

Response to Reviewer 1:

General comments

This paper presents observations of NMHCs, OVOCs, O₃, and other reactive trace gases made at a site in the Yellow River Delta during a winter-spring period and a summer period in 2017. The study area is very interesting because it is one of the largest oil and natural gas (O&NG) exploration areas in China. And it is a part of the North China Plain; a region suffers from severe air pollution. Some of the NMHCs and OVOCs samples were taken near oil wells and petrochemical industrial areas. The authors derived emission profiles of VOCs from oil fields. Such emission profiles were not available in China before. The concentrations of VOCs in ambient air over the site were very high due to large emissions from O&NG exploration in the Yellow River Delta. The authors also studied the atmospheric oxidative capacity, radical budget, and ozone formation mechanism at the observation site using a box model constrained by measurements. The results show that O₃ formation was mainly NO_x-controlled due to high-VOCs and low-NO_x conditions. OVOCs played a dominant role in OH reactivity and were the major source of RO_x radicals. The low NO_x level in summer limited the radical recycling.

The observational data reported in this paper are valuable. The emission profiles of VOCs from O&NG exploration are highly needed in air quality studies and emission control. The results from the box model study are interesting and important for such a special area. This paper is well written and within the scope of ACP. I recommend publication of this paper in ACP after the following minor points are appropriately addressed.

Response: we thank the reviewer for the positive comments and constructive suggestions to improve our manuscript. We have carefully considered all the review comments and revised the manuscript accordingly. Below we provide the original reviewer's comments *in black italic*, with our responses and changes in the manuscript in blue and red, respectively.

Specific comments and suggestions:

1. After reading this paper the readers would like to know the impacts of large VOCs emission in the Yellow River Delta on the air quality over the surrounding area. The summer concentration of NO_x at the study site was low. However, the NO_x levels over many other parts of the North China Plain are much higher. Photochemical O₃ production may be very different when transported high-VOCs plume mixed with high-NO_x air. To address this 3D simulation is needed, which may be out of the scope of this paper. But I think some discussions in this aspect are necessary.

Response: thanks for the suggestion. We agree with the reviewer that it is important to assess the impacts of oilfield VOC emissions on the regional air quality in the surrounding areas, and

it is indeed an initial objective of this project. As the reviewer indicated, 3-D model simulations and emission inventory of oilfield emissions are needed to address this issue, which is out of the scope of this paper. A separate work that aims at developing an oilfield emission inventory of VOCs and assessing its impacts on regional ozone pollution by WRF-Chem model is now underway. The following discussions have been added in the revised manuscript to address this aspect.

“Nonetheless, the oilfield emissions of VOCs may have high potential to affect the regional air quality in the polluted YeIRD and even the surrounding NCP regions, where the ambient NO_x are usually abundant. The oilfield emitted VOCs may significantly contribute to the formations of O_3 and secondary organic aerosol on a regional scale. To address this issue, an oilfield emission inventory of VOCs and NO_x as well as 3-dimensional chemical transport model simulations are needed. So far, the oilfield emission has not been included by the emission inventories in China. More efforts are urgently needed to develop accurate oilfield emission inventory and evaluating their impacts on the regional air quality and climate.”

