products, denote methacrolein and methyl vinyl ketone, respectively.

3. Your model underestimates OH concentration under low NO conditions. I am very surprised that you claim that this is due to an unknown chemical X species, without even loosing a word about possible interferences in the OH measurements. Such increasing OH interferences with decreasing NO concentrations have been identified unequivocally with different FAGE instruments, and an experimental technique has been developed to quantify such possible interferences, this needs to be discussed. And even though some FAGE systems might be more prone to this interference than others, the FAGE community seems to agree on, that occasional measurements with such a pre-injector system are indispensable during field campaigns, especially when low NO concentrations are expected during the campaign. Looking at your above-mentioned paper describing a field campaign a few months before this one, it seems that you had already developed such a pre-injector system at the time of the campaign, because you had already used it. So why did you not use it in this campaign? In my opinion it is idle to discuss OH measurements that are underestimated by the model at low NO conditions, as long as OH-interference to an unknown species has been excluded by experiments using a pre-injector.

Reply

Thanks for your suggestions, the pre-injector system did not be applied in this campaign, but it is believed that the interference in OH measurement in this campaign was negligible by analyzing the PKU-LIF system and the environmental conditions during the campaign.

PKU-LIF system has been applied to measure HOx concentrations for several campaigns. We used the pre-injector system to quantify the possible interferences since 2014, including the campaigns conducted in Wangdu site (Tan et al., 2017), Heshan site (Tan et al., 2019), Huairou site (Tan et al., 2018), Taizhou site (Ma et al., 2022, in review, ACPD), and Chengdu site (Yang et al., 2021). No significant internal interference was found in the prior studies, demonstrating that the accuracy of the PKU-LIF system has been determined for several times.

Moreover, the potential interference may exist when the sampled air contained alkenes, ozone, and BVOCs (Mao et al., 2012; Fuchs et al., 2016; Novelli et al., 2014), indicating the environmental conditions, especially O_3, alkenes and isoprene, are important to the OH interferences. To further explore the potential interference in this campaign, we take Wangdu campaign as an example to compare the major environmental conditions between the prior campaigns and Shenzhen campaign here. During the Wangdu campaign, the chemical modulation tests were conducted on 29 June, 30 June, 02 July, and 05 July 2014, respectively (Tan et al., 2017). The daily mean O_3, alkenes (ethene, butadiene and other anthropogenic dienes, internal alkenes and terminal alkenes) and isoprene concentrations during the daytime on 29 June were 94.1, 3.8, 1.9 ppb, those on 30 June were 92.2, 2.7, and 1.9 ppb, those on 02 July were 52.9, 1.5, and 0.5 ppb, and those on 05 July were 68.5, 2.4, and 0.9 ppb. The O_3, alkenes and isoprene concentrations on 29 June were highest among those on 29 June, 30 June, 02 July and 05 July, and thus the potential interference on 29 June can be considered the highest among the four days. The results indicated that the potential interference during the daytime in Wangdu was negligible.

Here, we also showed the major parameters related to OH interference in Shenzhen in Table S2 in the Supplementary Information. The daily mean O_3 and isoprene concentrations during the daytime in Shenzhen were within 8.6-91.7 ppb and 0.1-1.0 ppb, which were both lower than those on 29 June in Wangdu. In terms of the alkenes, only 10,16-17 October 2018 in Shenzhen campaign were higher than that observed on 29 June in Wangdu, but the O_3 concentrations on the three days in Shenzhen were only 21.9, 13.9, and 8.6 ppb, and the isoprene concentrations on the three days in Shenzhen were only 0.3, 0.2, and 0.1 ppb, respectively. Overall, the environmental condition in Shenzhen was less conducive to generating potential OH interference than that in Wangdu. Therefore, it is not expected that OH measurement in this campaign was affected by the internal interference.

We have added the description of interval interference in Section 2.2 and the Supplementary Information.

Table S2: The daily mean O_3, alkenes (ethene, butadiene and other anthropogenic dienes, internal alkenes and terminal alkenes) and isoprene concentrations during the daytime (08:00-17:00) in the STORM campaign in this study.