2. *Section 2.2 should include details about the calibrations and data quality.*

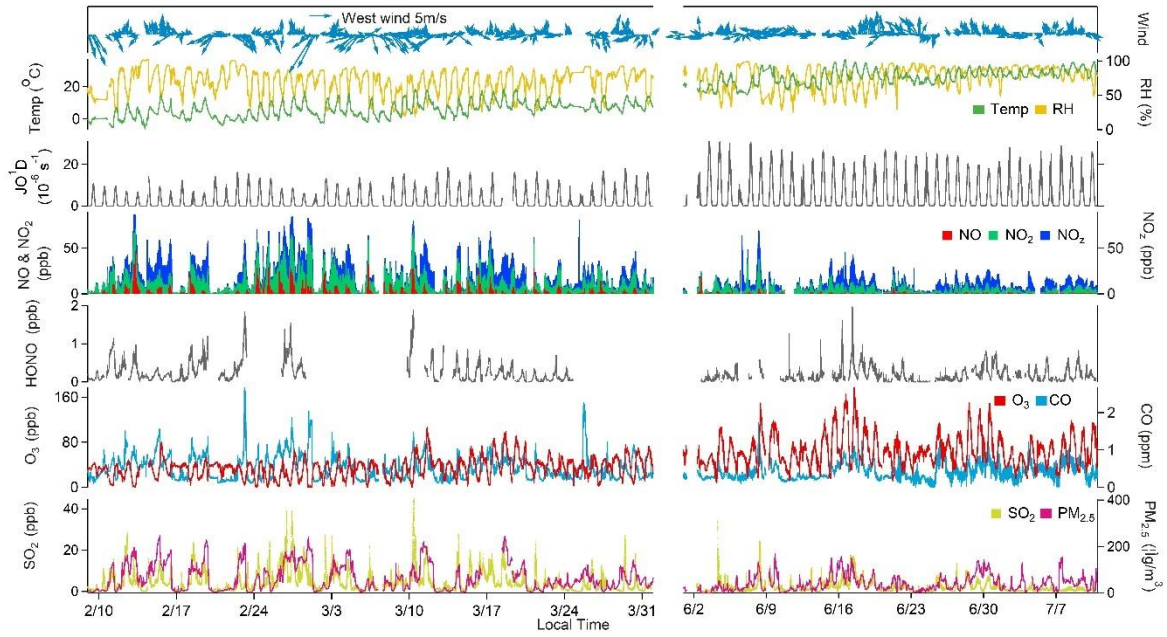
Response: the following descriptions have been provided in the revised manuscript.

“These trace gas analyzers were calibrated manually every three days during the measurement campaigns, including zero and span checks as well as conversion efficiency calibration of the MoO catalytic converter, with additional zero calibration automatically done every four hours for the CO instrument.”

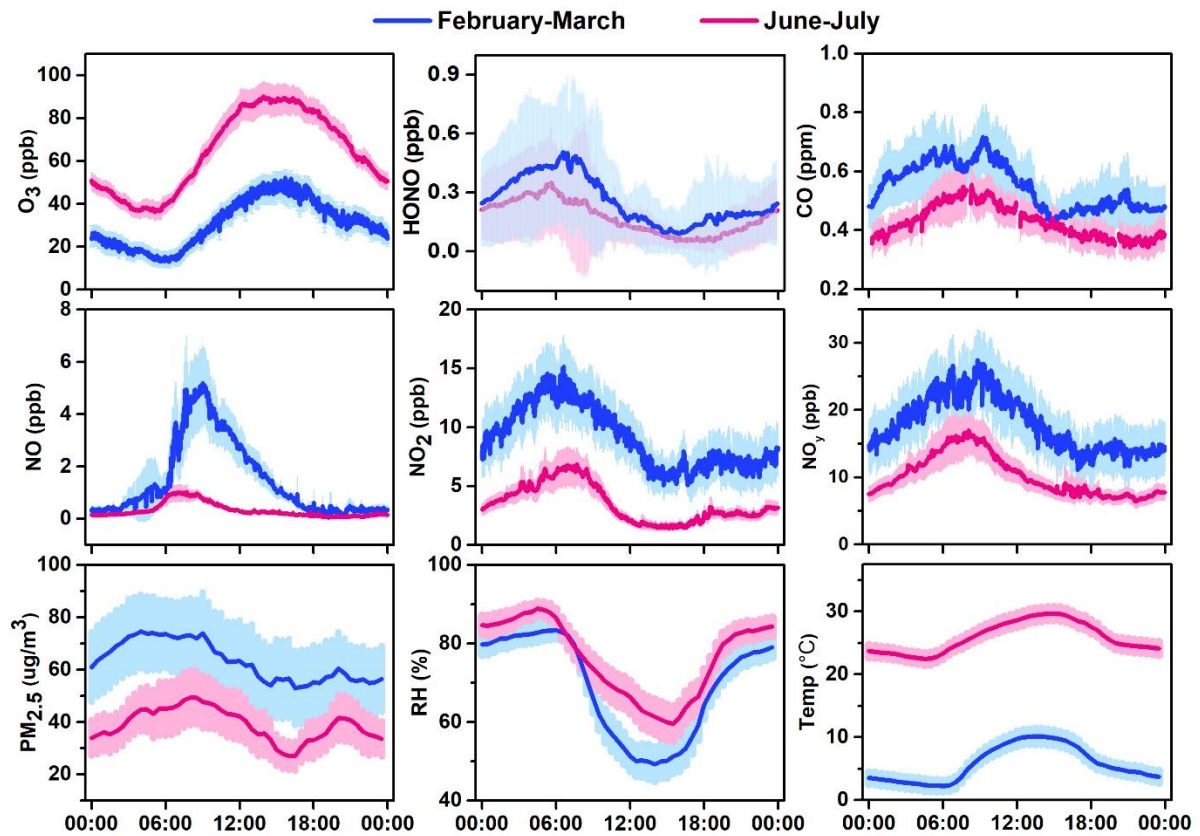
“All of the above measurement techniques have been successfully applied in many previous studies, and the detailed measurement principles, detection limits, quality assurance and quality control procedures can be found elsewhere (Xue et al., 2016; Simpson et al., 2016; Yang et al., 2018; Li et al., 2018).”

3. *Although HONO and OVOCs were observed, no observational data of these are presented. Since these species are very important in your studies of atmospheric oxidative capacity and radical chemistry, I do not think these observational data can be omitted. I think HONO data should be included in Figures 2 and 3, and OVOCs data should be either presented in Figure 4 or in an extra figure.*

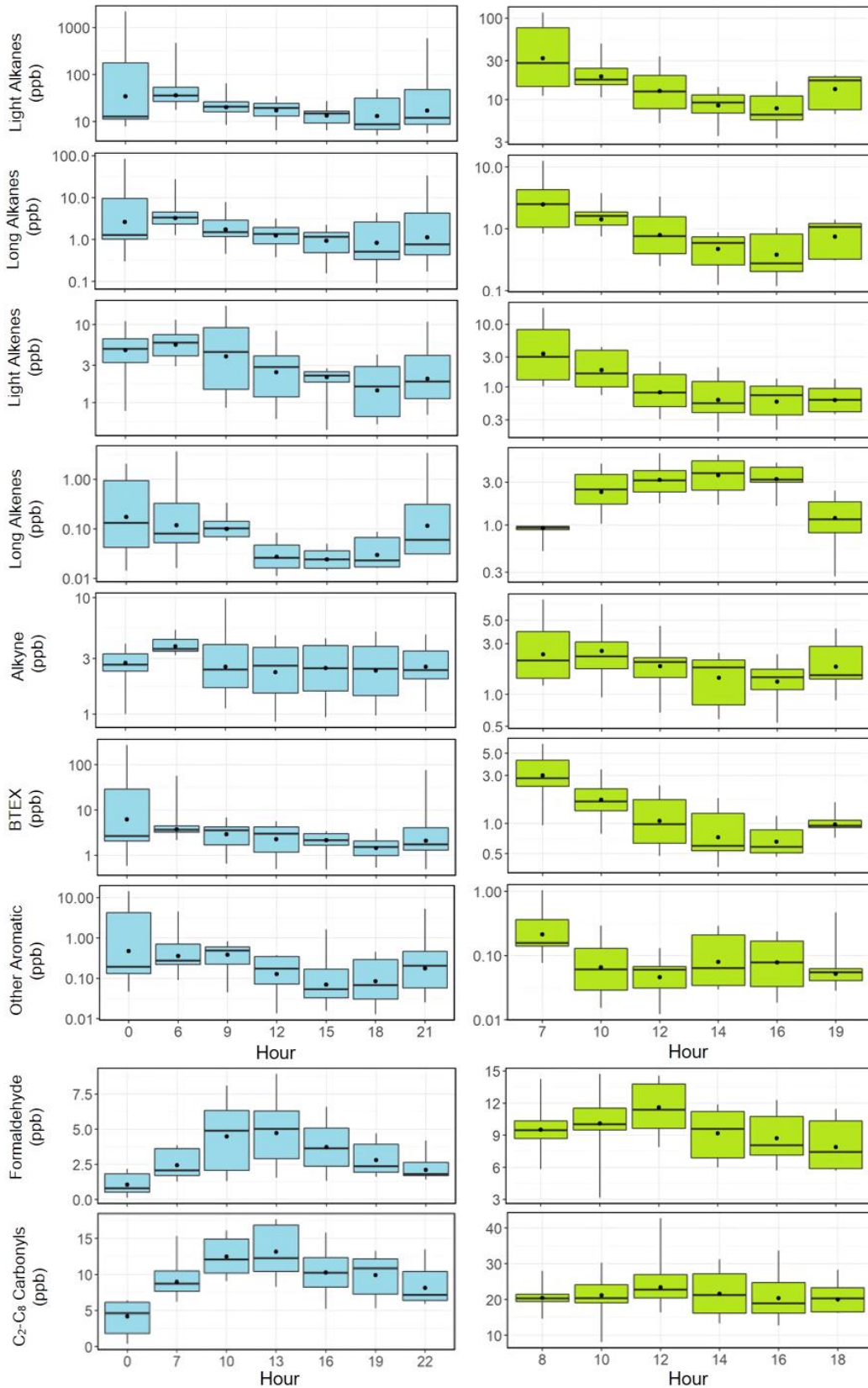
Response: in the revised manuscript, the HONO data has been included in Figures 2 and 3, and the OVOC data has been presented in Figure 4. The revised figures are as follows.