Date / Species	10-05	10-06	10-07	10-08	10-09	10-10	10-11	10-12	10-13	10-14	10-15	10-16
O_3 (ppb)	81.4	83.8	91.7	86.7	48.1	21.9	30.2	42.6	46.8	38.7	40.2	13.9
Alkenes (ppb)	1.4	1.8	3.6	2.3	3.2	5.4	2.9	2.4	2.6	1.4	1.6	4.9
Isoprene (ppb)	0.4	0.4	0.4	0.5	0.4	0.3	0.1	0.3	0.4	0.4	0.6	0.2

Date / Species	10-17	10-18	10-19	10-20	10-21	10-22	10-23	10-24	10-25	10-26	10-27	10-28
O_3 (ppb)	8.6	16.2	39.4	45.8	47.2	25.2	40.9	36.5	55.2	56.5	60.9	60.8
Alkenes (ppb)	4.7	3.2	2.1	1.3	1.2	2.5	2.9	2.7	1.2	3.4	1.7	1.7
Isoprene (ppb)	0.1	0.1	0.5	0.3	0.8	0.8	0.4	0.3	0.5	1.0	0.6	0.8

Revision

(1) Section 2.2:

Additionally, prior studies reported that OH measurement might be affected by the potential interference, when the sampled air contained ozone, alkenes and BVOCs (Mao et al., 2012; Fuchs et al., 2016; Novelli et al., 2014), indicating the environmental conditions are important to the production of interference. The pre-injector is usually used to test the potential OH interference, and has been applied to our PKU-LIF system to quantify the possible interferences for several campaigns, including the campaigns conducted in Wangdu, Heshan, Huairou, Taizhou and Chengdu sites (Tan et al., 2017; Tan et al., 2019; Tan et al., 2018; Yang et al., 2021). No significant internal interference was found in the prior studies, demonstrating the accuracy of the PKU-LIF system has been determined for several times. Moreover, to further explore the potential interference in this campaign, we compared the major environmental conditions, especially O_3, alkenes and isoprene, between Shenzhen and Wangdu sites, as shown in the Supplementary Information. The environmental condition in Shenzhen was less conducive to generating interference than that in Wangdu, and the details were presented in the Supplementary Information. Therefore, it is not expected that the OH measurements in this campaign were affected by the internal interference.

(2) The detailed information on potential OH interference was added in the Supplementary Information:

We compared the environmental conditions in Shenzhen and Wangdu sites. The chemical modulation tests, which was applied to test the potential OH interference, were conducted on 29 June, 30 June, 02 July and 05 July 2014 in Wangdu (Tan et al., 2017). During the campaign in Wangdu, the daily mean O_3, alkenes (ethene, butadiene and other anthropogenic dienes, internal alkenes and terminal alkenes) and isoprene concentrations during the daytime on 29 June were 94.1, 3.8, 1.9 ppb, those on 30 June were 92.2, 2.7, and 1.9 ppb, those on 02 July were 52.9, 1.5, and 0.5 ppb, and those on 05 July were 68.5, 2.4, and 0.9 ppb, respectively. The O_3, alkenes and isoprene concentrations on 29 June were the highest among those on 29 June, 30 June, 02 July and 05 July, and thus the potential interference on 29 June can be considered the highest among the four days. The chemical modulation results indicated that the potential interference during the daytime in Wangdu was negligible (Tan et al., 2017).

As shown in Table S2, the O_3, alkenes and isoprene concentrations in Shenzhen were within 8.6-91.7 ppb, 1.2-5.4 ppb, and 0.1-1.0 ppb, respectively. The O_3 concentrations in Shenzhen (8.6-91.7 ppb) were lower than those on 29 June (94.1 ppb) and 30 June (92.2 ppb) in Wangdu. Similarly, the isoprene concentrations in Shenzhen (0.1-1.0 ppb) were also lower than those on 29 June (1.9 ppb) and 30 June (1.9 ppb) in Wangdu. In terms of the alkenes, only the concentrations on 10, 16-17 October 2018 (4.7-5.4 ppb) in Shenzhen were higher than that observed on 29 June (3.8 ppb) in Wangdu, but the O_3 concentrations on the three days in Shenzhen were only 21.9, 13.9, and 8.6 ppb, and the isoprene concentrations on the three days in Shenzhen were only 0.3, 0.2, and 0.1 ppb, respectively.

Overall, the environmental condition in Shenzhen was less conducive to generating potential OH interference than that in Wangdu. Therefore, it is not expected that OH measurement in this campaign was affected by the internal interference.

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