Revised Figure 2. Time series of major trace gases, PM_{2.5}, and meteorological parameters measured at the study site during February-March and June-July 2017.



Revised Figure 3. Average diurnal patterns of major trace gases, PM_{2.5}, and meteorological parameters at the study site during February-March and June-July 2017. Error bars indicate the half standard deviation of the mean (blue line: February-March, red line: June-July).



Revised Figure 4. Average diurnal variations of light alkanes, long-chain alkanes, light alkenes, long-chain alkenes, alkyne, BTEX, other aromatics, formaldehyde, and C₂-C₈ carbonyls at the study site (left column: February-March, right column: June-July).

4. P13, L1-4 and Figure 11: why is the “ $\text{NO}+\text{HO}_2 = \text{NO}_2+\text{OH}$ ” reaction not included as a source of OH? If you have any reason not to include this reaction in OH production, you should not state “Photolysis of OVOCs is identified as the dominant radical source” (L2-3) because your Figure 11a shows OVOCs photolysis has only a minor contribution to OH production.

Response: here we only focus on the PRIMARY RO_x radical sources, and the “ $\text{NO}+\text{HO}_2 = \text{NO}_2+\text{OH}$ ” reaction was treated as a radical recycling process in the present study. The contribution of this recycling process to the OH production was also evaluated and presented in Figure 12. For clarity, the original statements have been modified as follows in the revised manuscript.

“Figure 11 presents major primary sources of OH, HO_2 and RO_2 radicals quantified in the YelRD region, and the detailed RO_x radical budget is summarized in Figure 12. Photolysis of OVOCs is identified as the dominant primary RO_x radical source, with daytime (6:00-18:00 LT) average production rates of 2.15 ± 1.40 ppbv h^{-1} for HO_2 (of which 1.10 ± 0.79 ppbv h^{-1} is from formaldehyde alone) and 0.86 ± 0.53 ppbv h^{-1} for RO_2 , respectively.”

5. Section 6, first paragraph and P9, L18-20: your measurements show a rapid morning increase of O_3 concentration. This increase may not only be resulted from photochemistry but also from vertical mixing. I suggest that you integrate the net O_3 production rate in Figure 13 to get a diurnal profile of O_3 based on box model simulations and compare it with the observed diurnal profile shown in Figure 3.

Response: thanks for the helpful suggestion. Indeed, the observed morning increase of O_3 concentrations can be due to both photochemistry and vertical mixing. We have examined the detailed budget of O_3 changes. The observed rate of change in O_3 concentrations at the study site (R_{meas}) was the result of chemistry (R_{chem} ; including production and destruction), deposition (R_{deps}), and transport (R_{trans} ; including horizontal and vertical transport). R_{chem} and R_{deps} were calculated by the observation-constrained chemical box model, and R_{meas} can be derived from the observed diurnal profiles of O_3 concentrations. The calculated results for the nine ozone episodes are shown below. During four episodes, downward intrusion of O_3 -laden residual layer air was clearly illustrated, as indicated by the large positive R_{trans} value in the morning. However, the downward mixing mainly occurred during the early morning period (i.e., 5:00-7:00 LT), whilst the observed O_3 increase in the mid- and late morning should be owing to the photochemical production. For clarity, the following discussions have been added in the revised manuscript.

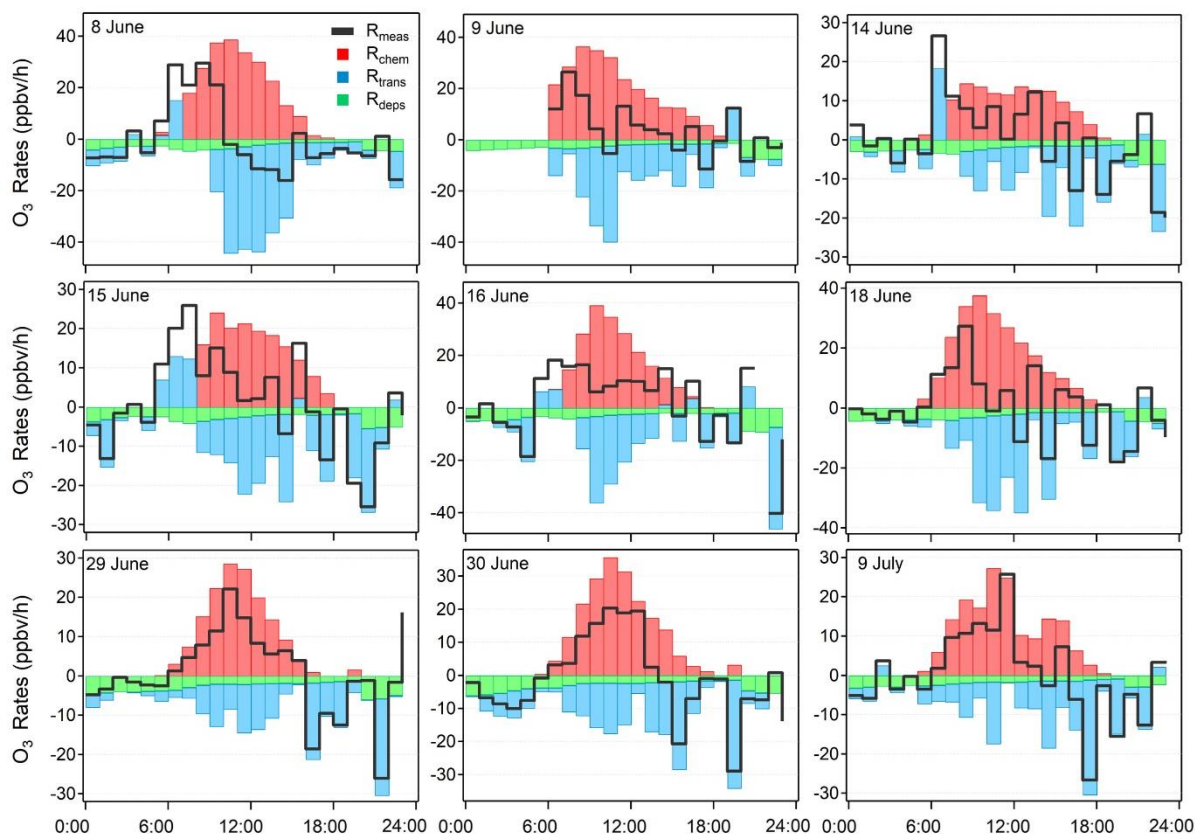


Figure R1. The observed rate of change in O₃ concentrations (R_{meas}) and the contributions from photochemistry (R_{chem}), transport (R_{trans}), and deposition (R_{deps}) in the YelRD during the nine selected O₃ episodes.

“A noteworthy result is the fast accumulation of O₃ during the morning period. For example, the average increases in O₃ concentrations in the morning (06:00–12:00 LT) were 49.2 ppbv and 30.2 ppbv in summer and winter-spring, respectively. The early morning (i.e., 05:00–07:00 LT) O₃ increase may be attributed to the downward intrusion of O₃-laden residual layer air (see Fig. S1), while the rapid O₃ increase throughout the morning period suggests the strong in-situ photochemical formation in this VOC-rich area.”

6. Some of the box model results can be compared with those from Chinese megacities reported by Tan et al. (2019). [Tan et al., Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: a case study based on box model simulation, *Atmos. Chem. Phys.*, 19, 3493–3513, 2019.]

Response: the findings of Tan et al. (2019) have been compared with our box model results in the revised manuscript. The revisions are as follows.

“In comparison, a recent study illustrated the importance of HONO and formaldehyde

photolysis in four polluted Chinese megacities (Beijing, Shanghai, Guangzhou and Chongqing), which accounted for ~50% of the total primary RO_x source (Tan et al., 2019).”

“This is quite different from those derived from the polluted urban areas, where the RO_x+NO_x reactions generally dominate the radical termination processes (Tan et al., 2019).”

Tan, Z., Lu, K., Jiang, M., Su, R., Wang, H., Lou, S., Fu, Q., Zhai, C., Tan, Q., Yue, D., Chen, D., Wang, Z., Xie, S., Zeng, L., and Zhang, Y.: Daytime atmospheric oxidation capacity in four Chinese megacities during the photochemically polluted season: a case study based on box model simulation, *Atmos. Chem. Phys.*, 19, 3493–3513, 2019.

7. P3, L15-18: *when it comes to long-term trends of surface ozone in China, “Ma et al., Significant increase of surface ozone at a rural site, north of eastern China, Atmos. Chem. Phys.*, 16, 3969-3977, 2016” is one of the few important papers and should be cited.

Response: this reference has been cited in the revised version.

8. P4, L23-26: *“In view of the regional scale, the observation site is constrained by both aged continental air masses transported from the Beijing-Tianjin-Hebei region and clean marine air from the Bohai Sea, making it an excellent platform to study the interaction between anthropogenic pollution and the natural background air in the North China Plain (NCP)”. I do not think you can really sample “clean marine air from the Bohai Sea” or “natural background air” because you are so close to the oil wells.*

Response: the study site can receive the marine air from the Bohai Sea when the air comes from exactly the east, although southwesterly winds generally dominated in summer in the present study. The original statements have been revised as follows.

“In view of the regional scale, the observation site is constrained by both aged continental air masses transported from the Beijing-Tianjin-Hebei region and marine air from the Bohai Sea.”

9. P4, L27-P5, L2.: *these sentences belong to section 2.2.*

Response: agree, and the original sentences have been separated as follows.

“Details of the sampling site can be found elsewhere (Zhang et al., 2019). Source samples were also collected from the nearby oil and gas wells to obtain the source profiles of VOCs from the oil field.” (This sentence is still at the end of Section 2.1)

“All in-situ measurement instruments were housed in a temperature-controlled container, and the sampling inlets were mounted on top of the container with an altitude of about 5 m above the ground.” (This sentence has been moved to Section 2.2)

10. P5, L14: *what is “SHARP”? This abbreviation should be explained.*

Response: we have explained and changed the sentence in the revised manuscript as follows:

“PM_{2.5} mass concentrations were measured using a Synchronized Hybrid Ambient Real-time Particulate monitor (SHARP; Thermo Scientific Model 5030).”

11. P5, L21-30: *did you use O₃ scrubbers when taking NMHCs samples?*

Response: we didn't use O₃ scrubbers when taking NMHCs samples. The following statements have been added in the revised manuscript to state the potential uncertainty for our VOC observations.

“Note that O₃ scrubbers were not used ahead of the canisters during the sampling, and the sampled canisters were shipped to the UCI for analysis immediately after the individual field campaign. Some reactive VOC compounds (such as alkenes) may be decayed more or less during the time span from sampling to lab analysis. Thus, one should keep in mind that the VOC observations in this study may be subject to some uncertainty and the reactive compounds may be underestimated to some extent.”

12. P7, L20-21: *“Photolysis frequencies within the model were adjusted by the solar zenith angle and the measured J(NO₂) (Saunders et al., 2003).” Why did you adjust photolysis frequencies within the model when you had the measured values?*

Response: we are sorry that the original statement is misleading. In the model, the unmeasured photolysis frequencies (we only measured J for NO₂, HCHO, O¹D, HONO and NO₃) were calculated as a function of solar zenith angle (Saunders et al., 2003), and then were scaled with the measured J(NO₂) values (based on the ratio of measured J(NO₂) to calculated J(NO₂)). The statement has been revised as follows in the revised version.

“Unmeasured photolysis frequencies within the model were calculated as a function of the solar zenith angle (Saunders et al., 2003), and then were scaled with the measured J(NO₂).”

13. P9, L14-17: *this statement applies only to summer.*

Response: this statement has been revised as follows.

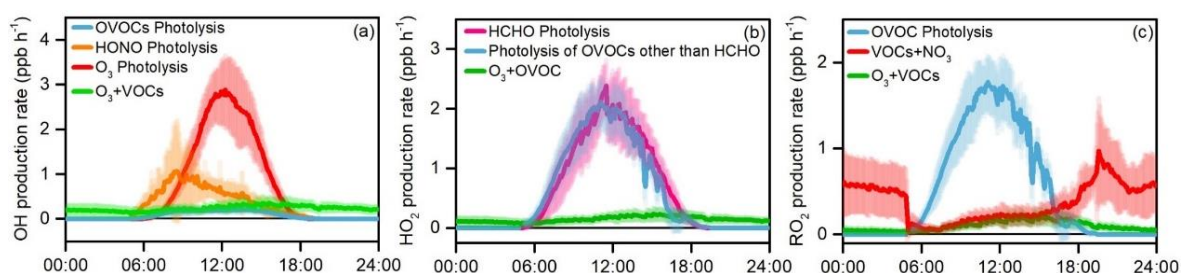
“VOCs generally showed higher levels during the nighttime or the early morning and lower mixing ratios during the day, with long-chain alkenes (comprising isoprene, 3-methyl-1-butene, 2-methyl-1-butene, alpha-pinene, and beta-pinene) as an exception that shows an opposite diurnal pattern in summer (Fig. 4).”

14. P9, L26-28: can you estimate errors in the so obtained emission profiles?

Response: the so obtained oilfield emission profiles may be subject to errors (or uncertainties) due to the limited size of source samples (i.e., 18). More comprehensive studies by taking much more samples are needed to better characterize the VOC emissions from the oilfield in China.

15. Figure 11b: Since you single out HCHO photolysis, “OVOCs Photolysis” here should be changed to “Photolysis of OVOCs other than HCHO” or similar.

Response: Figure 11b has been revised as suggested.



Revised Figure 11. Simulated average primary production rates of (a) OH, (b) HO₂, and (c) RO₂ during the summertime O₃ pollution episodes. The error bars indicate the standard deviations of the mean.